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ETHANOL/WATER, PHYSICAL AND CHEMICAL PROPERTIES FOR SEPARATION PROCESS DESIGN

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ETHANOL/WATER, PHYSICAL AND CHEMICAL PROPERTIES FOR SEPARATION PROCESS DESIGN

Brian Maiorella, Harvey Blanch, and Charles Wilke

May 1982

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ETHANOL/WATER, PHYSICAL AND CHEMICAL PROPERTIES
FOR SEPARATION PROCESS DESIGN

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Berkeley, California 94720

May 1, 1982

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1 Introduction

Accurate property data are essential for the design and evaluation of new ethanol/water separation processes. Important physical, chemical, and thermodynamic properties of ethanol, water, and their mixtures are compiled here. Property data are also included for major fermentation by-products which can affect the ethanol/water separation design. Data for selected separating agents are also included.

Preparation of data for this compilation involved four steps:
1) Where available, data were collected from the chemical literature;
2) All data were critically reviewed (as in the case for ethanol/water-vapor/liquid equilibrium data, where thermodynamic consistency testing was used to eliminate faulty data sets); 3) Data were correlated and computer routines developed to allow ready application in process screening and design; and 4) Where important data were not available in the literature (as in the effect of biological components and whole yeast cells on ethanol/water equilibrium properties), new experiments were conducted to collect the required data.

For vapor/liquid equilibria, the model to be used will be the general thermodynamic relationship:

\[ Y_i \phi_i \rho_{\text{total}} = X_i \gamma_i \phi \rho_{\text{liq}} \exp[p_{\text{total}} \rho_{\text{liq}}/(RT)] \]  

(1-1)

where:
Many of the correlations given in the following sections are chosen to lead to this overall model.

To be of the greatest use in process screening and design, property data must be in computer usable form. The integrated computational package of Prausnitz, et al. (1) is a versatile system for thermodynamic property evaluation and is used widely in industry. Whenever possible, correlations and new computer subroutines have been chosen to be compatible with this package. Where correlations used in this package were found inferior to others available (such as for liquid densities) both correlations are included.

2. Pure Component Property Data

This section presents basic physical property constants for ethanol and water. Values of these basic properties are well agreed upon. Several of these basic property values will be used in the development of correlations for the further properties discussed in subsequent sections.
Ethanol basic property data are summarized in Table 1. Water basic property data are summarized in Table 2.

3 Nonideal Vapor Phase--The Fugacity Coefficient

3.1 Introduction

The fundamental thermodynamic equation of vapor liquid equilibrium is:

\[ f_i^{\text{vap}} = f_i^{\text{liq}} \]  \hspace{1cm} (3-1)

where \( f_i \) = fugacity of component \( i \) in the specified phase.

For an ideal system, Raoult's law expresses the vapor/liquid equilibrium relationship as:

\[ Y_i p_{\text{total}} = X_i p_i^{\text{pure}} \]  \hspace{1cm} (3-2)

where:

- \( Y_i \) = mole fraction of component \( i \) in the vapor phase
- \( X_i \) = mole fraction of component \( i \) in the liquid phase
- \( p_{\text{total}} \) = system total pressure
- \( p_i^{\text{pure}} \) = vapor pressure of pure component \( i \) at the system temperature.

For the vapor phase, this is equivalent to assuming the ideal gas law.

Raoult's law fails for all but the simplest systems. At low to moderate pressures (less than 5 bar) the activity coefficient is
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>General Properties:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formula</td>
<td>C$_2$H$_5$OH</td>
<td></td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>46.069</td>
<td>1,2,3,4,5</td>
</tr>
<tr>
<td>Normal Boiling Point</td>
<td>351.47°K</td>
<td>1,2,3,4,5</td>
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<tr>
<td>Melting Point</td>
<td>159.05°K</td>
<td>1,2,3,4,5</td>
</tr>
<tr>
<td>Density$_{20}$</td>
<td>0.7893</td>
<td>2,3,4</td>
</tr>
<tr>
<td>Flash Point</td>
<td>282-284°K</td>
<td>2,3,4</td>
</tr>
<tr>
<td>Surface Tension (298°K)</td>
<td>23.1 dyne/cm</td>
<td>2,4</td>
</tr>
<tr>
<td>Association Parameter</td>
<td>1.40</td>
<td>1</td>
</tr>
<tr>
<td><strong>Critical Properties:</strong></td>
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<td></td>
</tr>
<tr>
<td>Critical Temperature</td>
<td>516.26°K</td>
<td>1,4,5</td>
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<tr>
<td>Critical Pressure</td>
<td>63.835 bar</td>
<td>1,4,5</td>
</tr>
<tr>
<td>Critical Volume</td>
<td>167 L/kmole</td>
<td>1,4,5</td>
</tr>
<tr>
<td>Critical Compressibility</td>
<td>0.248</td>
<td>1,4,5</td>
</tr>
<tr>
<td>Pitzer Acentric Factor</td>
<td>0.635</td>
<td>5</td>
</tr>
<tr>
<td><strong>Molecular Properties:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dipole Moment</td>
<td>1.69 Debye</td>
<td>1,5</td>
</tr>
<tr>
<td>Radius of Gyration</td>
<td>2.2495 Å</td>
<td>1,5</td>
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<tr>
<td><strong>Thermodynamic Properties:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat of Combustion (298°K)</td>
<td>326.8 kcal/gmole</td>
<td>2,4</td>
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<tr>
<td>Heat of Fusion</td>
<td>1.152 kcal/gmole</td>
<td>2,4</td>
</tr>
<tr>
<td>Heat of Formation (298°K)</td>
<td>-56.12 kcal/gmole</td>
<td>2,5</td>
</tr>
<tr>
<td>Gibbs Energy of Formation (298°K)</td>
<td>-40.22 kcal/gmole</td>
<td>2,5</td>
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</tbody>
</table>
Table 2
Water Basic Property Data

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>General Properties:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formula</td>
<td>H$_2$O</td>
<td>1,2,3,5</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>18.016</td>
<td>1,2,3,5</td>
</tr>
<tr>
<td>Normal Boiling Point</td>
<td>373.15°K</td>
<td>1,2,3,5</td>
</tr>
<tr>
<td>Melting Point</td>
<td>273.15°K</td>
<td>1,2,3,5</td>
</tr>
<tr>
<td>Density$_{20}^0$</td>
<td>1.000</td>
<td>2,3</td>
</tr>
<tr>
<td>Surface Tension (298°K)</td>
<td>73. dyne/cm</td>
<td>2</td>
</tr>
<tr>
<td>Association Parameter</td>
<td>1.70</td>
<td>1</td>
</tr>
<tr>
<td><strong>Critical Properties:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Critical Temperature</td>
<td>647.37°K</td>
<td>1,5</td>
</tr>
<tr>
<td>Critical Pressure</td>
<td>221.20 bar</td>
<td>1,5</td>
</tr>
<tr>
<td>Critical Volume</td>
<td>56.0 L/kgmole</td>
<td>1,5</td>
</tr>
<tr>
<td>Critical Compressibility</td>
<td>0.229</td>
<td>1,5</td>
</tr>
<tr>
<td>Pitzer Acentric Factor</td>
<td>0.344</td>
<td>5</td>
</tr>
<tr>
<td><strong>Molecular Properties:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dipole Moment</td>
<td>1.83 Debye</td>
<td>1,5</td>
</tr>
<tr>
<td>Radius of Gyration</td>
<td>0.6150 Å</td>
<td>1,5</td>
</tr>
<tr>
<td><strong>Thermodynamic Properties:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat of Fusion</td>
<td>1.435 kcal/gmole</td>
<td>2,3</td>
</tr>
<tr>
<td>Heat of Formation (298°K)</td>
<td>-57.80 kcal/gmole</td>
<td>2,5</td>
</tr>
<tr>
<td>Gibbs Energy of Formation (298°K)</td>
<td>-56.64 kcal/gmole</td>
<td>2,5</td>
</tr>
</tbody>
</table>

References
1,2,3,5
1,2,3,5
1,2,3,5
2,3
1
1,5
1,5
5
1,5
2,3
2,5
generally incorporated to account for liquid phase nonideality, but no correction is made for the vapor phase. For the system ethanol/water, however, polar interactions increase the vapor phase nonidealities and even at 1 bar pressure, a fugacity correction is necessary.

\[ \phi_i y_i p_{\text{total}} = y_i X_i f_{\text{ref,liq}} \]  \hspace{1cm} (3-3)

where:

- \( \phi_i \) = component \( i \), gas phase fugacity coefficient
- \( y_i \) = component \( i \), liquid phase activity coefficient
- \( f_{\text{ref,liq}} \) = reference fugacity for component \( i \) in the liquid at standard state conditions for \( y_i \)

In this section, the Hayden-O'Connell virial equation correlation for fugacity coefficients is outlined and evaluated for the system ethanol/water. A later section considers the liquid phase nonidealities.

3.2 The fugacity coefficient from an equation of state

The fugacity coefficient is a function of temperature, composition and pressure. It relates nonidealities in the vapor phase pressure/volume/temperature relationship and hence, a model for the fugacity coefficient can be developed from any gas phase equation of state which adequately models the vapor P,V,T behavior. In this way, the well developed vapor equation of state correlations may be applied rather than developing an entirely new fugacity correlation.
The relationship between the fugacity coefficient and vapor phase P,V,T relations can be developed directly from the definitions of fugacity coefficient and fugacity:

\[ \phi_i = f_i/Y_i p_{\text{total}} \]  
\[ [(\partial \ln f_i)/(\partial P)]_T = V_i/RT \]  

and with suitable thermodynamic manipulations (7), we find

\[ RT (\ln(f_i/PY_i)) = RT \ln \phi_i = \int_0^P [(\partial V/\partial n_i)_T,P,n_j - (RT/P)] dP \]
\[ = -\int_{-\infty}^V [(\partial P/\partial n_i)_{T,V,n_j} - (RT/V)] dV - RT \ln Z \]  

Any suitable equation of state may now be substituted, and fugacity coefficient correlations have been developed based on the Redlich-Kwong, Sugie Lu, Lee-Erbar-Edmunster, Benedict-Webb-Rubin, Pitzer and virial equations of state (5). Only for the virial equation are rigorous thermodynamic relations known for relating mixed component vapor properties to the pure component properties, therefore, this equation has been chosen as the starting point in most recent correlations for the fugacity coefficient.

The virial equation is given as

\[ Z = PV/(RT) = 1 + B'(T)/V + C'(T)/V^2 + ... \]
Expressed in pressure explicit form and truncated after one term, the virial equation reduces to

\[ Z = 1 + \frac{BP}{RT} \]  

(3-8)

where:

- \( P \) = system pressure
- \( T \) = system temperature
- \( R \) = ideal gas constant
- \( Z \) = compressibility.

and the second virial coefficient for a mixture is given by the rule:

\[ B = \sum_{i=1}^{n} \sum_{j=1}^{n} Y_i Y_j B_{ij}(T) \]  

(3-9)

derived from statistical mechanics arguments.

This truncated virial equation accurately models the \( P,V,T \) behavior of ethanol and water systems (and others) up to about one half their critical density (at which point further terms must be retained). This is well beyond the pressure range of likely distillation and extraction processes. Substituting the virial equation into equation 3-6 (with the appropriate differentiations) yields the desired relation:

\[ \ln \rho_i = [2 \sum_{j=1}^{n} (Y_j B_{ij}) - B](P/RT) \]  

(3-10)
thus, requiring only an expression for the virial coefficients.

3.3 Virial coefficient correlation: The Hayden-O'Connell correlation

The second virial coefficient is a correction to the ideal gas law to consider vapor phase pair interactions. As such, the virial coefficient can be directly related to the interaction energy between molecular pairs as expressed by a pair potential:

\[
B = \frac{1}{2} N \int_{0}^{\infty} \int_{0}^{\pi/2} \int_{0}^{2\pi} \left(1 - e^{-\frac{\phi}{kT}}\right) r^2 \sin \phi \, d\phi \, dr \quad (3-11)
\]

where:
\[
\phi \quad \text{the molecular pair potential function}
\]
\[
r \quad \text{molecular separation distance}
\]
\[
k \quad \text{Boltzmann constant}
\]
\[
N \quad \text{Avogadro's number}
\]

For a simple system with only the classical electrostatic forces (no polar or association contributions) the molecular interactions will be made up of bound, metastable bound and free types (Fig. 1), and corresponding contributions to the virial coefficient can be considered (7). With no association, the metastable and bound contributions have been correlated with the critical properties, dipole moment (\(\mu\)), and a molecular size parameter (8).

The free (repulsive, molecular volume) contribution to the virial coefficient has also been correlated for nonpolar nonassociating
Figure 1. Intermolecular pair potential contributions as used in the Hayden-O'Connell Model.
molecules using only critical properties and the Pitzer acentric factor (to correct for molecular nonspherocity) (9,10). None of these correlations are adequate for the evaluation of virial coefficient for the polar ethanol/water system.

The limitations of previous correlations are overcome by the modification of Hayden and O'Connell (11). In this model, pair interactions are represented in two parts, a classical electrostatic contribution and the nonclassical contribution arising from polar and association effects. In this way, equations of the forms already developed can be used to correlate most effects. To apply these equations in finding the classical contributions for polar molecules, pseudo-polar reduced properties were developed. For the nonspheroicity correction to the free contribution, the Pitzer acentric factor is replaced with the mean radius of gyration (which is not altered by molecular polarity as is the Pitzer factor) and nonpolar changes to the critical temperature and pressure are cancelled by using a molecular dipole moment angle averaging correction to the interaction energy and molecular size correlations.

To complete the correlation for polar and associating components, Hayden and O'Connell developed correlations to account for these additional effects. The polar (attractive) contribution to the free contribution was correlated by empirically fitting data for polar, nonassociating compounds. The association contribution to the bound contribution was then correlated as an equilibrium constant for the association reaction in terms of an association (or solvation for
unlike molecules) parameter. For unlike pair interactions, suitable mixing rules were developed.

The necessary equations for the calculation of virial coefficients for both polar and nonpolar systems are given below:

**Virial Coefficient Segment Contributions:**

\[
B_{ij}^{\text{Total}} = B_{ij}^{\text{Free}} + B_{ij}^{\text{Dimerized}} \quad (3-12)
\]

\[
B_{ij}^{\text{Free}} = B_{ij}^{\text{Free,Nonpolar}} + B_{ij}^{\text{Free,Polar}} \quad (3-13)
\]

\[
B_{ij}^{\text{Dimerized}} = (B_{ij}^{D,\text{Metastable}} + B_{ij}^{D,\text{Bound}}) + B_{ij}^{D,\text{Associative}} \quad (3-14)
\]

**Free, Nonpolar Contribution:**

\[
B_{ij}^{\text{Free,Nonpolar}} = b_{o,ij} \left(0.94 - \frac{1.47}{T_{ij}^*} - \frac{0.85}{(T_{ij}^*)^2} + \frac{1.015}{(T_{ij}^*)^3}\right) \quad (3.15)
\]

[Correlation developed from data for nonpolar hydrocarbons]

where:

\[
\frac{1}{T_{ij}^*} = \frac{\epsilon_{ij}}{kT} - 1.6 \omega_{ij} \quad (3-16)
\]

\[
\frac{\epsilon_{ij}}{k} = \text{corrected nonpolar pseudo-interaction energy}
\]

\[
\frac{\epsilon_{ij}}{k} = \left(\frac{\epsilon_{ij}}{k}\right)^' \left[1 - \xi_{ij} c(1)_{ij} \left[1 - \frac{\epsilon_{ij} (1 + c(1)_{ij})}{2}\right]\right] \quad (3.17)
\]

angle averaging correction

(polar contribution removal)
\[
\frac{\varepsilon_{ii}}{k} = T_{c_i} \left\{ 0.748 + 0.91 \omega_{ii} \right\} - T_{c_i} \left\{ \frac{0.4n_{ij}}{2+20 \omega_{ii}} \right\} \quad (3-18)
\]

\[\text{standard form for non-polar components} \quad \text{non-polar components correction}\]

\[
\frac{\varepsilon_{ij}}{k} = \left( \frac{\varepsilon_{ij}}{k} \right)^{\prime} \left( 1 + \xi_{ij} C(1)_{ij} \right) \quad (3-19)
\]

\[\text{angle averaging correction}\]

\[T_{c_i} = \text{Critical temperature}\]

\[P_{c_i} = \text{Critical pressure}\]

\[
\frac{\varepsilon_{ij}}{k} = 0.7 \left[ \left( \frac{\varepsilon_{ij}}{k} \right)^{\prime} \left( \frac{\varepsilon_{jj}}{k} \right)^{\prime} \right]^{1/2} + \left\{ 0.6 \left\{ \frac{1}{1/(\varepsilon_{ii}/k)} + \frac{1}{1/(\varepsilon_{jj}/k)} \right\} \right\} \quad (3-20)
\]

\[\omega_{ii} = \text{nonpolar pseudoacentric factor}\]

\[
\omega_i = 0.006026 R_i^{\prime} + 0.02096 (R_i^{\prime})^2 - 0.001366 (R_i^{\prime})^3 \quad (3-21)
\]

\[R_i^{\prime} = \text{radius of gyration of component i (Å)}\]

\[
\omega_{ij} = \frac{1}{2} \left( \omega_{ii}^{\prime} + \omega_{jj}^{\prime} \right) \quad (3-22)
\]

\[
C(1)_{ij} = \frac{16 + 400 \omega_{ij}^{\prime}}{10 + 400 \omega_{ij}^{\prime}} \quad \text{and} \quad C(1)_{ii} = \frac{16 + 400 \omega_{ii}^{\prime}}{10 + 400 \omega_{ii}^{\prime}} \quad (3-23)
\]

\[\text{angle averaging correction term}\]

\[
\xi_{ii} = 0 \text{ for } \omega_i < 1.45 \quad \text{angle averaging correction term} \quad (3-24)
\]
or

\[
\xi_{ii} = \frac{1.7941 \times 10^7 (\omega_i)^4}{\left[2.882 - \frac{1.882 \omega_i}{0.03 + \omega_i}\right] T_{ci} (\sigma_{ii}^0)^6 (\varepsilon_{ii}/k)^1} \quad \text{for } \omega_i \geq 1.45 \quad (3.25)
\]

\[
\xi_{ij} = \frac{(\omega_i)^2 (\varepsilon_{jj}/k)^{2/3} (\sigma_{ij}^0)^4}{(\varepsilon_{ij}/k)^{1/3} (\sigma_{ij}^0)^6} \quad \text{for } \omega_i \geq 2 \text{ and } \omega_j = 0 \quad (3.26)
\]

or

\[
\xi_{ij} = \frac{(\omega_j)^2 (\varepsilon_{ii}/k)^{2/3} (\sigma_{ij}^0)^4}{(\varepsilon_{ij}/k)^{1/3} (\sigma_{ij}^0)^6} \quad \text{for } \omega_j \geq 2 \text{ and } \omega_i = 0 \quad (3.27)
\]

or

\[
\xi_{ij} = 0 \quad \text{for all other values of } \omega_i, \omega_j \quad (3.28)
\]

\[
b_{o,ij} = 1.26184 (\sigma_{ij}^0)^3 \quad \text{and} \quad b_{o,ii} = 1.26184 (\sigma_{ii}^0)^3 \quad (3.29)
\]

\[\sigma_{ij} = \text{effective nonpolar potential parameter (potential well width, or loosely, molecular size)}\]

\[
\sigma_{ii} = \sigma_{ii}^0 \left(1 + \xi_{ii} C(2)_{ii}\right)^{1/3} \quad (3.30)
\]

angle averaging correction

\[
\sigma_{ii} = (2.44 - \omega_{ii}) \left(1.0133 T_{ci} P_{ci}^{-1}\right)^{1/3} \quad (3.31)
\]

[standard nonpolar molecule, molecule size parameter]

\[
\sigma_{ij}^0 = (\sigma_{ii} \cdot \sigma_{jj})^{1/2} \quad (3.32)
\]

\[
\sigma_{ij} = \sigma_{ij}^0 \left(1 - \xi_{ij} C(2)_{ij}\right) \quad (3.33)
\]
\[ C(2)_{ij} = \frac{3}{10 + 400 \omega_{ij}} \] angle averaging correction term (3-34)

**Free, Polar Contribution:**

\[ B_{ij,\text{Free},\text{Polar}} = -b_{0,ij} \nu_{ij}^{*'} \left( 0.74 - \frac{3.0}{T_{ij}^{*}} + \frac{2.1}{(T_{ij}^{*})^2} + \frac{2.1}{(T_{ij}^{*})^3} \right) \] (3.35)

[empirical correlation developed from polar nonassociating molecule data]

where:

\[ \nu_{ij}^{*'} = \text{empirical correlational parameter for free, polar contribution} \]

\[ \nu_{ij}^{*'} = \nu_{ij} \text{ for } \nu_{ij} < 0.04 \] (3-36)

or \[ \nu_{ij}^{*'} = 0 \text{ for } 0.04 \leq \nu_{ij} < 0.25 \] (3-37)

or \[ \nu_{ij}^{*'} = \nu_{ij} - 0.25 \text{ for } \nu_{ij} \geq 0.25 \] (3-38)

\[ \nu_{ij} = \text{reduced effective dipole moment} \]

\[ \nu_{ij} = \frac{7243.8 \nu_{ij} \nu_{ij}}{(e_{ij}/k)(\sigma_{ij})^3} \] (3-39)

**Metastable and Bound Contributions:**

\[ B_{ij,\text{Metastable}} + B_{ij,\text{Bound}} = b_{0,ij} A_{ij} \exp \left( \frac{\Delta H_{ij}}{(kT/e_{ij})} \right) \] (3-40)

[Deduced from Stockmayer potential function]

where:

\[ A_{ij} = -0.3 - 0.05 \nu_{ij}^{*} \] (3-41)
\[ \Delta H_{ij} = 1.99 + 0.2 (u_{ij}^*)^2 \]  \hspace{1cm} (3-42)

**Associative (Chemical) Contribution:**

\[ B_{ij}^{\text{Associative}} = b_{0,ij} E_{ij} \left[ 1 - \exp \left( \frac{1500 n_{ij}}{T} \right) \right] \]  \hspace{1cm} (3-43)

[Treating association as a reaction at equilibrium]

where:

\[ E_{ij} = \exp \left( n_{ij} \left[ \frac{650}{(e_{ij}/k) + 300} - 4.27 \right] \right) \] for \( n_{ij} < 4.5 \)  \hspace{1cm} (3-44)

or

\[ E_{ij} = \exp \left( n_{ij} \left[ \frac{42,800}{(e_{ij}/k) + 22,400} - 4.27 \right] \right) \] for \( n_{ij} \geq 4.5 \)  \hspace{1cm} (3-45)

(carboxylic acids)

Only six readily available properties are required to use the Hayden-O'Connell correlation. Extensive tables of these properties are provided in the appendices of both *The Properties of Gases and Liquids* (5) and *Computer Calculation for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibrium* (1) as well as in other sources. Where measured properties are not available, predictive methods can be used (5). Required property data for ethanol and water are summarized in Table 3.

**3.4 Alternative correlations**

Alternative relations have been developed to correlate the second virial coefficient for polar systems (12-19). Hayden compares his correlation with those of Nothnagel, Tsonopoulos, Black and Kreglenski. For water and alcohol, the Hayden-O'Connell correlation is superior to all but the equation of Tsonopoulos which requires fitting coefficients. The Hayden-O'Connell correlation is more general and
Table 3
Property Data for Hayden-O'Connell Correlation

<table>
<thead>
<tr>
<th>Property</th>
<th>Ethanol</th>
<th>Cross</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{critical}}$ ($^\circ\text{K}$)</td>
<td>516.26</td>
<td>--</td>
<td>647.37</td>
</tr>
<tr>
<td>$P_{\text{critical}}$ (bar)</td>
<td>63.835</td>
<td>221.20</td>
<td></td>
</tr>
<tr>
<td>Radius of Gyration ($\text{Å}$)</td>
<td>2.250</td>
<td>0.615</td>
<td></td>
</tr>
<tr>
<td>Association Parameter</td>
<td>1.40</td>
<td>1.70</td>
<td></td>
</tr>
<tr>
<td>Solvation Parameter</td>
<td>--</td>
<td>1.55</td>
<td>--</td>
</tr>
<tr>
<td>Dipole Moment (Debye)</td>
<td>1.69</td>
<td>--</td>
<td>1.83</td>
</tr>
</tbody>
</table>

With these units, $B_{ij}$ will be given in cm$^3$/gmole
is the correlation employed in the Prausnitz computer equilibrium calculation package (1). As shown in the following evaluative section, the correlation is excellent.

3.5 Fugacity coefficient computer implementation

In ETOH (the ethanol/water equilibrium package) (Appendix 1), the Hayden-O'Connell correlation is used in determining fugacity coefficients. The virial coefficients are calculated in subroutine TDEP (modeled after subroutine BIJS2 in the more general Prausnitz package (1)), and the fugacity coefficients are calculated in PDEP (modeled after subroutine PHIS2 of Prausnitz). For a printout of the virial and fugacity coefficients, MODE-24 should be set equal to 1 when the ETOH package is called.

3.6 Fugacity correlation--critical evaluation

Second virial coefficients for ethanol and water (but not their mixtures) are available in the literature (20-25). Subroutine TDEP of the ETOH package was used to predict virial coefficients for the ethanol/water system and the results are plotted against measured values in Figure 2. The various contributions to the virial coefficients are presented in Table 4.

Vapor phase P,V,T measurements become very difficult at low pressure (less than 500 mmHg)—corresponding to low temperature. For the data of Kretschmer and Wiebe (20), the authors indicate an expected uncertainty in B of only 5 cm$^3$/g mol at 373 K and above, but an uncertainty of greater than 100 cm$^3$/g mol at 313 K and below. As can be seen in the figure, the correlation agrees well with the data at
Figure 2. Pure component and cross virial coefficients for the system ethanol/water.
Table 4
Second Virial Coefficient Contributions

<table>
<thead>
<tr>
<th>Contributions</th>
<th>Ethanol</th>
<th></th>
<th></th>
<th>Cross</th>
<th></th>
<th></th>
<th>Water</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303.15°K</td>
<td>333.15°K</td>
<td>363.15°K</td>
<td>303.15°K</td>
<td>333.15°K</td>
<td>363.15°K</td>
<td>303.15°K</td>
<td>333.15°K</td>
<td>363.15°K</td>
</tr>
<tr>
<td>( b_{\text{Free}} )</td>
<td>-121.8</td>
<td>-88.6</td>
<td>-62.2</td>
<td>-90.5</td>
<td>-57.2</td>
<td>-33.7</td>
<td>-63.6</td>
<td>-36.6</td>
<td>-18.3</td>
</tr>
<tr>
<td>( b_{D,\text{Metastable+Bound}} )</td>
<td>-450.9</td>
<td>-365.2</td>
<td>-306.4</td>
<td>-243.1</td>
<td>-202.0</td>
<td>-173.1</td>
<td>-245.4</td>
<td>-198.9</td>
<td>-166.9</td>
</tr>
<tr>
<td>( b_{D,\text{Associative}} )</td>
<td>-1400.3</td>
<td>-749.8</td>
<td>-444.9</td>
<td>-1427.3</td>
<td>-715.1</td>
<td>-401.5</td>
<td>-1486.9</td>
<td>-697.0</td>
<td>-370.2</td>
</tr>
<tr>
<td>( B )</td>
<td>-1973.0</td>
<td>-1203.6</td>
<td>-813.5</td>
<td>-1760.9</td>
<td>-974.3</td>
<td>-608.3</td>
<td>-1795.9</td>
<td>-932.5</td>
<td>-555.4</td>
</tr>
</tbody>
</table>
moderate temperature, deviating most at low temperatures where the uncertainty in the data is greatest. Fortunately, the fugacity coefficient varies as exponential (P) and larger errors can be tolerated in the virial coefficients at lower pressure, and hence lower temperature.

At 373°K (the temperature at the base of an atmospheric pressure ethanol/water distillation column) the discrepancies between correlation for $B_{\text{ethanol}}$ and $B_{\text{water}}$ are $-3.10$ and $-19.50$ cm$^3$/gmol. At the respective vapor pressures of the components at these temperatures, these deviations would result in deviations in the fugacity coefficients for the pure components of only $0.0002$ in $0.9487$ and $0.0006$ in $0.9850$, respectively. Even for the point at 313.15°K, where the deviation is the greatest between experiment and correlation, a difference of only $0.0029$ in $0.9854$ results.

Figure 3 shows the plot of ethanol and water fugacity coefficients versus mole fraction ethanol in the vapor phase at various pressures and saturation conditions, as calculated with subroutine PDEP of ETOH. The temperatures 303 through 383°K cover the likely range for ethanol water separation systems, and it is clear from the substantial deviations from ideality ($\phi \neq 1$) that vapor phase nonidealities cannot be neglected. The vapor fugacity coefficient must be considered in any ethanol/water vapor/liquid equilibrium evaluation.

4 Liquid Specific Volumes

4.1 Alternative density formulations

Ethanol and water densities are necessary for design. The specific volume is also required for the Poynting correction to the vapor/liquid
Figure 3. Fugacity coefficients for the system ethanol/water.
equilibrium relation. Use of a general correlation form which can be applied to other components (preferably without fitting new data) is desirable. Numerous corresponding states formulations have been developed including the Tyn and Calus (26), Chueh and Prausnitz (27) Yamada and Gunn (28), and Rackett (29) equations. Spencer and Danner (30) evaluated the various liquid density equations. For nonpolar liquids these equations could predict liquid densities to within from 1 to 5 percent accuracy. Substantially larger errors were found for polar liquids.

To predict accurately polar liquid densities, Spencer and Danner (30) proposed a modification to the Rackett (31) corresponding states formulation, employing a single fitting parameter. This modified Rackett parameter is now tabulated for a large number of fluids (1,31) and it can be estimated knowing only the fluid normal boiling point. The modified Rackett equation is general (applying to both nonpolar and polar fluids) and is the form used in the Prausnitz equilibrium computation package (1).

4.2 The modified Rackett equation

The modified Rackett formulation is given by:

\[ V_i^L = \frac{RT_c}{Z_{R_i}} \left( \frac{P_c}{P_i} \right) \]  

(4-1)

with

\[ \tau = 1 + \left[ 1 - \frac{T}{T_c} \right]^{0.286} \]

for \( T/T_c \leq 0.75 \)

or

\[ 1.6 + 0.00693/\left[ (T/T_c) - 0.655 \right] \]

for \( T/T_c > 0.75 \)
and

\[ \rho_i = \frac{(MW)_i}{(V_1^L)} \]  \hspace{1cm} (4-2)

where

\[ V_1^L = \text{molar volume of pure liquid } i \]
\[ T_{c_i} = \text{critical temperature of } i \]
\[ P_{c_i} = \text{critical pressure of } i \]
\[ R = \text{ideal gas constant} \]
\[ Z_{R_i} = \text{modified Rackett parameter for } i \]
\[ \rho_i = \text{mass density of pure liquid } i \]
\[ (MW)_i = \text{component } i, \text{molecular weight}. \]

For ethanol and water, the modified Rackett parameters given by Spencer and Danner are 0.2520 and 0.2380, respectively.

4.3 Liquid density computer implementation

In ETOH, the modified Rackett formula is used in determining liquid densities in subroutine TDEP (modeled after subroutine MVOL in the Prausnitz package (1)). For a printout of the molar specific volumes MODE-24 should be set equal to 1 when the ETOH package is called.

4.4 Density correlation—critical evaluation

Rackett correlation liquid density predictions are plotted along with measured densities for ethanol (4) and water (32) for temperatures up to near the fluid normal boiling points in Figure 4. The average errors for ethanol and water, respectively, are 0.0188 g/cm³ and 0.0336 g/cm³. For computation of the Poynting corrections to the vapor/liquid equilibrium equation, these accuracies are adequate. Further, the modified Rackett relations retain accuracy at elevated
Figure 4. Rackett liquid density correlation for ethanol and water.
temperature (for up to $T/T_{c_1} = 0.85$) and can be used in the design of supra-atmospheric pressure distillation systems.

For design at ordinary pressure, greater accuracy in the density specification may be necessary. For the temperature range of Figure 4, the simple numerical fits for ethanol (1) and water (33) may be used:

\[
\rho_{\text{ethanol}} = 0.80632 - 0.00085365 (T) - 10^{-8}(T)^2 - 2 \times 10^{-9}(T)^3
\]

\[
\rho_{\text{water}} = 1.0000326 + 2.3459 \times 10^{-5}(T) - 6.1070 \times 10^{-6}(T)^2 + 1.7334 \times 10^{-8}(T)^3
\]

The ethanol density correlation reproduces the data with an average deviation of $\pm 0.00014$. The maximum deviation for the water correlation is $\pm 0.00015$.

5 Vapor Pressures and the Reference Fugacity

5.1 Vapor pressure correlations

Pure component vapor pressures are needed for design and also in establishing the liquid phase reference fugacities for vapor/liquid equilibrium determinations. The variation in pure component vapor pressure with temperature is given by the thermodynamically rigorous Clapeyron equation:

\[
d(ln p_{\text{sat}})/d(1/T) = -\Delta H_{\text{vap}}/R(Z_{\text{vap}} - Z_{\text{liq}})
\]

where:
Numerous vapor pressure correlations have been developed based on differing assumptions for the terms $\Delta H_{vap}$ and $(Z_{vap} - Z_{liq})$ (not generally known a priori as functions of temperature) (34-36). A detailed review is provided by Miller (37).

A particularly simple solution to the Clapeyron equation (good over relatively small range of $T$) is the Antoine equation (38):

$$\ln P_{\text{sat}} = A - \frac{B}{C + T}$$  \hspace{1cm} (5-2)

Predictive methods have been devised for the Antoine constants ($A, B, C$), but these are best fit directly to experimental data (39).

5.2 Antoine correlation--critical evaluation

Antoine constants for ethanol and water at normal temperatures are given in Table 5. Figure 5 compares the correlation with the experimentally measured vapor pressure of Ambrose and Sprake (ethanol) (41) and the steam tables (water) (42). In both cases the fit is excellent and further refinements of the equations are not necessary. Antoine constants are also tabulated for most other typical solvents (5).
Table 5

Antoine Constants for Ethanol and Water

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp. Range</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>0-100°C</td>
<td>18.91198</td>
<td>3803.99</td>
<td>231.48</td>
</tr>
<tr>
<td>Water</td>
<td>0-60°C</td>
<td>18.66855</td>
<td>4030.182</td>
<td>235.0</td>
</tr>
<tr>
<td>Water</td>
<td>60-150°C</td>
<td>18.34426</td>
<td>3841.20</td>
<td>228.0</td>
</tr>
</tbody>
</table>

For $\ln P_{sat} = A - \frac{B}{C+T}$, \( P_{sat} \equiv \text{mm Hg} \), \( T \equiv ^\circ C \)

References 4, 5, 40.
Figure 5. Antoine vapor pressure correlation for ethanol and water.
5.3 Zero pressure reference fugacity derivation

The general relation for vapor/liquid equilibrium may be expressed as:

\[ Y_i \phi_i p_{\text{total}} = [X_i \gamma_i (T, p_{\text{ref}}) f_{i, \text{0,liquid,pref}}] \exp[(p_{\text{total}} - p_{\text{pref}}) V_{i, \text{liq}}/(RT)] \] (5-3)

where:

\( \gamma_i (T, p_{\text{pref}}) \) = liquid phase activity coefficient of component at system temperature evaluated at reference pressure.

\( f_{i, \text{0,liquid,pref}} \) = reference fugacity for component i in the liquid at the standard state conditions \((T, p_{\text{pref}})\) of the activity coefficient.

A particularly convenient choice of reference pressure is \( p_{\text{pref}} = 0 \). This simplifies the Poynting correction term to:

\[ \text{Poynting correction} = \exp[(p_{\text{total}} V_{i, \text{liq}})/(RT)] \] (for \( p_{\text{pref}} = 0 \)) (5-4)

For this choice of reference pressure, it then follows (setting \( X_i = Y_i = \gamma_i = 1 \)) that:

\[ f_{i, \text{0,liquid}} = P_{i, \text{sat}} \phi_i \exp[-(P_{i, \text{sat}} V_{i, \text{liq}})/(RT)] \] (5-5)

where:
### 5.4 Zero pressure reference fugacity correlation

Having developed expressions for $P_{i}^{\text{sat}}$, $\phi_{i}^{\text{sat}}$ and $V_{i}^{\text{liquid}}$ for ethanol and water, we can evaluate the zero pressure reference fugacity. For computational efficiency, Prausnitz has fit the reference fugacity directly to the form:

\[
\ln f_{i}^{0,\text{liq}} = (C_{1,i}) + [(C_{2,i})/(T)] + [(C_{3,i})(T)] + \\
[(C_{4,i})(\ln T)] + [(C_{5,i})(T^2)]
\] (5-6)

In the normal temperature range, this numerical fit is equivalent to evaluation of $f_{i}^{0,\text{liq}}$ according to equation 5-5. Further, at high pressures, the Lyckman correlation (43) was used to predict values of $P_{i}^{\text{sat}}$ to insure reasonable values for $f_{i}^{0,\text{liq}}$ up to $T/(T_{c,i}) = 1.8$. Extensive tables of constants for equation 5-6 have been compiled (6) and values for ethanol and water are presented in Table 6.

### 5.5 Reference fugacity--computer implementation

In ETOH (Appendix 1), the reference fugacities are computed in subroutine TDEP (modeled after subroutine PURF in the Prausnitz package (1)). Pure component vapor pressures can be generated using ETOH by calling BDPT with $X_1 = 1$ (ethanol) or $X_1 = 0$ (water).
Table 6
Zero Pressure Reference Fugacity Equation Constants

<table>
<thead>
<tr>
<th></th>
<th>Ethanol</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \ln f_i^{0, \text{liquid}} )</td>
<td>( = c_1 + \frac{c_2}{T} + c_3 i + c_4 i T + c_5 i T^2 )</td>
<td></td>
</tr>
<tr>
<td>( c_1 )</td>
<td>-90.909919</td>
<td>57.041588</td>
</tr>
<tr>
<td>( c_2 )</td>
<td>-3465.8735</td>
<td>-7004.8416</td>
</tr>
<tr>
<td>( c_3 )</td>
<td>-0.062301392</td>
<td>0.0035888444</td>
</tr>
<tr>
<td>( c_4 )</td>
<td>20.486493</td>
<td>-6.66893878</td>
</tr>
<tr>
<td>( c_5 )</td>
<td>( 2.0664221 \times 10^{-5} )</td>
<td>( -8.5054287 \times 10^{-7} )</td>
</tr>
</tbody>
</table>
5.6 Reference fugacity correlation—critical evaluation

Pure component vapor pressures generated by the ETOH package are presented in Table 7. The agreement with measured values (see Fig. 5) is excellent.

6 Vapor/Liquid Equilibrium: The Activity Coefficient

6.1 Hydrogen bonding and liquid phase nonidealities

The hydroxyl group is dominant in imparting many of ethanol's anomalous physical properties. Polarizability and hydrogen bonding result from the small size and dominant hydroxyl group of the molecule. These effects are most evident in the liquid phase where ethanol is largely dimerized by hydrogen bonding (44). Hydrogen bonding is even stronger in water, and water molecules associate in the liquid phase in ordered groupings of typically five molecules (45). Abnormally high boiling point, heat of vaporization and entropy of vaporization are all manifestations of the strong associations of ethanol and water.

The unusual vapor/liquid equilibrium behavior of ethanol/water mixtures is also largely attributable to liquid phase nonidealities resulting from molecular association effects (100). As either ethanol is added to pure water, or water to ethanol, the ordered molecular grouping of the pure fluids is disrupted and new orderings formed. Association effects lead to the formation of the ethanol/water azeotrope (as well as azeotropes between ethanol and other solvents).

It is beyond the capability of present day statistical mechanics liquid phase perturbation theories to account quantitatively for the complex association effects observed for ethanol/water mixtures (46).
Table 7

Computer Generated Pure Component Vapor Pressures

<table>
<thead>
<tr>
<th>ETHANOL</th>
<th>WATER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (mm Hg)</td>
<td>Temperature (°K)</td>
</tr>
<tr>
<td>19.0758</td>
<td>280.0</td>
</tr>
<tr>
<td>26.4653</td>
<td>285.0</td>
</tr>
<tr>
<td>36.2567</td>
<td>290.0</td>
</tr>
<tr>
<td>49.0775</td>
<td>295.0</td>
</tr>
<tr>
<td>65.6764</td>
<td>300.0</td>
</tr>
<tr>
<td>86.9375</td>
<td>305.0</td>
</tr>
<tr>
<td>113.8932</td>
<td>310.0</td>
</tr>
<tr>
<td>147.7385</td>
<td>315.0</td>
</tr>
<tr>
<td>189.8427</td>
<td>320.0</td>
</tr>
<tr>
<td>241.7622</td>
<td>325.0</td>
</tr>
<tr>
<td>305.2504</td>
<td>330.0</td>
</tr>
<tr>
<td>382.2682</td>
<td>335.0</td>
</tr>
<tr>
<td>474.9915</td>
<td>340.0</td>
</tr>
<tr>
<td>585.8183</td>
<td>345.0</td>
</tr>
<tr>
<td>717.3739</td>
<td>350.0</td>
</tr>
<tr>
<td>872.5146</td>
<td>355.0</td>
</tr>
<tr>
<td>1054.330</td>
<td>360.0</td>
</tr>
<tr>
<td>1266.145</td>
<td>365.0</td>
</tr>
</tbody>
</table>
To predict vapor/liquid equilibrium behavior, therefore, we must rely on well based liquid phase models with constants fit to accurate equilibrium data.

6.2 Ethanol/water equilibrium data evaluation

The ethanol/water system has been extensively studied and many vapor/liquid equilibrium data are available in the literature (see Tables 8 and 9 for a compilation of data sources). Often, though, the literature data are highly scattered and the data of different researchers are in disagreement. Before an equilibrium model can be developed, accurate data must be selected and faulty data removed.

The Gibbs-Duhem relation (eq. 6-1) (70) is a rigorous thermodynamic relationship between the activity coefficients of all components in a mixture and, hence, must be obeyed by correct ethanol/water equilibrium data.

$$\left[ \frac{\Delta H^E}{R(T)^2} \cdot dT \right] - \left[ \frac{\Delta V^E}{RT} \cdot dP \right] + \sum_{i} x_i \frac{d \ln \gamma_i}{d T} = 0 \tag{6-1}$$

where $\Delta H^E$ and $\Delta V^E$ are the excess heat and volume of mixing, respectively. An integral (area) test of equilibrium data can be developed from the Gibbs-Duhem relation for isothermal or isobaric data sets (71,72). The criteria for thermodynamic consistency of binary equilibrium data are then:

For Isobaric data sets:

$$\int_{0}^{1} \ln \frac{\gamma_1}{\gamma_2} \, dx = \int_{x_1=0}^{x_1=1} \frac{\Delta H^E}{RT^2} \, dT \tag{6-2}$$
Table 8
Ethanol/Water Equilibrium Data Sources
Constant Temperature

<table>
<thead>
<tr>
<th>Researchers</th>
<th>Date</th>
<th>Temperature (°K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dulitskaya</td>
<td>1945</td>
<td>323.15</td>
<td>47</td>
</tr>
<tr>
<td>Jones, Shoenborn, Colburn</td>
<td>1943</td>
<td>323.15, 333.15</td>
<td>48</td>
</tr>
<tr>
<td>Dornte</td>
<td>1929</td>
<td>298.15</td>
<td>49</td>
</tr>
<tr>
<td>Udovenko, Fatkulina</td>
<td>1952</td>
<td>313.15, 323.15, 333.15</td>
<td>50</td>
</tr>
<tr>
<td>Wrewski</td>
<td>1939</td>
<td>312.91, 327.96, 347.94</td>
<td>51</td>
</tr>
<tr>
<td>Pemberton, Mash</td>
<td>1977</td>
<td>303.15, 323.15, 343.15, 363.15</td>
<td>52</td>
</tr>
<tr>
<td>Mertl</td>
<td>1972</td>
<td>313.15, 328.15, 343.15</td>
<td>53</td>
</tr>
<tr>
<td>Goller, Wicke</td>
<td>1947</td>
<td>283.15, 288.15, 293.15, 298.15</td>
<td>54</td>
</tr>
<tr>
<td>Nikolskaya</td>
<td>1946</td>
<td>298.15, 323.15, 348.15</td>
<td>55</td>
</tr>
<tr>
<td>Linderstroem-Lang, Vaslow</td>
<td>1968</td>
<td>298.17</td>
<td>56</td>
</tr>
<tr>
<td>d'Avila, Silva</td>
<td>1970</td>
<td>283.15, 288.15, 293.15, 298.15, 303.15</td>
<td>57</td>
</tr>
<tr>
<td>Bar-David, Dodge</td>
<td>1959</td>
<td>423.15, 473.15, 523.15</td>
<td>58</td>
</tr>
</tbody>
</table>
Table 9
Ethanol/Water Equilibrium Data Sources
Constant Pressure

<table>
<thead>
<tr>
<th>Researchers</th>
<th>Date</th>
<th>Pressure (mm Hg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beebe, Coulter, Lindsay, Baker</td>
<td>1942</td>
<td>95, 190, 380, 760</td>
<td>59</td>
</tr>
<tr>
<td>Carey, Lewis</td>
<td>1932</td>
<td>760</td>
<td>60</td>
</tr>
<tr>
<td>Dalager</td>
<td>1969</td>
<td>760</td>
<td>61</td>
</tr>
<tr>
<td>Jones, Shoeborn, Colburn</td>
<td>1943</td>
<td>760</td>
<td>48</td>
</tr>
<tr>
<td>Kauer, Bittrich</td>
<td>1968</td>
<td>760</td>
<td>62</td>
</tr>
<tr>
<td>Svoboda, Hynek, Pick</td>
<td>1968</td>
<td>745</td>
<td>63</td>
</tr>
<tr>
<td>Kirschbaum, Gerstner</td>
<td>1939</td>
<td>50, 100, 250, 500, 740, 760</td>
<td>64</td>
</tr>
<tr>
<td>Novella, Tarraso</td>
<td>1952</td>
<td>760</td>
<td>65</td>
</tr>
<tr>
<td>Rius</td>
<td>1959</td>
<td>706</td>
<td>66</td>
</tr>
<tr>
<td>Carey, Lewis</td>
<td>1932</td>
<td>760</td>
<td>67</td>
</tr>
<tr>
<td>Stabnikov, Matyushev, Protsyuk, Yushchenko</td>
<td>1972</td>
<td>380, 760</td>
<td>68</td>
</tr>
<tr>
<td>Otsuki, Williams</td>
<td>1953</td>
<td>760</td>
<td>69</td>
</tr>
</tbody>
</table>
For Isothermal data sets:

\[
\int_{0}^{1} \ln \frac{\gamma_1}{\gamma_2} \, dx_1 = \int_{x_1=0}^{x_1=1} \frac{\Delta V^E}{RT} \, dP
\]  

(6-3)

\(\Delta H^E\) is not a priori known as a function of composition for the ethanol/water system, hence, for the isobaric equation, no simplifications can be made and isobaric data can not be readily tested for thermodynamic consistency (72). For isothermal data sets, however, the second integral can be approximated to zero with great confidence as \(\Delta V^E\) is extremely small compared to \(RT\).

Given the correlations thus far developed for the vapor phase fugacity coefficients \((\phi_i)\) and for the zero pressure reference fugacities \((f_i^0, \text{ref})\), \(\gamma_i\) can be evaluated according to:

\[
\gamma_i = \frac{Y_i \phi_i p_{\text{total}}}{X_i f_i^0, \text{ref}}
\]  

(6-4)

The thermodynamic consistency of individual data sets can then be tested by trapezoidal rule integration of equation 6-3 in the simplified form of equation 6-5 and expressing the activity coefficients as in equation 5 using the reported composition \((X, Y)\), pressure \((P)\) and temperature \((T)\) data.

\[
\sum_{n=2}^{N} \frac{1}{2} \left[ \ln \frac{\gamma_1}{\gamma_2}_n + \ln \frac{\gamma_1}{\gamma_2}_{n-1} \right] x \left[ X_n - X_{n-1} \right] = A
\]  

(6-5)

where:
N = number of data points beginning at $x_1 = 0$ and going to $x_1 = 1$

The sum in equation 6-5 should ideally equal zero, and Prausnitz suggests $|A| < 0.02$ for the consistency criterion (70).

Consistency with the Gibbs-Duhem relation is a necessary, but not sufficient condition for determining the validity of equilibrium data sets. Further, the integral test described tests only whole data sets and cannot distinguish individual faulty data points (Van Ness, Byer and Gibbs have devised a far more complex test for specific points within a data set (73,74)).

Given the limitations of the consistency test, it was used as an initial screening tool to eliminate obviously faulty data sets and select passing sets for further evaluation. The test was performed using program CONTEST (Appendix 2). Figure 6 shows graphically the integration of equation 6-5 for the data of Pemberton and Mash (52). The difference in areas above and below the $\ln (y_1/y_2) = 0$ line is only $A = 0.0026$ and these data were chosen for further evaluation. For Figure 7 (data of Jones, Shoenborn and Colburn (48)) the difference in area is $A = -0.0419$ and the data are scattered. This second data set was eliminated.

The Pemberton-Mash data were collected at the British National Physical Laboratory in 1977 using a sophisticated static equilibrium cell measuring device. The researchers claim accuracies as follows:

1) Temperature to within $\pm 1\, \text{m}^\circ\text{K}$
2) Pressure to the greater of $\pm 0.02$ percent or $\pm 2.6\, \text{Pa}$.
3) Composition to $\pm 0.046$ percent.
Figure 6. Thermodynamic consistency test of the equilibrium data of Pemberton and Mash.


\[ A = [A_1 - A_2] = 0.0026 \]

\[ \ln \left( \frac{\gamma_{\text{Ethanol}}}{\gamma_{\text{water}}} \right) \]

\[ x_{\text{Ethanol}} \]

\[ A_1 \]

\[ A_2 \]
Figure 7. Thermodynamic consistency test of the equilibrium data of Jones, Schoenborn and Colburn.

Jones, Schoenborn, Colburn - Ind. Eng. Chem., 35, 666 (1943)

$323.15 \text{ K}$

$A = [A_1 - A_2] = 0.0419$
Isothermal data was taken for pure ethanol and water plus 24 intermediate concentrations. Data were taken covering the required range of temperatures and pressures.

The data of Pemberton and Mash were chosen for use in developing the activity coefficient model.

6.3 The activity coefficient: models for the excess Gibbs energy

The Gibbs Duhem relation constrains the choice of models for vapor liquid equilibria. Any mathematical representation for the activity coefficients must be consistent with:

$$\sum X_i \ln \gamma_i = 0 \text{ (at constant } T, P)$$  \hspace{1cm} (6-6)

The excess Gibbs energy of mixing is given by:

$$G^E = RT \sum_i X_i \ln \gamma_i$$  \hspace{1cm} (6-7)

so that for a binary system:

$$RT \ln \gamma_1 = G^E + X_2 \left[ \frac{\partial G^E}{\partial X_1} \right]_{T,P}$$

$$RT \ln \gamma_2 = G^E - X_1 \left[ \frac{\partial G^E}{\partial X_1} \right]_{T,P}$$  \hspace{1cm} (6-8)

These relations provide the necessary link to statistical mechanics theories which can be used to model the activity coefficients. Any molecular interaction model for the Gibbs energy (consistent with equation 6-6) can be used to correlate liquid phase activity coefficients.
Common models for the excess Gibbs energy are summarized by Gmehling and Onken (75). As an initial screening, the equilibrium data fitting program of Anderson (1,76) (after some modification to allow handling of larger data sets) was used to fit two and three parameter Wilson (77), NRTL (78), and UNIQUAC (79), and two parameter Van Laar (80) and Margules (81) models to correlate an isothermal ethanol/water data set (see Figure 8). All of these models, except the two parameter NRTL and Margules, were sufficiently flexible to fit the data (including predicting the azeotrope). Of these models, the UNIQUAC equation is based on the most fully developed molecular interaction theory, and in fact, the UNIQUAC model can be shown to reduce to the other models upon appropriate simplifying assumptions (79).

The UNIQUAC, Wilson, and NRTL equations share the advantage that they can predict multicomponent equilibria using only binary fit parameters. The Wilson and UNIQUAC equations have the further advantage that group contribution theories have been developed to allow the prediction of the necessary binary parameters when experimental data are lacking (this could be important, for instance, in establishing a preliminary screening program for solvents to be used in an ethanol extraction scheme). Finally, the UNIQUAC (but not the Wilson) model can predict miscibility gaps (again important in extraction system design). Based on these considerations, the UNIQUAC equation was chosen for modeling the ethanol/water activity coefficients.

6.4 The UNIQUAC model

The derivation of the UNIQUAC model is described by Maurer and Prausnitz (82). The UNIQUAC activity equation is based on an extension
Figure 8. Comparison of various models in fitting isothermal ethanol/water equilibrium data.
of Guggenheim's statistical mechanics model (83) to assess the excess Helmholtz energy of mixing at constant temperature and volume, which (for nonelectrolyte solutions) can substitute for the excess Gibbs free energy at constant temperature and pressure, and hence yield the activity (84). The liquid is envisioned as a three dimensional lattice of molecular segments with nearest neighbor interactions and described by a partition function. Large molecules may have many segments filling several lattice sites and the number of nearest interacting neighbors is related to the lattice coordination number (Z), the molecular volume (r_i), and molecular surface area (q_i). Z is generally chosen equal to 10. The molecular size parameters (r_i and q_i) can be determined from pure component data for van der Waals volume and surface area (85) and are tabulated for most common molecules (1). The model, in addition, accounts for nonathermal mixing by considering the local average environment of each molecule type rather than the overall average molar concentration (following Scott (86)). The local compositions (x_{ij}) are related to the overall composition (X_i) through Boltzmann type factors. This recognizes the tendency, for instance, of similar molecules (all polar or all nonpolar) to group (and interact) together, and of dissimilar molecular species to separate. Thus, the model considers molecular interactions on the microscopic scale at which they take place. These cross species interactions are given by two binary energy parameters for each pair of species, and these adjustable parameters must be determined by fitting experimental vapor/liquid equilibrium data.
When the UNIQUAC equation for the excess Gibbs energy is differentiated according to equation 6-8, the desired relation for the activity coefficients results. The activity coefficient is made up by two contributions (equation 6-9) with molecular size and shape differences lumped in the combinatorial part and energetic interactions lumped in the residual. \( \phi_i \) and \( \epsilon_i \) represent the volume and surface area fractions, respectively, for component \( i \). \( \epsilon_i \) is a modified surface area fraction over which the energetic interactions operate (as introduced by Anderson (87)). For most molecules, \( \epsilon_i = \epsilon_i' \) but for water and alcohols, the small hydroxyl group dominates the energetic interaction so that the apparent surface of energetic interaction \( q'_{21} \) is smaller than the actual molecular surface area \( q_{21} \).

\[
\ln \gamma_i = \ln \gamma_i^{\text{combinatorial}} + \ln \gamma_i^{\text{residual}} \\
\ln \gamma_1 = \ln \frac{\phi_2}{x_1} + \frac{7}{2} q_2 \ln \frac{\phi_1}{\phi_2} + \phi_2 (\epsilon_1 - \frac{r_1}{r_2}) + C q_1 \left[ - \ln (\epsilon_1' + \epsilon_2') + \frac{\phi_2^{T_21}}{\epsilon_1' + \epsilon_2' - \frac{\phi_1^{T_12}}{\epsilon_1' + \epsilon_2'}} - \frac{\phi_2^{T_12}}{\epsilon_2' + \epsilon_1^{T_12}} \right] \\
\ln \gamma_2 = \ln \frac{\phi_2}{x_2} + \frac{7}{2} q_2 \ln \frac{\phi_2}{\phi_2} + \phi_2 (\epsilon_2 - \frac{r_2}{r_1}) + C q_2 \left[ - \ln (\epsilon_2' + \epsilon_1') + \frac{\phi_1^{T_12}}{\epsilon_2' + \epsilon_1^{T_12}} - \frac{\phi_1^{T_12}}{\epsilon_1' + \epsilon_2^{T_21}} \right]
\]

where:
\[ \varepsilon_1 = \frac{Z}{2} (r_1 - q_1) - (r_1 - 1) \]
\[ \varepsilon_2 = \frac{Z}{2} (r_2 - q_2) - (r_2 - 1) \]

\[ \phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \quad \phi_2 = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2} \]

\[ \phi_1' = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2} \quad \phi_2' = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2} \]

\[ \phi_1'' = \left[ \phi_1'' \tau_{12} \right] / \left[ \phi_2'' + \phi_1'' (\tau_{12}) \right] \]

and where (for the ethanol water system):

- \( Z \) (coordination number) = 10
- \( r_1 \) (ethanol structural size parameter) = 2.11
- \( r_2 \) (water structural size parameter) = 0.92
- \( q_1 \) (ethanol structural area parameter) = 1.97
- \( q_2 \) (water structural area parameter) = 1.40
- \( q_1' \) (ethanol modified area parameter) = 0.92
- \( q_2' \) (water modified area parameter) = 1.00

\( \tau_{12} \) and \( \tau_{21} \) are the UNIQUAC parameters. The major temperature dependence of these parameters can be removed if they are expressed as
\[ \tau_{12} = \exp \left( \frac{-\Delta U_{12}}{CRT} \right) \]
\[ \tau_{21} = \exp \left( \frac{-\Delta U_{21}}{CRT} \right) \]  

\( \Delta U_{12}/R \) and \( \Delta U_{21}/R \) are then the final parameters which are found by fitting equilibrium data.

C is the UNIQUAC third parameter—set equal to one according to the original development (yielding the two parameter UNIQUAC equation), but allowed to vary (remaining positive) in the modification of Maurer (82).

6.5 A temperature dependent extension of UNIQUAC—fitting the ethanol/water system

As can be seen in Fig. 8, the two parameter UNIQUAC equation can accurately represent isothermal ethanol/water equilibrium behavior at 323.15°K. To correctly predict the variation of important equilibrium properties (such as azeotrope composition) with pressure, however, the basic UNIQUAC model must be extended to incorporate temperature dependence in the UNIQUAC parameters.

The basic thermodynamic relationship for the variation of activity coefficient with temperature is:

\[ \left( \sum_{i=1}^{m} x_i \ln \gamma_i \right)_{p,x} = - \frac{H^E}{RT^2} \]  

and

\[ \sum_{i=1}^{m} x_i \ln \gamma_i \]

(6-17)
\[
\left( a \left( \sum_{i=1}^{m} x_i \ln \gamma_i \right) \right)_{P,X} = \frac{-S^E}{R}
\]

where \( H^E \) is the excess heat of mixing and \( S^E \) is the excess entropy of mixing. For the ethanol/water system, the heat of mixing is a complex function of temperature and pressure (see section 7) and neither an athermal solution (\( H^E = 0 \) so that \( \ln \gamma_i \) is independent of \( T \)) or a regular solution (\( S^E = 0 \) so that \( \ln \gamma_i \propto \frac{1}{T} \)) simplification can be applied.

Prausnitz (1) suggests that where the temperature dependence of activity coefficients cannot be neglected, the dependence can often be accounted for by representing the characteristic energies in the form:

\[
\Delta U_{12} = a_{12} + \frac{b_{12}}{T}
\]

(6-18)
Thomsen (88), however, has tested several systems using:

\[
\Delta U_{12} = a_{12} + \frac{b_{12}}{\sqrt{T}}
\]

(6-19)
\[
\Delta U_{12} = a_{12}T
\]

(6-20)
\[
\Delta U_{12} = a_{12} \exp(b/T)
\]

(6-21)
as well as equation 6-18. All these forms gave similar improvement in the overall equilibrium correlation.
To find the temperature dependence of the activity coefficients for the ethanol/water system, rather than \textit{a priori} assuming a possibly too restrictive form for the UNIQUAC interaction energy parameters, the Pemberton data was used to fit the UNIQUAC equation at six temperatures (298.15, 303.15, 323.15, 343.15, 363.15, 383.15°K) corresponding to the pressure range 60 to 1070 mm Hg. The resulting values of $(\Delta U_{12}/R)$ and $(\Delta U_{21}/R)$ are shown vs temperature in Figure 9. Both parameters vary smoothly over the range studied. $\Delta U_{21}$ could be fit approximately in the form of equation 6-18, but $\Delta U_{12}$ is better fit in a parabolic form. A five term polynomial expansion was chosen to fit both $\Delta U_{12}$ and $\Delta U_{21}$ (equations 22 and 23) through the range of interest. This polynomial can fit both interaction energy forms quite accurately and is readily differentiated (this is advantageous in calculating the heat of mixing as in section 7.3).

\begin{align*}
\Delta U_{12}/R &= -10845.010853 + 144.454638358(T) \\
&\quad -0.69258910446(T)^2 + 0.00143459625212(T)^3 \\
&\quad -1.096233611 \times 10^{-6} (T)^4 \quad (6-22) \\

\Delta U_{21}/R &= 38765.541772 - 475.052110708(T) \\
&\quad + 2.14108540923(T)^2 - 0.00420316593674(T)^3 \\
&\quad + 3.054583612 \times 10^{-6} (T)^4 \quad (6-23)
\end{align*}
Figure 9. Temperature dependence of the UNIQUAC interaction energy parameters for the system ethanol/water.
6.6 Ethanol/water equilibrium model—computer implementation and critical evaluation

The overall model for pure ethanol/water vapor/liquid equilibrium is given by the general relation

$$y_i \phi_i \rho_{total} = x_i \gamma_i f_i^0 \text{liquid} \exp \left( \frac{P_{total} V_i \text{liq}}{RT} \right) \quad (6-24)$$

$\phi_i$, $V_i \text{liq}$ and $f_i^0 \text{liq}$ are given by the correlations of sections 3, 4, and 5. The modified (temperature dependent) UNIQUAC equation for $\gamma_i$ provides the final necessary relation.

Subroutine TXDEP of the ETOH program (based on ACTIV2 of the Prausnitz package (1)) calculates the activity coefficients. Subroutine BDPTM is a driver routine which calls the other subroutines of the ETOH package (Appendix 1) using equation 6-24 to make bubble and dew-point calculations. (For the ethanol/water system, given any two of $P$, $T$, $X$, $Y$, the other two are found).

A telling test of the overall equilibrium model is the prediction of isobaric data. The model was developed from isothermal data sets while a single isobaric data set covers a range of temperatures.

Figures 10 through 22 compare model predictions with data for the ethanol/water vapor/liquid equilibrium at various pressures from 50 mmHg to 760 mmHg. At the higher pressures agreement is excellent. At low pressures, there is some discrepancy between the data of Kirschbaum (64) and the data of Beebe (59). The Kirschbaum data are in good agreement with the data of other researchers at higher pressures. The equilibrium model accurately predicts the low pressure equilibrium behavior as given by Kirschbaum.
Figure 10. UNIQUAC model fit to ethanol/water equilibrium data.
Figure 11.

P = 760 (mm of Hg)

2-Parameter UNIQUAC Fit
Jones, Shoenborn and Colburn
Ind. Eng. Chem. 35, 666 (1943)
Figure 12.

2-Parameter UNIQUAC Fit

J.S. Carey and W.K. Lewis
Ind. Eng. Chem. 24, 892 (1932)

\[ P = 760 \text{ (mm of Hg)} \]
Figure 13.

2-Parameter UNIQUAC Fit
E.C. Novella and J.M. Tarraso
An. de Fisica y Quimica 488, 397 (1952)
Figure 14.

2-Parameter UNIQUAC Fit
Svoboda, Hynek and Pick

$P = 745$ (mm of Hg)
Figure 15:

Gas Mole Fraction of Ethanol

Liquid Mole Fraction of Ethanol

P = 740 (mm of Hg)

2-Parameter UNIQUAC Fit

E. Kirschbaum and F. Gerstner

Verfahrenstechnik 1, 10 (1939)
Figure 16.

2-Parameter UNIQUAC Fit
E. Kirschbaum and F. Gerstner
Verfahrenstechnik 1, 10 (1939)
Figure 17.

2-Parameter UNIQUAC Fit
Beebe, Coulter, Lindsay and Baker
Ind. Eng. Chem. 34, 1501 (1942)
Figure 18.
Figure 19.
P = 100 (mm of Hg)

2-Parameter UNIQUAC Fit
E. Kirschbaum and F. Gerstner
Verfahrenstechnik, 1, 10 (1939)

Figure 20.
Figure 21.
Figure 22.

P = 50 (mm of Hg)

Gas Mole Fraction of Ethanol

Liquid Mole Fraction of Ethanol

2-Parameter UNIQUAC Fit
E. Kirschbaum and F. Gerstner
Verfahrenstechnik I, 10 (1939)
An even more difficult test of the model is its ability to predict the variation in the azeotrope composition with pressure. Figure 23 shows the model prediction compared with the data of Pemberton and Mash (52), and the data of Beebe (59). The Pemberton-Mash data are more reliable. The model accurately predicts the azeotropic composition down to about 200 mmHg but does not predict the disappearance of the azeotrope at very low pressures. Figures 24 and 25 show the predicted equilibrium curves at 50 and 100 mmHg expanded near the azeotropic composition. The curves closely follow the data of Kirschbaum (64) (differing by less than 0.001 mole fraction), but in this region the curves are almost parallel to the \( Y = X \) line and very small errors in the equilibrium prediction can give a large apparent error in prediction of the azeotrope composition.

The equilibrium model closely predicts the slope of the data curves in the range from \( X = 0.70 \) to \( 0.85 \) mole fraction. This is crucial for prediction of the required reflux ratio in an ethanol/water distillation and for this purpose, as well as for generating plate counts for column design, this model is quite satisfactory.

6.7 Further improvements to the equilibrium model

The ethanol/water equilibrium model described, provides the necessary accuracy for detailed separation process design. For specific applications (such as predicting the exact variation in azeotropic composition with pressure) further improvements are necessary.
Figure 23. Effect of pressure on ethanol/water azeotrope composition.
Figure 24. UNIQUAC model prediction of ethanol/water equilibrium for high ethanol concentration.
Figure 25.

E. Kirschbaum, F. Gerstner
Verfahrenstechnik I, 10 (1939)
To predict the disappearance of the azeotrope at low pressure, the temperature versus UNIQUAC parameter correlation could be continued down to lower temperatures (the data of d'Avila and Silva (57) could be used down to 283.15°K). Likewise, the correlation could be extended to predict high pressure equilibrium behavior (correlating the UNIQUAC parameters with the data of Bar-David and Dodge (58)).

Another means to improve the activity coefficient correlation is to apply the extended three parameter UNIQUAC form (C not held fixed at C = 1.0). Using the same strategy as in establishing the two parameter correlation, isothermal data were independently fit at six temperatures. The resulting three coefficients are plotted versus temperature in Figures 26, 27 and 28. Maurer (82) suggests that for a given system the third parameter should be reasonably stable, with a value of C = 0.7 giving improvement for most systems over C = 1.0. It was hoped that a single optimal value of C could be found for the ethanol/water system, but C varies widely with temperatures (from 0.47 to 1.89). Further, \( \Delta U_{12}/R \) no longer varies smoothly with temperature.

Accepting the UNIQUAC third parameter as temperature dependent, the variation in the three parameters with temperature can be fit approximately by:

\[
\Delta U_{12}/R = -89.328445 + 24.275419 \beta + 68.69882 \beta^2 + 14.59371 \beta^3 - 10.421989 \beta^4 - 4.5220483 \beta^5
\]  

(6.25)
Figure 26. Parameter 1

Parameter 2

Parameter 3

Temperature dependence for the three parameter UNIQUAC model.
\[ \Delta U_{21}/R = 327.38164 + 198.60022 \beta + 152.99377 \beta^2 \]
\[ - 8.512191 \beta^3 - 58.20737 \beta^4 + 0.75478520 \beta^5 \]
\[ + 7.0619251 \beta^6 \]

\[ C = 1.3325301 - 0.76270750 \beta - 0.32100718 \beta^2 \]
\[ + 0.22672759 \beta^3 + 0.13847213 \beta^4 - 0.03136680 \beta^5 \]
\[ - 0.01708429 \beta^6 \]

with \( \beta = -16.030588 + 0.04705824 T \)

\( T \equiv \text{°K} \)

The temperature dependent three parameter model does predict the disappearance of the azeotrope (at \( P \approx 50 \text{ mmHg} \)) but spurious maxima in the azeotrope versus temperature correlation also result. The overall improvement in the correlation is marginal. A further difficulty with the three parameter model is that no longer can binary parameters be used in predicting multicomponent phase equilibria. This is a major handicap as the correlations of section 9 cannot be applied with the three parameter equation to predict the equilibrium behavior in the presence of fermentation by-products or added extractive agents. For these reasons, the two parameter correlation should be preferred.

7 Thermal Properties – Vapor and Liquid Enthalpies

7.1 Enthalpy path relations

The enthalpy (like the other fundamental thermodynamic relations) is a state function. Any path may be used in relating the enthalpies
of two end states. One convenient method for the correlation of enthalpies is to refer all enthalpies to an ideal state. Paths are then chosen whereby the various nonideal contributions are added to reach the final real state.

7.2 Gas phase enthalpies: $C^0_p$ and virial corrections

Pure component gasses at 0°C (273.15°K) and zero pressure (i.e., the ideal gas state at 0°C) is chosen as the standard state. To represent the enthalpy of an actual gas relative to this ideal standard state, path terms can be summed for the effect of temperature (still at zero pressure) and then for the effects of pressure and for mixing effects in multicomponent systems. The temperature effect on enthalpy (at zero pressure) is given by $C^0_p$ with:

$$H_{i,0,vap} = \sum_{i=1}^{m} (Y_i \int_{273.15}^{T} C^{0}_{p_i} \, dT)$$

(7-1)

where:

$H_{i,0,vap}$ = the ideal gas (zero pressure) enthalpy relative to the zero pressure, 0°C, standard gas state

$C^{0}_{p_i}$ = the ideal gas specific heat of component i.

$C^{0}_{p_i}$ is a function of temperature and can be determined by flow calorimetric measurements at several low pressures and extrapolating the results to zero pressure (89). The heat capacity is a monotonic function of temperature and Prausnitz (1) gives correlations for water and many organic vapors using the general form:
\[ C_p^0 = D_1 + D_2/T + D_3\cdot T + D_4 \ln T \]  \hspace{1cm} (7-2)

with \( C_p^0 \equiv (\text{standard state specific heat}) \text{ kcal/kgmole}^*\text{K} \)

\( T \equiv ^*\text{K} \)

Values of the constants for ethanol and water are given in Table 10. This equation accurately fits the data for both ethanol (90) and water (91) (Figure 29).

The path term to account for vapor nonidealities of the mixed system at system pressure is given rigorously by:

\[ \Delta H = \int_0^P \left[ V - T \left( \frac{\partial^2 V}{\partial T^2} \right)_{P,Y} \right] \, dP \]  \hspace{1cm} (7-3)

where:

- \( P \) = system pressure
- \( V \) = mixture molar volume.

This correction term can now be evaluated by substituting any equation of state which adequately represents the mixture \( P,V,T \) behavior.

Applying the virial equation (as already developed in section 3 for correlation of the vapor fugacities),

\[ \Delta H = P \sum_{i=1}^{m} \sum_{j=1}^{m} Y_i Y_j \left[ B_{ij} - T \left( \frac{d B_{ij}}{dT} \right) \right] \]  \hspace{1cm} (7-4)

At low pressures, this correction is small (15 percent at \( 370^*\text{K} \) and 1 bar). The correlation of equation 7-4 accurately predicts this
Table 10
Zero Pressure Vapor Specific Heat

<table>
<thead>
<tr>
<th></th>
<th>Ethanol</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>D_1</td>
<td>$-1.7797 \times 10^2$</td>
<td>6.1122</td>
</tr>
<tr>
<td>D_2</td>
<td>$5.0472 \times 10^3$</td>
<td>$2.1460 \times 10^2$</td>
</tr>
<tr>
<td>D_3</td>
<td>$-1.1213 \times 10^{-2}$</td>
<td>$3.2756 \times 10^{-3}$</td>
</tr>
<tr>
<td>D_4</td>
<td>$3.1568 \times 10^1$</td>
<td>$3.7823 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

$C_p^0 = D_1 + D_2/T + D_3 T + D_4 \ln T$

$C_p^0 \equiv \text{kcal/kgmole} \cdot \text{°K} \quad T \equiv \text{°K}$
Figure 29. Temperature dependence of the ideal gas specific heat $C_p^0$ of ethanol and water.
correction for the limited data of Counsell, Fenwick and Lees (90) for pure ethanol up to 1 bar. Unfortunately, data is not available for the ethanol/water mixture and the mixture correction of equation 7-4 cannot be tested.

7.3 Liquid phase enthalpies: $\Delta H_{\text{vap}}$ and $\Delta H_{\text{mix}}$

7.3.1 Liquid enthalpy, general relationship

By appropriate path choice, liquid phase enthalpies may also be related to a 0°C ideal gas (zero pressure) reference state. The enthalpy is then given by:

$$H_{\text{liq}} = \sum_{i=1}^{m} x_i H_{i,0,\text{vap}} - \sum_{i=1}^{m} x_i \Delta H_{\text{vap},i}^{0} - \Delta H_{\text{mix}}^{0}$$

$$+ \sum_{i=1}^{m} x_i P (V_i - T \frac{dV_i}{dT})$$

The term $x_i H_{i,0,\text{vap}}$ corrects from 0°C to the system temperature (in the gas phase) for each of the components. The ideal vapor is then condensed to its ideal liquid components (at zero pressure and with no excess heat of mixing effects) releasing $x_i \Delta H_{\text{vap},i}^{0}$ for each component. The ideal liquid components are mixed at zero pressure, giving up $\Delta H_{\text{mix}}^{0}$. The final term accounts for the effect of pressure on the mixed liquid. At low pressures (to ~5 bar) the liquid is essentially incompressible and this term can be neglected. The first term is evaluated from $C_{p,i}^{0}$ as in section 7.2. New correlations are required for $\Delta H_{\text{vap}}^{0}$ and $\Delta H_{\text{mix}}^{0}$. 
7.3.2 Zero pressure heat of vaporization

The Clapeyron equation (see equation 5-1) provides an exact link between the heat of vaporization and the vapor pressure versus temperature relationship. Applying the Clapeyron relation, the (hypothetical) heat of vaporization of a component at zero pressure is related to the zero pressure reference fugacity by:

\[ \Delta H^0_{vap,i} = RT^2 \left( \frac{d \ln f_{0,i,liq}}{dT} \right) \]  (7-6)

As in section 5, the zero pressure reference fugacities for ethanol and water can be correlated according to (1):

\[ \ln f_{0,i,liq} = C_{1,i} + C_{2,i} (T)^{-1} + C_{3,i}(T) + C_{4,i}(\ln T) + C_{5,i}(T)^2 \]  (7-7)

The zero pressure heat of vaporization is then given by:

\[ \Delta H^0_{vap,i} = R \left[ -C_{2,i} + C_{3,i}(T)^2 + C_{4,i}(T) + 2C_{5,i}(T)^3 \right] \]  (7-8)

with

\[ \Delta H^0_{vap,i} \equiv \text{kcal/kgmole}^\circ \text{K} \]
\[ T \equiv \text{^\circ K} \]
\[ R \equiv 1.9872 \text{ kcal/kgmole}^\circ \text{K} \]

The constants for ethanol and water are given in Table 6.

At low temperatures (and corresponding saturation pressures) the effect of pressure on the heat of vaporization is small, and \( \Delta H^0_{vap} \) closely follows the true \( \Delta H_{vap} \) at saturation pressure. At higher temperatures the deviation is large (Figure 30).
Figure 30. Zero pressure heat of vaporization for ethanol and water.
7.3.3 Heat of mixing

The heat of mixing is rigorously related to vapor-liquid equilibrium properties through:

\[
\left( \frac{a(G^E/T)}{a(1/T)} \right)_P X = \Delta H_{\text{mix}} \tag{7-9}
\]

Expressing the excess Gibbs energy in terms of activity coefficients,

\[
\Delta H_{\text{mix}} = -RT \sum_{i=1}^{m} \chi_i \left( \frac{\alpha \ln \gamma_i}{\alpha T} \right)_P X \tag{7-10}
\]

In section 6, the \( \gamma_i \) were expressed relative to \( f_i^{O, \text{liquid}} \), i.e., the zero pressure reference state. Hence, if we use \( \gamma_i \) as calculated in section 6, \( \Delta H_{\text{mix}} \) calculated with equation 7-10 will be at the zero pressure reference state (\( \Delta H_{\text{mix}}^0 \)) as required for evaluation of the liquid enthalpy by equation 7-5.

Substituting the standard UNIQUAC form for \( \gamma_i \) and differentiating gives (92):

\[
\Delta H_{\text{mix}}^0 = -RT \sum_{i=1}^{m} \left[ \sum_{j=1}^{m} \frac{q_i' \chi_i' \sum_{j=1}^{m} \epsilon_j' \tau_{ji} \ln \tau_{ji}}{\sum_{j=1}^{m} \epsilon_j' \tau_{ji}} \right] \tag{7-11}
\]

This form (with \( \tau_{ji} \) independent of temperature) is generally inadequate for prediction of \( \Delta H_{\text{mix}}^0 \). The general approach of correlating \( \Delta H_{\text{mix}} \) with a model for the activity coefficient can be successful, however, when parameters are fitted to enthalpy (not equilibrium) data. (93).
For the ethanol/water system, sufficient high quality equilibrium data were available to determine the temperature dependence of the UNIQUAC energy parameters. When the new temperature dependent UNIQUAC equation for \(\gamma_i\) (see section 6) is substituted into equation 7-10, a model for the complex heat of mixing behavior of the ethanol/water system results.

\[
\Delta H_{\text{mix}}^0 = -RT \left[ q_1 x_1 \left\{ \left( \frac{-\theta_2}{\theta_1 + \theta_2 \tau_{21}} \right) \left[ \frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}} \right] \right\} \right. \\
\left. + q_2 x_2 \left\{ \left( \frac{-\theta_1}{\theta_2 + \theta_1 \tau_{12}} \right) \left[ \frac{\tau_{12}}{\theta_2 + \theta_1 \tau_{12}} \right] \right\} \right]
\]

\[
\left( \frac{\theta_1}{\theta_1 + \theta_2 \tau_{21}} \right) \left[ \frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}} \right] p, x \\
+ \left( \frac{\theta_2}{\theta_2 + \theta_1 \tau_{12}} \right) \left[ \frac{\tau_{12}}{\theta_2 + \theta_1 \tau_{12}} \right] p, x
\]

\[
\frac{\theta_1}{\theta_1 + \theta_2 \tau_{21}} \left[ \frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}} \right] p, x \\
+ \left( \frac{\theta_2}{\theta_2 + \theta_1 \tau_{12}} \right) \left[ \frac{\tau_{12}}{\theta_2 + \theta_1 \tau_{12}} \right] p, x
\]

\[
\theta_1 = \frac{q_1 x_1}{q_1 x_1 + q_2 x_2} \\
\theta_2 = \frac{q_2 x_2}{q_1 x_1 + q_2 x_2}
\]

\[
q_1 = 0.92 \\
q_2 = 1.00
\]

with \(\Delta H_{\text{mix}}^0\) \(\equiv\) kcal/kgmole

\(R \equiv 1.9872\) kcal/kgmole*K
\[ \tau_{ij} = \exp \left( \frac{-\Delta U_{ij}}{RT} \right) \]  

(7-14)

\[ \left[ \frac{\partial \tau_{ij}}{\partial T} \right]_{P,X} = -\exp \left( \frac{-\Delta U_{ij}}{RT} \right) \left[ \frac{\partial}{\partial T} \left( \frac{\Delta U_{ij}}{RT} \right) \right]_{P,X} \]  

(7-15)

Using the new temperature dependent form for \( \Delta U_{ij}/R \) developed from equilibrium data (section 6.5):

\[ \Delta U_{12}/R = \varepsilon_{12} + m_{12}(T) + n_{12}(T)^2 + o_{12}(T)^3 + p_{12}(T)^4 \]  

(7-16)

and

\[ \Delta U_{21}/R = \varepsilon_{21} + m_{21}(T) + n_{21}(T)^2 + o_{21}(T)^3 + p_{21}(T)^4 \]  

then:

\[ \left[ \frac{\partial \Delta U_{ij}}{\partial T} \right]_{P,X} = \frac{\partial}{\partial T} \left[ \left( \frac{\varepsilon_{ij}}{T} \right) + (m_{ij}) + (n_{ij})T + (o_{ij})T^2 + (p_{ij})T^3 \right] \]

\[ = -\frac{\varepsilon_{ij}}{T^2} + n_{ij} + 2(o_{ij})T + 3(p_{ij})T^2 \]  

(7-17)

and finally:

\[ \left[ \frac{\partial \tau_{ij}}{\partial T} \right]_{P,X} = -\tau_{ij} \left\{ -\frac{\varepsilon_{ij}}{T^2} + n_{ij} + 2(o_{ij})T + 3(p_{ij})T^2 \right\} \]  

(7-18)

Using the constants \( \varepsilon_{ij} \) through \( p_{ij} \) evaluated from equilibrium data (see equations 6-22 and 6-23) the model is complete.

A computer program, HMIXING (Appendix 3), has been developed to implement this model. Subroutine HMIX, given the temperature and mole...
fraction of ethanol, computes the zero pressure heat of mixing. For moderate pressures (less than ~5 bar) the effect of pressure on heat of mixing is negligible.

Model predictions for the heat of mixing versus temperature and composition are given in Figure 31. These can be compared with the calorimetric results of Larkin (Figure 32) (94).

The ethanol/water system is extremely nonideal, showing both exothermic and endothermic mixing behavior. At intermediate temperatures, the isothermal mixing curves are actually sigmoidal, with both positive and negative deviations at the same temperature. A combination of association and dissociation reactions for the polymeric ethanol and water liquid components is simultaneously present. The modified UNIQUAC model correctly represents the form of this complex behavior, but quantitatively underestimate the extremes of nonideality. The compositions at maxima and minima are accurately predicted, but the corresponding $\Delta H^0_{\text{mix}}$ values are underestimated (by as much as 30 percent at 323.15°K).

This is an extreme test of the modified UNIQUAC model. These enthalpy predictions are made based on interaction parameters fit solely to the vapor/liquid equilibrium behavior. Further, the $\Delta H^0_{\text{mix}}$ relation uses derivatives of the UNIQUAC $\gamma$ relations—demanding even greater accuracy for good results. The ability of the model to predict the complex form of the $\Delta H^0_{\text{mix}}$ behavior is very encouraging and suggests that with further good experimental data to improve the temperature dependent UNIQUAC parameter fit, that more exact quantitative agreement might be expected.
Figure 31. Modified UNIQUAC Model for Heat of Mixing

Figure 32. Colorimetric data of Larkin, J. Chem. Thermo., 7, 137 (1975)

Heat of mixing for the system ethanol/water.
Values of $\Delta H^0_{\text{mix}}$ are always small compared to $\Delta H^0_{\text{vap}}$ (150 kcal/kgmole versus 10,000 kcal/kgmole) and the predictions of the UNIQUAC model will generally be adequate for use in distillation design. Where more accurate values are required (as possibly in extraction system design) Larkin (94) gives a numerical correlation for the heat of mixing (for the temperature range 298.15 to 383.15°K):

$$\Delta H_{\text{mix}} = 0.239X(1-X)\sum_{i=1}^{m} a_i(X)^i$$ (7-19)

with

$$a_i = b_i + c_i(T) + d_i(T)^2$$ (7-20)

$i = 0, 0.5, 1.5, 2.5, 4.5$

<table>
<thead>
<tr>
<th>$a_i$</th>
<th>$b_i/10^5$</th>
<th>$c_i/10^3$</th>
<th>$d_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$</td>
<td>-3.63868</td>
<td>+1.83829</td>
<td>-2.32763</td>
</tr>
<tr>
<td>$a_{0.5}$</td>
<td>+9.25982</td>
<td>-4.83586</td>
<td>+6.37228</td>
</tr>
<tr>
<td>$a_{1.5}$</td>
<td>-14.04894</td>
<td>+7.51661</td>
<td>-10.11280</td>
</tr>
<tr>
<td>$a_{2.5}$</td>
<td>+10.91318</td>
<td>-5.89498</td>
<td>+7.98868</td>
</tr>
<tr>
<td>$a_{4.5}$</td>
<td>-2.79986</td>
<td>+1.50557</td>
<td>-2.03127</td>
</tr>
</tbody>
</table>

where:

$\Delta H_{\text{mix}} \equiv$ heat of mixing (at about the saturation pressure) in kcal/kgmole

$T \equiv ^\circ K$
$X$ = mole fraction ethanol in the liquid.

These equations generated the curves in Figure 32 correlating the Larkin data.

7.4 Simplified relations

Most design applications are at or near atmospheric pressure. The most commonly needed enthalpy values will then be liquid enthalpies and heats of vaporization at 1 atmosphere. If we neglect nonideal mixing effects (as were considered in the previous more complete relations) then simple correlations are available to predict the needed thermal properties.

7.4.1 $C_{latm}^p$

If the (hypothetical) ideal gas standard state is replaced by a (real) pure component, 1 atmosphere, $0^\circ C$ liquid standard state, and if nonideal mixing effects are neglected, then liquid phase enthalpies can be expressed as:

$$H_{latm,liq} = \sum_{i=1}^{m} (X_i \int_{273.15}^{T} C_{latm,liq}^p dT)$$  \hspace{1cm} (7-21)

$C_{latm,liq}^p$ for ethanol (4) and water (95) have been correlated as:

$$C_{ethanol}^{latm,liq} = 25.008 + 6.330 \times 10^{-2} (T-273.15)$$
$$+ 1.032 \times 10^{-3} (T - 273.15)^2$$  \hspace{1cm} (7-22)

$$C_{water}^{latm,liq} = 18.014 \times \left[ 0.996185 + 0.0002874 \left( \frac{T-173.15}{100} \right) \right]^{5.26}$$
$$+ 0.011160 \times 10^{-0.036} (T-273.15)$$  \hspace{1cm} (7-23).
with

\[ c_{P_i}^{\text{latm,liq}} \equiv \text{specific heat of pure component } i \text{ in the liquid phase at 1 atmosphere pressure (kcal/kgmole}^\circ \text{K)} \]

\[ T \equiv \text{Temperature in } ^\circ \text{K. Equations are valid for the range 273.15 to 373.15}^\circ \text{K} \]

The temperature dependence of \( c_{P_i}^{\text{latm,liq}} \) is small, and for most purposes the use of a constant representative value is quite adequate.

7.4.2 \( \Delta H_{vap} \)

The heat of vaporization is required for distillation flash calculations. Neglecting vapor phase nonidealities in mixing, and noting that for close boiling components the saturation pressure of the liquid mixture is close to the saturation pressure of any component, then:

\[ \Delta H_{vap} = \sum_{i=1}^{m} Y_i \Delta H_{vap,i} \tag{7-24} \]

Further, (again neglecting nonidealities and assuming operation at near 1 atm) the enthalpy of a saturated gas phase relative to the 0°C liquid standard state can be represented as:

\[ H_{\text{vapor}} = \sum_{i=1}^{m} (Y_i \int_{273.15}^{T} c_{P_i}^{\text{latm,liq}} \, dT) + \sum_{i=1}^{m} Y_i \Delta H_{vap,i} \tag{7-25} \]

The heats of vaporization for ethanol and water can be represented over a very wide temperature range by the general Pitzer corresponding states relation (96) (see Figure 33 (5)):
Figure 33. Pitzer correlation for heat of vaporization of ethanol and water.
\[
\frac{\Delta H_{\text{vap}}}{RT_c} = 7.08 \ (1-T_r)^{0.354} + 10.95\omega \ (1-T_r)^{0.456} \tag{7-26}
\]

where:

- \(\Delta H_{\text{vap}}\) = kcal/kgmole
- \(T_r\) = \(T/T_{\text{critical}}\) \(T_c\) in °K
- \(R\) = 1.9872 kcal/kgmole °K
- \(\omega\) = Pitzer acentric factor

\(T_c\) and \(\omega\) for ethanol and water are given in Tables 1 and 2.

For improved accuracy in the low pressure (50 mmHg to 2 atm) range, the simple empirical fits for ethanol (4) and water (97) can be used (see Figure 34, data of Counsell (90) and Polak (98) for ethanol, Keenan (42) for water):

- \(\Delta H_{\text{vap, ethanol}} = 10,424.3 - 10.7861 \ (T - 273.15) - 0.055277 \ (T-273.15)^2 \tag{7-27}\)
- \(\Delta H_{\text{vap, water}} = 14,568.1 - 22.0570 \ (T) + 0.0442725(T)^2 - 5.36506 \times 10^{-5} (T)^3 \tag{7-28}\)

Plewes (99) has developed enthalpy concentration diagrams for the ethanol/water system at 760 and 300 mmHg. These graphs can be readily applied for preliminary process evaluation.

8 Salt Effect on Ethanol/Water Equilibrium

8.1. Introduction

Dissolved species, especially salts, are known to perturb vapor/liquid equilibria. In some cases, such as potassium acetate in ethanol/water (101), the effect can be quite large (in this case
Figure 34. Empirical fit to heat of vaporization for ethanol and water.
eliminating the azeotrope). In most (but not all) instances, the dissolved species depresses the volatility of the solvent it is most soluble in, while augmenting the volatility of the solvent it is least soluble in, the effect increasing as the dissolved species concentration is increased. With the volatility difference between species increased, the separation efficiency is improved.

The "salt effect" on phase equilibrium is important for the ethanol/water system. Salts at high concentration have been added to distillation reflux to enhance ethanol relative volatility, break the azeotrope and allow production of a pure ethanol product from a single column (102). Salts have been added to dilute ethanol/water solutions to enhance the selectivity of organic solvents in extracting ethanol (103,104). Finally, the dissolved components naturally present in a fermenting beer or wine can affect the relative volatility of ethanol and water. In new processes, like vacuum or flash-fermentation (105), which selectively remove ethanol from the fermenting broth (thus concentrating the remaining nonvolatile components), this effect may become important. Even microbial cells can affect the apparent relative volatility of ethanol and water.

8.2 Models for the salt effect

The addition of a dissolved species further complicates the already complex water/ethanol interactions which determine equilibrium behavior. Various models have been set forth, from the simple qualitative hydration approach to quantitative attempts based on electrostatic or van der Waals theories.
According to the simple hydration model (106,107,108,109), salt molecules will associate preferentially with the solvent in which they are more soluble. Generally, this will be the more polar solvent (in this case water). The water molecules will form a hydration shell around each ion, thus "t ieing up" the ion's hydration number of water molecules. Salts are nonvolatile—hence, the volatility of ion-molecule complexes is essentially zero. The vapor composition is then determined by the solution in regions remote from the binding ions. The bulk liquid remote from ions is now depleted in water molecules. The nonaqueous solvent (ethanol) concentration in these regions is relatively enhanced compared to the pure ethanol/water system and thus, the volatility of ethanol in the salted system is relatively enhanced.

This simple model neglects entirely interactions between the dissolved species and the nonaqueous solvent. To be useful in quantitative predictions, hydration numbers should be independent of the nonaqueous solvent chosen and the same as those for pure water in the solute. However, these conditions are not generally met (110, 111). This model cannot explain "salting in" (volatility depression) of nonaqueous solvents observed for some salts. Finally, this model cannot explain the disappearance of an azeotrope caused by salting. If the salt acts only by binding water molecules and thus increasing the effective ethanol concentration in the bulk of the liquid, then the ethanol/water azeotrope should still occur, and should appear at a lower total ethanol concentration in the liquid.
Electrostatic theories have been used to attempt quantitative predictions of the salt effect. The activity coefficient of the nonaqueous solvent is corrected by an added term for the electrostatic contribution to the chemical potential. This correction is derived from the Helmholtz work function in discharging the ions from pure aqueous solvent and recharging them into the actual mixed solvent solution containing the nonaqueous component. The electrostatic theory was first applied by Debye and McAuley (112) with many later refinements (113,114,115,116).

Electrostatic models do predict the general trends that smaller ions (higher charge density) are more effective in salting out, and that less polar nonaqueous solvents are the most affected. However, the models do not predict the many observed anomalies and departures from these general rules. Salting in is not explained. Quantitative predictions of the enhancement due to a particular salt cannot be made to closer than a factor of two (117,118,119,120).

The limitations of the electrostatic models arise from their simplified view of the solvent as a structureless dielectric continuum with ion interactions measured only by their effect on dielectric properties. All other types of forces, and the effect of ions in orienting the solvent structure, are ignored (111,113).

Salting in can be explained when short range van der Waals forces are considered (121). Using the London formula for the dispersion potential, Bockris, Bowler-Reed and Kitchener (122) developed a quantitative expression for the van der Waals contributions to the salt
effect. This is then added to the electrostatic contribution (119). While this model can predict salting into of the nonaqueous solvent, the model is not successful at quantitatively predicting the degree of the salt effect (122).

As it is still beyond the capability of any theory using only measurable pure component properties to predict quantitatively the complex effect of dissolved solutes on vapor/liquid equilibrium behavior, we must rely instead on well-based models with constants fit to accurate equilibrium data for the mixed system.

Considering only electrostatic effects but allowing for nonspherocity and induced dipole effects, the activity coefficient of the nonaqueous solvent in a salted solution can be represented by a power series in the concentrations of the salt and nonaqueous solvent (115, 119):

\[
\ln \gamma_i = \sum_{\ell, m=0}^{\infty} k_{\ell, m} x_i^m x_s^\ell
\]

where:

\(x_i\) and \(x_s\) are mole fractions of the nonaqueous solvent and of the salt, respectively.

When the interaction constants \((k_{\ell, m})\) are calculated from pure component properties using electrostatic principles (115), the model fails to quantitatively predict salting phenomena. If, however, the constants are fit to experimental equilibrium data, then a valuable predictive model results. \(x_i\) is then generally taken as the
nonaqueous solvent concentration on a salt free basis and the fit constants reflect (in a complex way) all the various force effects of the salt on the components of the solution.

At high dilution, equation 8-1 reduces to:

\[ \ln \gamma_i = k_{0,0} + k_{0,1} X_i + k_{1,0} X_S \]  \hspace{1cm} (8-2)

Assuming a similar expression for the effect of the salt on water, a very simple relation for the enhancement of nonaqueous solvent volatility by a salt can be derived (123):

\[ \ln \frac{K_s}{K_0} = (k_{0,1}^i - k_{0,1}^w) X_S \]  \hspace{1cm} (8-3)

where \( k_{0,1}^i \) and \( k_{0,1}^w \) are constants as in equation 8-2 but from the calculation of \( \gamma_i \) and \( \gamma_w \) (activity coefficient for the nonaqueous solvent and water), respectively.

\( K_s \) and \( K_0 \) are solvent relative volatilities with and without salt.

\[ K_s = \frac{Y_i^S/X_i^S}{Y_w^S/X_w^S} \]  \hspace{1cm} (8-4)

with \( X_i \) and \( X_w \) given on a salt free basis. \( k_{0,1}^i \) is a measure of the effect of the salt on the nonaqueous solvent. \( k_{0,1}^w \) is a measure of the effect of the salt on the water component of the solution. The difference between these factors is referred to simply-
as the enhancement factor \( k \), and is a measure of the effect of the salt on the relative volatilities of the solvents.

\[
\ln \frac{K_S}{K_0} = k \chi_S
\]  

This simple relation is a limiting law (for low salt and fixed nonaqueous solvent concentration only). Further, it should be valid only when the change in boiling point due to the salt is small so that the activity coefficients computed with and without salt are at the same temperature—again this is true for low salt concentration.

8.3 Volatility enhancements at high salt and ethanol concentration—literature data

Despite its apparent limitations, the simple model of equation 8-5 has been applied successfully to many systems even at salt saturation conditions (119,123). Table 11 summarizes reported experimental evaluations of the salt effect for the system ethanol/water. The data are actually quite limited in that almost all are for salts at saturation and data are rarely available for ethanol concentrations below 10 mole percent (salt free basis).

Johnson and Furtner (123) applied equation 8-5 to the ethanol/water system with 12 different salts at saturation as well as to 12 other systems with methanol and n-propanol replacing ethanol. The values of \( k \) for the 24 systems tested were all remarkably constant and a single value of \( k \) for each system was able to predict the entire equilibrium curve duplicating the data to within approximately one mole percent.
Table 11
Studies of Salt Effect on Ethanol Volatility

<table>
<thead>
<tr>
<th>Salt</th>
<th>Salt Concentration</th>
<th>Effect on Ethanol Volatility</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Nitrate</td>
<td>Saturation</td>
<td>Enhance</td>
<td>124,125</td>
</tr>
<tr>
<td>Potassium Nitrate</td>
<td>Sat.</td>
<td>Enhance</td>
<td></td>
</tr>
<tr>
<td>Sodium Sulfate</td>
<td>Sat.</td>
<td>Enhance</td>
<td></td>
</tr>
<tr>
<td>Potassium Sulfate</td>
<td>Sat.</td>
<td>Enhance</td>
<td></td>
</tr>
<tr>
<td>Ammonium Chloride</td>
<td>Sat.</td>
<td>Enhance</td>
<td>123,126</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>Sat.</td>
<td>Enhance</td>
<td></td>
</tr>
<tr>
<td>Potassium Chloride</td>
<td>Sat.</td>
<td>Enhance</td>
<td></td>
</tr>
<tr>
<td>Sodium Nitrate</td>
<td>Sat.</td>
<td>Enhance</td>
<td></td>
</tr>
<tr>
<td>Lead Nitrate</td>
<td>Sat.</td>
<td>Enhance</td>
<td></td>
</tr>
<tr>
<td>Mercuric Chloride</td>
<td>Sat.</td>
<td>Depress</td>
<td></td>
</tr>
<tr>
<td>Mercuric Bromide</td>
<td>Sat.</td>
<td>Depress</td>
<td></td>
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<tr>
<td>Mercuric Iodide</td>
<td>Sat.</td>
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<td></td>
</tr>
<tr>
<td>Barium Nitrate</td>
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<td>Enhance</td>
<td></td>
</tr>
<tr>
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<td>Enhance</td>
<td></td>
</tr>
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<td>Ammonium Sulfate</td>
<td>Sat.</td>
<td>Enhance</td>
<td></td>
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<td>Cuprous Chloride</td>
<td>Sat.</td>
<td>Enhance</td>
<td></td>
</tr>
<tr>
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<td>Sat.</td>
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<td>Barium Nitrate</td>
<td>Sat.</td>
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<td></td>
</tr>
<tr>
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<td>Enhance</td>
<td></td>
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<td>128</td>
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<tr>
<td>Potassium Iodide</td>
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<td>Enhance</td>
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</tr>
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</tr>
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<tr>
<td>Sodium Iodide</td>
<td>Sat.</td>
<td>Enhance</td>
<td>131</td>
</tr>
<tr>
<td>Sodium Bromide</td>
<td>Sat.</td>
<td>Enhance</td>
<td></td>
</tr>
<tr>
<td>Potassium Iodide</td>
<td>Sat.</td>
<td>Enhance</td>
<td></td>
</tr>
<tr>
<td>Potassium Bromide</td>
<td>Sat.</td>
<td>Enhance</td>
<td></td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>Sat.</td>
<td>Enhance</td>
<td>132</td>
</tr>
<tr>
<td>Mercuric Chloride</td>
<td>Sat.</td>
<td>Depress</td>
<td></td>
</tr>
</tbody>
</table>
Table 11 (continued)

<table>
<thead>
<tr>
<th>Salt</th>
<th>Salt Concentration</th>
<th>Effect on Ethanol Volatility</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium Chloride</td>
<td>Sat.</td>
<td>Enhance</td>
<td>133</td>
</tr>
<tr>
<td>Ammonium Chloride</td>
<td>Sat.</td>
<td>Enhance</td>
<td></td>
</tr>
<tr>
<td>Potassium Chloride</td>
<td>Sat.</td>
<td>Enhance</td>
<td></td>
</tr>
<tr>
<td>Sodium Nitrate</td>
<td>Sat.</td>
<td>Enhance</td>
<td></td>
</tr>
<tr>
<td>Lithium Chloride</td>
<td>Sat.</td>
<td>Enhance</td>
<td>134</td>
</tr>
<tr>
<td>Sodium Bromide</td>
<td>0.0244 to 0.1197 mole fraction</td>
<td>Enhance</td>
<td>135</td>
</tr>
<tr>
<td>Ammonium Chloride</td>
<td>0.0150 to 0.1070</td>
<td>Enhance</td>
<td></td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>0.0049 to 0.0501</td>
<td>Enhance</td>
<td></td>
</tr>
<tr>
<td>Potassium Acetate</td>
<td>Sat.</td>
<td>Enhance</td>
<td>101</td>
</tr>
<tr>
<td>Sodium Acetate</td>
<td>Sat.</td>
<td>Enhance</td>
<td>137</td>
</tr>
<tr>
<td>Calcium Acetate</td>
<td>Sat.</td>
<td>Depress</td>
<td>137</td>
</tr>
<tr>
<td>Barium Acetate</td>
<td>Sat.</td>
<td>Enhance/Depress*</td>
<td></td>
</tr>
<tr>
<td>Sodium Acetate</td>
<td>0.75 to 3 g/L</td>
<td>Enhance</td>
<td>138</td>
</tr>
</tbody>
</table>

*Volatility enhancement at low ethanol concentration crossing over to depression at high ethanol concentration.
throughout. The values of $k$ found for the ethanol/water system measured with salts at saturation are summarized in Table 12. There is no apparent underlying basis for the success of equation 8-5 (which was derived only as a limiting law for the case of dilute salts) in modeling the behavior of the wide range of systems of Table 12 under the more complex conditions of salts at saturation. The derivation of equation 8-5 from the more general form of equation 8-1 suggests that a more complex relation should be required.

Johnson and Furter offer a partial explanation for the constancy of $k$ in a balancing between changes in the components $k_{0,1}^i$ and $k_{0,1}^w$, reflecting a cancelling of opposing effects on the vapor/liquid equilibrium. Using data for the system ethanol/water/ammonium chloride at various values of ethanol and salt concentration (not just salt at saturation), they plot $k_{0,1}^i$ and $k_{0,1}^w$ (calculated separately) and show that they both vary strongly with the salt concentration. The variations tend, however, to cancel almost exactly giving a constant value for $k$ (the difference $k_{0,1}^i-k_{0,1}^w$).

Table 13 summarizes the order of effect of various ions (119, 123). The order found by Johnson and Furter for volatility enhancement by ions on the ethanol/water system is in good agreement with the order found for several systems with polar nonaqueous solvents. The order also corresponds roughly with the predictions of the electrostatic theory that smaller ions (higher charge density) should have a greater effect. The exact effectiveness order found, however, is not
Table 12
Enhancement Factors for Salts at Saturation*

<table>
<thead>
<tr>
<th>Salt</th>
<th>Enhancement Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium Chloride</td>
<td>8.3</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>11.1</td>
</tr>
<tr>
<td>Potassium Chloride</td>
<td>9.7</td>
</tr>
<tr>
<td>Sodium Nitrate</td>
<td>6.9</td>
</tr>
<tr>
<td>Lead Nitrate</td>
<td>8.1</td>
</tr>
<tr>
<td>Mercuric Chloride</td>
<td>-1.4</td>
</tr>
<tr>
<td>Mercuric Bromide</td>
<td>-2.1</td>
</tr>
<tr>
<td>Mercuric Iodide</td>
<td>0.2</td>
</tr>
<tr>
<td>Barium Nitrate</td>
<td>4.6</td>
</tr>
<tr>
<td>Potassium Sulfate</td>
<td>2.3</td>
</tr>
<tr>
<td>Ammonium Sulfate</td>
<td>8.1</td>
</tr>
<tr>
<td>Cuprous Chloride</td>
<td>5.5</td>
</tr>
</tbody>
</table>

*Results of Johnston and Furter (123)
### Table 13
Ions in Decreasing Order of Effectiveness

<table>
<thead>
<tr>
<th>Cations</th>
<th>Ionic Radius (angstroms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>0.65</td>
</tr>
<tr>
<td>Sodium</td>
<td>1.00</td>
</tr>
<tr>
<td>Potassium</td>
<td>1.33</td>
</tr>
<tr>
<td>Lead</td>
<td>1.18</td>
</tr>
<tr>
<td>Barium</td>
<td>1.38</td>
</tr>
<tr>
<td>Ammonium</td>
<td>----</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.72</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Anions</th>
<th>Ionic Radius (angstroms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate</td>
<td>----</td>
</tr>
<tr>
<td>Chloride</td>
<td>1.80</td>
</tr>
<tr>
<td>Bromide</td>
<td>1.96</td>
</tr>
<tr>
<td>Nitrate</td>
<td>----</td>
</tr>
<tr>
<td>Iodide</td>
<td>2.20</td>
</tr>
</tbody>
</table>
identical even for all neutral polar nonaqueous solvents and can be very different for strongly acidic or basic solvents. The anomalous behavior of mercuric ion has been related to its covalent bonding properties (123).

Data are not available for ethanol/water/strong acid systems (HCl, H₂SO₄) but for similar systems (139) the effect of H⁺ ions is very small and can be neglected at ordinary pH. This apparent contradiction of the principle that small ions should have a large effect is explained when we consider the tendency of water ordinarily to be in a small fraction dissociated. H⁺ ions, thus, make up a part of the ordinary structure of the water nonaqueous solvent system and can fit into the normal structure when added at low concentration without causing disruptions.

Very little information is available on the effect of mixed salts on ethanol/water relative volatility. For many nonpolar systems at low salt and nonaqueous solvent concentration, the effect of multiple salts is approximately additive (119, 140) so that:

\[ \ln \frac{K_s}{K_o} = \sum_{j=1}^{m} k_j X_j \]  

(8-6)

where \( X_j \) and \( k_j \) are the mole fraction and enhancement factor for the \( j \)th salt component added.

This additivity of effects has also been reported for a limited number of polar nonaqueous solvent systems (141, 142). For the
ethanol/water system the only data are for mixed halide salts at saturation (131). At low ethanol concentration (< 0.40 mole fraction) the additivity roughly holds, but near the azeotrope a synergy is found such that mixed salts enhance the ethanol relative volatility by significantly more than their simple additive effects even after taking into account the enhanced solubility of the mixed salts compared to the salts added separately.

While equation 8-5 has proved successful in correlating the effects of a wide range of simple salts in the ethanol/water system at saturation, it does fail for many important cases. Particularly problematic are the acetate salts and sugars. Some acetates are very soluble in the ethanol/water system and are among the most effective salts in breaking the azeotrope to allow a simple one column extractive distillation. Sugars (sucrose and glucose) are present in wines and beers during fermentation and distillation.

For the system ethanol/water/potassium acetate at saturation, Meranda and Furter (101) found large enhancements (with the azeotrope completely eliminated), but the value of k varied by a factor of three as ethanol concentration was decreased from $X = 0.9$ to $X = 0.1$. This led to much further study of the family of acetate salts at salt saturation. The variation of k with ethanol composition was confirmed for potassium acetate and also found true when methanol replaced ethanol (137). For the system ethanol/water/sodium acetate at saturation a large enhancement was also found, but the values of k were approximately constant with varying ethanol concentration (137).
Bedrossian and Cheh (138) then applied equation 8-5 to the sodium acetate system under conditions of varying levels of salt at low concentrations (0.75 to 3.0 g/L). Under these conditions (unlike the behavior at salt saturation) the value of k was found to vary very significantly with ethanol concentration as shown in Figure 35. As the ethanol concentration is decreased, k initially slowly decreases, but at low ethanol concentrations (similar to those found in a fermenting broth) the value of k rises by a factor of five.

Further anomalous behavior is found for barium and calcium acetate at saturation (137). At low ethanol concentrations barium acetate enhances ethanol relative volatility, but at high ethanol concentrations barium acetate depresses ethanol volatility causing salting in. Although calcium acetate is more soluble in water than ethanol, it causes salting in at all ethanol concentrations.

The anomalous behaviors of the acetate family cannot be described by equation 8-5 with a single k value for each salt. Potassium acetate is known to form two different hydrates and at least one alcoholate (136). These special associations may help explain this salt's strong effect on relative volatility. Sodium acetate is very soluble in both ethanol and water and this results in very large (> 30°C) boiling temperature rises for the saturated system over the salt free system. This invalidates the use of equation 8-5 since the volatilities with and without salt are no longer measured at approximately the same temperature and this may help explain the difference in results between the experiments at saturation and at low salt concentrations (where the boiling rise is small).
Figure 35. Effect of sodium acetate on ethanol/water relative volatility.

1.5 g/l Sodium Acetate
Data of Bedrossian and Cheh

 Enhancement Factor, k

 Mole Fraction Ethanol (Salt-free basis)
Sugars will generally be present only at low concentrations (except at the beginning of batch fermentation) and hence have little effect. Kharin and Perelyyin (143) studied the effect of sucrose on ethanol relative volatility and again found k to vary widely with the ethanol concentration (Figure 36) causing salting in at low ethanol concentrations (less than 0.06 mole fraction) and salting out at moderate concentrations. Similar behavior has been observed for a limited number of other systems (e.g., pyridine/water with sodium sulfate (114)).

Recent work by Jaques and Furter (135) raises further questions as to the broad applicability of equation 8-5. In this work, equation 8-5 was tested under the conditions for which it was derived—constant nonaqueous solvent concentration and varying low salt concentration. For both ethanol and methanol systems, the equation worked very well giving nearly constant k values (Figure 37). However, the values of k found under these conditions of low salt concentration (~0.02 to 0.12 mole fraction) were consistently lower than those found for the salts at saturation (Table 14).

The difficulties cited lead to important conclusions for the use of equation 8-5. For azeotropic distillation design (using salts at saturation) equation 8-5 can be used with k values taken from the literature. For most systems of simple salts, k will not vary substantially with ethanol concentration at salt saturation and some extrapolation is acceptable. For complex or highly soluble salts (such as potassium and sodium acetate) further care must be taken to apply
Figure 36. Effect of sucrose on ethanol/water relative volatility.
Figure 37. Effect of ammonium chloride on ethanol/water relative volatility.
Table 14
Enhancement Factor for Dilute Salt Solutions and Solutions at Salt Saturation

<table>
<thead>
<tr>
<th>Salt</th>
<th>Enhancement Factor k At Saturation</th>
<th>Enhancement Factor k Dilute Salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Chloride</td>
<td>11.1</td>
<td>8.3</td>
</tr>
<tr>
<td>Potassium Chloride</td>
<td>9.7</td>
<td>7.8</td>
</tr>
<tr>
<td>Ammonium Chloride</td>
<td>8.3</td>
<td>5.3</td>
</tr>
<tr>
<td>Sodium Bromide</td>
<td>---</td>
<td>6.7</td>
</tr>
</tbody>
</table>
the equation only at the conditions for which the experimental k value was measured.

The limited data for salts at less than saturation concentration suggests that k values determined at saturation cannot be applied at less than saturation. The data for sodium acetate also suggests that while k may be nearly invariant with X in the moderate ethanol concentration range, that volatility enhancement may be disproportionately large at the low (<0.02 mole fraction) ethanol concentrations typical of a fermentation broth.

8.4 Volatility enhancement at low salt and ethanol concentration

8.4.1 Volatility enhancement in fermentation systems

During wine production, ethanol is stripped from the wine by CO₂ evolved in the fermentation. In industrial ethanol production, ethanol is initially concentrated in a stripping still. In new fermentation processes such as flash fermentation (105) or extractive fermentation (145), ethanol is removed from the fermenting broth (by flashing under vacuum or by extraction, respectively) continuously as it is produced. In all of these processes the ethanol is removed from a solution containing dissolved species and the effect of these species on the ethanol/water equilibrium should be considered.

Table 15 presents the composition of a grape must (the crushed grape juice which is fermented to produce wine) (146). The concentration of inorganics is low and these will have little effect. Only the carbohydrates (sugars) are present in large concentration and the data of Kharin and Perelyyn (143) can be used to estimate their effect on
Table 15
Composition of a Grape Must

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount Range (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>70 - 85</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>12 - 28</td>
</tr>
<tr>
<td>Total Acids</td>
<td>0.3 - 1.3</td>
</tr>
<tr>
<td>Tannin</td>
<td>0.0 - 0.2</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.01 - 0.20</td>
</tr>
<tr>
<td>Ash</td>
<td>0.2 - 0.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ash Constituent</th>
<th>Amount Range (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.001 - 0.030</td>
</tr>
<tr>
<td>K</td>
<td>0.400 - 2.000</td>
</tr>
<tr>
<td>Ca</td>
<td>0.040 - 0.150</td>
</tr>
<tr>
<td>Mg</td>
<td>0.050 - 0.200</td>
</tr>
<tr>
<td>Al</td>
<td>0.001 - 0.040</td>
</tr>
<tr>
<td>Na</td>
<td>0.050 - 0.200</td>
</tr>
<tr>
<td>Mn</td>
<td>0.000 - 0.050</td>
</tr>
<tr>
<td>Cl</td>
<td>0.030 - 0.150</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.100 - 0.420</td>
</tr>
<tr>
<td>S$_4$O$_4$</td>
<td>0.028 - 0.330</td>
</tr>
</tbody>
</table>
the ethanol volatility and hence on the volatility losses (which constitute a substantial pollution problem) during fermentation.

Table 16 presents the composition of a typical stillage from molasses (147). Stillage is the concentrated product remaining after ethanol has been distilled away and contains the spent yeast (solids). Table 17 presents the composition of a fermentation beer produced in continuous fermentation using the semisynthetic medium of Cysewski (Table 18) (148). Again the concentrations of dissolved inorganic components are low and should have only a very small effect on ethanol/water equilibrium.

Proposed new fermentation processes will concentrate the dissolved species and, for these processes, the effect of the dissolved components may become important. In vacuum fermentation, the feed solution is continuously added to a fermentor under vacuum. Fermentation takes place in the broth and ethanol is boiled away as it is produced (to eliminate end product inhibition). Nonvolatile feed components which are not metabolized, build up in the fermentor. A small liquid bleed is taken to remove dead cells and regulate the extent of buildup of components to levels below where they would inhibit the fermentation reaction. It is desirable, however, to maintain the bleed as small as possible to take most of the product in the concentrated purified vapor form. Likewise, in conventional fermentation, to reduce the liquid waste disposal load, stillage is now recycled (with added substrate) to the fermentor, again concentrating nonvolatile dissolved species (149). Similar concentration effects occur in extractive and
### Table 16
Composition of a Stillage from Fermentation of Molasses

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Solids</td>
<td>61.0</td>
</tr>
<tr>
<td>Total N</td>
<td>0.87</td>
</tr>
<tr>
<td>Total P (as P$_2$O$_5$)</td>
<td>0.099</td>
</tr>
<tr>
<td>K (as K$_2$O)</td>
<td>11.4</td>
</tr>
<tr>
<td>Cl</td>
<td>6.0</td>
</tr>
<tr>
<td>Ca</td>
<td>0.8</td>
</tr>
<tr>
<td>Mg</td>
<td>0.23</td>
</tr>
<tr>
<td>S0$_4$</td>
<td>2.5</td>
</tr>
<tr>
<td>Total Reducing Sugars</td>
<td>0.9%</td>
</tr>
<tr>
<td>Total Proteins</td>
<td>0.4%</td>
</tr>
</tbody>
</table>
Table 17
Composition of a Fermentation Beer
(after yeast cell removal)

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total N *</td>
<td>1.760</td>
</tr>
<tr>
<td>Free SO₄</td>
<td>0.051</td>
</tr>
<tr>
<td>Cl</td>
<td>3.38</td>
</tr>
<tr>
<td>Na</td>
<td>0.838</td>
</tr>
<tr>
<td>K</td>
<td>0.863</td>
</tr>
<tr>
<td>P</td>
<td>0.202</td>
</tr>
<tr>
<td>Mg</td>
<td>0.246</td>
</tr>
<tr>
<td>Ca</td>
<td>0.029</td>
</tr>
<tr>
<td>Free NH₃ (as N)</td>
<td>0.455</td>
</tr>
<tr>
<td>Reducing Sugars (as Glucose)</td>
<td>1.0</td>
</tr>
</tbody>
</table>

* Soluble protein based on bound nitrogen is approximately 8.1 g/L.
Table 18
Fermentation Medium

<table>
<thead>
<tr>
<th>Component</th>
<th>(g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose (anhydrous)</td>
<td>100.0</td>
</tr>
<tr>
<td>Yeast extract (Difco)</td>
<td>8.5</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>1.32</td>
</tr>
<tr>
<td>MgSO$_4$•7H$_2$O</td>
<td>0.11</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>0.06</td>
</tr>
<tr>
<td>Anti-foam (General Electric AF60)</td>
<td>0.2 ml</td>
</tr>
<tr>
<td>Tap water</td>
<td>Make up to 1 liter</td>
</tr>
</tbody>
</table>
membrane extractive fermentation processes. In one proposed extraction process, potassium chloride is actually added to the fermentation broth to enhance the ethanol/water extractive separation (103).

Table 19 summarizes levels at which various salts (present in most feeds) become inhibitory (150). These inhibitory levels will set the limits for operation of the fermentation and are the maximum concentrations that need be considered in assessing effects on volatility enhancement.

8.4.2 Experimental procedure

New data is needed to assess the effects of dissolved components—both salts and biological components—on ethanol volatility in new fermentation schemes. Ethanol concentrations will be limited to less than 0.04 mole fraction (the limit of total end product inhibition) and typically to 0.02 mole fraction (where inhibition is small). Salt concentrations will be well below saturation.

An Othmer equilibrium still (151) (Ace Glass No. 6681B) was used to measure volatility enhancements at conditions similar to those of a concentrated fermentation beer (Figure 38). The method of still operation was similar to that of Johnson and Furter (132) who used a still to determine enhancement effects of salts at saturations. 400 ml of the liquid to be tested was charged to the roughly 800 ml still body. The liquid was heated by a thermosyphon heater tube wrapped outside with a heating tape and controlled with a variac. To prevent bumping, a Nichrome wire coil was placed inside the thermosyphon tube to provide nucleation sites for boiling. A very slow boiling rate was used to prevent splashing and entrained droplet carry over to the collector.
<table>
<thead>
<tr>
<th>Salt</th>
<th>Concentration at Onset of Inhibition* (gmole/L)</th>
<th>Concentration at High Inhibition** (gmole/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Chloride</td>
<td>0.291</td>
<td>0.457</td>
</tr>
<tr>
<td>Ammonium Chloride</td>
<td>0.117</td>
<td>0.466</td>
</tr>
<tr>
<td>Magnesium Sulfate</td>
<td>0.606</td>
<td>0.829</td>
</tr>
<tr>
<td>Magnesium Chloride</td>
<td>0.566</td>
<td>0.886</td>
</tr>
<tr>
<td>Potassium Chloride</td>
<td>0.549</td>
<td>1.654</td>
</tr>
<tr>
<td>Ammonium Sulfate</td>
<td>0.134</td>
<td>0.205</td>
</tr>
<tr>
<td>Potassium Phosphate</td>
<td>0.639</td>
<td>0.753</td>
</tr>
<tr>
<td>Calcium Chloride</td>
<td>0.074</td>
<td>0.238</td>
</tr>
</tbody>
</table>

* 20 percent reduction in cell mass production.
** 80 percent reduction in cell mass production.
Figure 38. Othmer equilibrium still used in vapor/liquid equilibrium studies.
The vapor was condensed in a refrigerated (1°C) condenser and collected in the 18 ml receiver. When the receiver is full, the excess condensate returns to the main still body via the overflow return line so that after sufficient time a steady state is achieved with the condensed vapor in equilibrium with the boiling liquid. The still was insulated and the vapor portion of the main body was wrapped outside with heating tape and maintained at 1-3°C higher than the boiling liquid to prevent refluxing.

The ethanol and water compositions of liquid and vapor products were determined by gas chromatography. The chromatograph injection port was fitted inside with a sleeve containing a glasswool plug to collect nonvolatile components and prevent them from fouling the column. The chromatograph was calibrated with known standards so that the ratio of water and ethanol peak areas measured by the thermal conductivity detector gave directly the mole fraction of ethanol (on a dissolved species free basis). Individual analyses varied by less than 5 percent and four or five analyses were made of each sample and the averages reported.

To test the experimental technique, pure ethanol/water samples (with no salts) were equilibrated in the still. Eight hours equilibration time was found inadequate but at 20 hours (the still left overnight) excellent agreement with literature values (Pemberton and Mash (52)) was achieved. A mass balance after the equilibration also showed the system to be closed. Figure 39 shows the results of this test along with results with added ammonium chloride at 0.012 mole fraction salt.
Figure 39. Ethanol/water relative volatility with and without added ammonium chloride salt.
8.4.3 Effect of salts at low ethanol concentration—NaCl, KCl, NH₄Cl

Experiments were conducted with dilute ~0.015 mole fraction (35g/L) ethanol solutions and with NaCl, KCl, and NH₄Cl at concentrations ranging from 0.00 to 0.02 mole fraction salts—as might be expected in a fermentation. When these results are plotted according to equation 8-5 (Figures 40-42) a straight line relationship results indicating a constant k value. These values are 14.5 for NaCl, 11.0 for NH₄Cl and 17.4 for KCl. In the case of all three salts, the values of k found at these dilute ethanol concentrations are substantially higher than those reported by Jaques and Furter (135) at higher ethanol concentrations. This behavior is very similar to that reported by Bedrossian and Cheh (138) for sodium acetate where k values were also elevated at low concentration. To test the effect of ethanol concentration on the enhancement factor, additional experiments were conducted holding the NH₄Cl concentration constant (at ~0.012 mole fraction) while increasing the ethanol concentration from 0.015 mole fraction to 0.114 mole fraction. These are the points shown in Figure 39. Results (summarized in Table 20) show that k does decrease with increasing ethanol concentration. The value of k = 4.0 obtained here at X_{eth} = 0.114 compares with the value of 5.3 of Jaques and Furter obtained at X_{eth} = 0.223, indicating that the enhancement may reach a minimum before returning to its constant value found at moderate ethanol concentrations. This again agrees with the behavior reported for sodium acetate (see Figure 35).
Figure 40. Effect of sodium chloride on ethanol/water relative volatility.
Figure 41. Effect of potassium chloride on ethanol/water relative volatility.
Figure 42: Effect of ammonium chloride on ethanol/water relative volatility.
Table 20

Variation of Enhancement Factor \( k \) with Ethanol Concentration for Ammonium Chloride at 0.012 mole fraction Salt

<table>
<thead>
<tr>
<th>Mole Fraction Ethanol</th>
<th>Enhancement Factor ( k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0152</td>
<td>12.6</td>
</tr>
<tr>
<td>0.0415</td>
<td>6.3</td>
</tr>
<tr>
<td>0.114</td>
<td>4.0</td>
</tr>
</tbody>
</table>
Since fermentation beers contain several dissolved components, it is important to determine if the additivity of effects expressed by equation 8-6 holds under conditions of dilute ethanol and salt concentration. Mixed NaCl/KCl solutions were equilibrated in the still and the enhancement effects determined. These are summarized in Table 21. Applying equation 8-6 to these solutions and using the k values determined for the salts individually gives:

**Solution 1:**
\[
\ln \frac{K_S}{K_O} = 0.0019 \times 17.41 + 0.0019 \times 14.52 = 0.0607
\]

**Solution 2:**
\[
\ln \frac{K_S}{K_O} = 0.0017 \times 17.41 + 0.0036 \times 14.52 = 0.0819
\]

which are both in very good agreement with the measured enhancement values. At these low salt concentrations interactions between different salts should be small and this additivity is as expected.

8.4.4 Effect of dissolved biological components--yeast extract

Yeast extract is the water soluble portion of autolysed yeast, composed of proteins, amino acids, peptides, salts and other components (Table 22) (152). It is similar in composition to the products released by lysed yeast cells in repeated cycling through a fermentation.

Large ions of unsymmetric charge distribution often cause salting in. This hydrotropism has been observed in many systems with salts such as sodium benzoate, sodium toluene sulfonate, and aniline nitrate.
Table 21
Volatility Enhancement in Mixed Salt Solutions

<table>
<thead>
<tr>
<th>Salt Mole Fraction</th>
<th>NaCl</th>
<th>KCl</th>
<th>$\chi_e$</th>
<th>$\gamma_e^O$</th>
<th>$\gamma_e^S$</th>
<th>$\ln \frac{K_s}{K_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0019</td>
<td>0.0019</td>
<td>0.0155</td>
<td>0.1568</td>
<td>0.1654</td>
<td>0.0636</td>
<td></td>
</tr>
<tr>
<td>0.0036</td>
<td>0.0017</td>
<td>0.0147</td>
<td>0.1504</td>
<td>0.1614</td>
<td>0.0836</td>
<td></td>
</tr>
</tbody>
</table>

$\gamma_e^O$ = Vapor mole fraction ethanol without salt.

$\gamma_e^S$ = Vapor mole fraction ethanol with salt added to the liquid.
### Table 22

**Typical Composition of Yeast Extract**

<table>
<thead>
<tr>
<th><strong>Nitrogen (percent)</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>10.3</td>
</tr>
<tr>
<td>Amino</td>
<td>5.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Salts (percent)</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.5</td>
</tr>
<tr>
<td>Ca</td>
<td>0.06</td>
</tr>
<tr>
<td>Fe</td>
<td>0.20</td>
</tr>
<tr>
<td>K</td>
<td>3.4</td>
</tr>
<tr>
<td>Mg</td>
<td>0.07</td>
</tr>
<tr>
<td>P</td>
<td>1.16</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Carbohydrates (percent)</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>16.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Amino Acids (percent)</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Arginine</td>
<td>3.5</td>
</tr>
<tr>
<td>Cystine</td>
<td>1.6</td>
</tr>
<tr>
<td>Histidine</td>
<td>1.5</td>
</tr>
<tr>
<td>Isoleucine</td>
<td>4.7</td>
</tr>
<tr>
<td>Leucine</td>
<td>6.4</td>
</tr>
<tr>
<td>Lysine</td>
<td>6.5</td>
</tr>
<tr>
<td>Methionine</td>
<td>2.0</td>
</tr>
<tr>
<td>Phenylalanine</td>
<td>3.5</td>
</tr>
<tr>
<td>Threonine</td>
<td>3.3</td>
</tr>
<tr>
<td>Tryptophane</td>
<td>1.0</td>
</tr>
<tr>
<td>Tyrosine</td>
<td>4.0</td>
</tr>
<tr>
<td>Valine</td>
<td>4.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Vitamins mcg/g</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Biotin</td>
<td>4</td>
</tr>
<tr>
<td>Choline</td>
<td>2000</td>
</tr>
<tr>
<td>Cyanocobalamin</td>
<td>0.0</td>
</tr>
<tr>
<td>Folic Acid</td>
<td>20</td>
</tr>
<tr>
<td>Niacin</td>
<td>400</td>
</tr>
<tr>
<td>Pantothenic Acid</td>
<td>100</td>
</tr>
<tr>
<td>Pyridoxine</td>
<td>30</td>
</tr>
<tr>
<td>Riboflavin</td>
<td>50</td>
</tr>
<tr>
<td>Thiamine</td>
<td>100</td>
</tr>
<tr>
<td>PABA</td>
<td>24</td>
</tr>
</tbody>
</table>
Prausnitz (144) explains this effect as an attraction of the nonelectrolyte molecules to the ion's large nonpolar end to reduce the concentration in the charged region. Some of the biological molecule fragments of the yeast extract were expected to have this hydrotropic effect.

Solubility data for amino acids and peptides in water and ethanol (156,157,158) supported this hypothesis for some components. Acetnaphthalide and benzamide--both with a polar residue attached to a large ring structure--are more soluble in ethanol than water and would be expected to depress ethanol relative volatility. Most of the common amino acids however (such as glycine, alanine, valine, tryosine, and leucine) show very high dipole moments (present at ordinary pH as dipolar zwitterions), are more soluble in water than ethanol, and should enhance ethanol relative volatility.

Results from equilibration in the Othmer still with yeast extract present showed substantial salting out. Figure 43 plots \( \ln \frac{K_s}{K_0} \) vs yeast extract composition in grams per liter (a mole fraction cannot be calculated without a representative molecular weight for the complex extract mixture). The resulting plot is roughly linear, with an effect on a weight basis slightly less than one half that found for pure KCl salt.

The concentration of charged species in the solution can be determined approximately by measuring the conductivity of the solution. The conductivity can be related directly to the solution condosity which is the molar concentration of an NaCl solution having the same
Figure 43. Effect of yeast extract on ethanol/water relative volatility.
specific conductance as the measured solution (2). The conductance of solutions of various dissolved ions is related by the Nernst-Einstein equation and is inversely proportional to the ions' diffusion coefficients (159). For all simple inorganic salts the molar concentration to achieve a given conductivity is similar, but for larger ions with large diffusion coefficients, the concentration needed to achieve a given conductance is higher. For the yeast extract solutions, therefore, the condosities will probably underestimate the actual ionic concentration. When enhancement is plotted against conductivity for the yeast extract solutions (Figure 44), a roughly linear relation is again found. The resulting k value based only on estimated charged species concentration is much larger (k = 76 vs. k = 17.4 for KCl) than the values obtained for pure salts. It must be concluded that noncharged species (including zwitterions) are having an effect along with the charged species in salting out ethanol, as expected from the amino acid solubility data.

8.4.5 Effect of pH and glucose

Fermentation beers are normally acidic (pH = 3 to 4). To test the effect of pH, an ethanol/water solution (X_e = 0.0150) was acidified with sulfuric acid to a pH of 2.88 and equilibrated in the still (results in Table 23). To within experimental error, no effect on volatility was observed. This is as expected since a pH of 2.88 corresponds to the extremely small concentration of only 2.4 x 10^-5 mole fraction. In a complex mixture such as a fermentation broth, pH may still have an effect as the protonation states of other species (and hence their effect on volatility) may be changed by changes in pH.
Figure 44. Effect of yeast extract (as measured by charged species concentration) on ethanol/water relative volatility.
Table 23

Effect of pH on Ethanol Volatility

<table>
<thead>
<tr>
<th>pH = 2.88</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_e = 0.0150$</td>
</tr>
</tbody>
</table>

Table 24

Effect of Glucose on Ethanol Volatility

<table>
<thead>
<tr>
<th>Glucose Concentration: 20 g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_e = 0.0156$</td>
</tr>
</tbody>
</table>
To confirm the applicability of the data of Kharin and Perelyyin (143) for sugars, a single experiment was conducted with 20 g/L glucose added to an ethanol/water mixture \( X_e = 0.0156 \) and equilibrated (results in Table 24). Salting in was observed with a \( k \) value of -11.3 which is comparable to the value of -11.9 reported for sucrose at low ethanol concentration (see Figure 36).

8.4.6 Ethanol volatility over a complex beer

A concentrated fermentation broth was prepared to test the change in apparent ethanol volatility over the complex mixture. A continuous culture was maintained using Cysewski's medium (Table 18) to produce a large sample of the broth. The initial broth composition was as given in Table 17 with a yeast cell concentration of 10 g/L. This beer was then concentrated fourfold by stripping with air under mild vacuum and at 60°C. The concentrated beer (with cells intact as examined microscopically) was diluted with ethanol and water in various amounts to produce beers of roughly constant ethanol concentration \( X_e = 0.015 \) mole fraction but increasing dissolved species concentrations. The actual amounts of each component mixed and degree of concentration over the original beer are summarized in Table 25. A final sample was prepared as above, but with yeast cells centrifuged out. Samples were then equilibrated in the still. Before injection into the G.C., the liquid samples were cooled and centrifuged (at 2°C to minimize volatile losses) to remove cells which could plug the G.C. prefilter.

Results are summarized in Table 26. For all the beer samples with cells present, a small degree of salting in was observed. This is
Table 25
Fermentor Beer Samples for Volatility Enhancement Studies

<table>
<thead>
<tr>
<th>4 Fold Concentrated Beer (ml)</th>
<th>95 Wt % Ethanol (ml)</th>
<th>Water (ml)</th>
<th>Concentration Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>27</td>
<td>298</td>
<td>0.75</td>
</tr>
<tr>
<td>300</td>
<td>27</td>
<td>73</td>
<td>3.00</td>
</tr>
<tr>
<td>373</td>
<td>27</td>
<td>0</td>
<td>3.73</td>
</tr>
<tr>
<td>300 (centrifuged)</td>
<td>27</td>
<td>73</td>
<td>3.00</td>
</tr>
<tr>
<td>Beer Concentration Factor</td>
<td>$X_e$</td>
<td>$Y^0_e$</td>
<td>$Y^s_e$</td>
</tr>
<tr>
<td>---------------------------</td>
<td>------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>0.75</td>
<td>0.0153</td>
<td>0.1552</td>
<td>0.1527</td>
</tr>
<tr>
<td>3.00</td>
<td>0.0160</td>
<td>0.1603</td>
<td>0.1304</td>
</tr>
<tr>
<td>3.73</td>
<td>0.0162</td>
<td>0.1614</td>
<td>0.1311</td>
</tr>
<tr>
<td>3.00*</td>
<td>0.0140</td>
<td>0.1450</td>
<td>0.1578</td>
</tr>
</tbody>
</table>

* Centrifuged beer - cell free
surprising as the glucose concentration in the most concentrated sample was only 4 g/L—not enough to explain the ethanol volatility depression, and all of the other components tested salt ethanol out. The single sample without cells present did show salting out as anticipated.

A first possible explanation might be an attraction of ethanol to the slightly charged (160) outer cell surface; hydrotropism at a grand scale. However, this explanation is inadequate as a complete ethanol monolayer over all the cells present in the threefold concentrated sample would reduce the bulk liquid ethanol concentration by only 2.6 x 10^{-3} g/L, far too little to account for the measured reduction in ethanol vapor composition which would require a bulk liquid composition reduction of 9.1 g/L. This explanation is feasible, however, if not only the cell outer wall surface, but also the cell internal membrane structure became available to adsorb ethanol—the cell becoming an ethanol "sponge" upon heating in the still. If the cells settled to the still bottom during equilibration, they would have been contacted directly with the more concentrated ethanol overflow returning from the condensate collector. An adsorption of 0.3 g ethanol/g cells (dry weight) would be necessary to account for the volatility depression effect. This is only one third the ethanol adsorption capacity of Amberlite (a common exchange resin).

The same results would have been seen in the event of ethanol absorption into the lipid cell membrane. The solubility of ethanol in most organic solvents increases substantially at high temperature
It is possible that under the high (boiling) temperature conditions in the still, ethanol may have been extracted into the cells. This would have reduced the bulk ethanol concentration during equilibration to give a low measured vapor composition. During centrifugation (at 2°C) the ethanol may have been released to the solution to return a high measured ethanol liquid concentration and show the apparent salting in.

Another possible explanation is the release of nonvolatile ethanol extractants (components which would reduce the ethanol volatility) from the cells during the twenty hours of equilibration in the still at boiling temperatures. After equilibration, the cells are still coherent bodies but are much smaller than the cells originally taken from the fermentor. This seems to be a reasonable explanation.

Finally, the presence of yeast cells may have interfered with mixing in the still, preventing equilibration. This seems unlikely though considering the twenty hour equilibration times used.

To better elucidate, an equilibration run was attempted under vacuum at 35°C to reduce temperature effects and prevent changes in the cells (cell morphology is not altered under vacuum in the vauferm process). Unfortunately, excessive bumping made this test impossible.

Applying either of the two likely explanations, the enhancement found for the beer without cells would be most appropriate to use in the analysis of a vauferm process (where high temperatures are not encountered). The volatility depression found for the complete beer would be expected in the case of atmospheric pressure (high
temperature) stripping in an ethanol stripping still processing whole beer.

8.5 Conclusions

The new data for volatility enhancement by salts in dilute ethanol solution demonstrates that equation 8-5 is applicable only at fixed ethanol concentration (a criterion applied in its derivation). The constancy of effectiveness factors "k" for many salts over the midrange of ethanol concentrations appears to result from a fortuitous balancing of salt effects on ethanol and water in this composition range.

Limited attempts have been made to include the effect of nonaqueous solvent concentration in correlations of the enhancement factor. Following Guyer (162), Bedrossian and Cheh (138) found for their data for sodium acetate that:

\[ \ln \left( \frac{y^s}{y^o} \right) \propto X_e \]  

(8-8)

at constant \( \frac{X_{\text{water}}}{X_{\text{salt}}} \)

with enhancement increasing as the ratio of equation 8-8 decreases. Jaques and Furter (163) have applied equation 8-1 retaining terms through the third order to derive a six constant equation similar to equation 8-5 but including a dependence on the nonaqueous solvent concentration. All six constants must be fit to data, and, not surprisingly, the equation correlates data quite well. For salts at
saturation, the Wilson equation has been applied with new pseudo-Wilson constants found for the ethanol and water components in the salt saturated solution (164). This method has the disadvantage that new constants must be fit to data for every salt concentration of interest.

A more promising approach to correlating the effect of dissolved components on phase equilibrium is the generalization of the UNIQUAC approach (82,165) to include dissolved components as species of zero volatility. Binary interaction energy parameters would then be found for all components in the solution (including dissolved species). This approach, along with a method to predict a priori the interaction coefficients, is now under development at the University of California, Berkeley (166).

Volutility effects in complex systems like fermentation beer are difficult to predict. Fortunately, the effects are generally small (as seen in Figure 39). Most beer (or wine) components will enhance ethanol volatility, but yeast cells present at high temperature depress ethanol volatility. These effects may be neglected for initial design purposes, or approximate corrections may be included based on the data of this report. For a sensitive final design, new equilibrium data should be taken over the actual broth of interest at the design conditions. Problems due to unwanted temperature effects could be eliminated by using a static mixing cell device (like that of Pemberton and Mash (52)) instead of a recirculating still. This would give vapor pressure vs total composition and temperature data from which
equilibrium compositions could be deduced by the method of Barker (167).

Dissolved components will have a large effect only when specifically added at high concentration as in extractive distillation or salt augmented liquid extraction (103). Effects due to naturally occurring dissolved components will be negligible compared to the effect of these added salts at high concentration. Literature reported enhancement values at saturation conditions can be used to evaluate extractive distillation systems and the values of this report can be used to evaluate liquid extraction from dilute ethanol solutions at fixed salt concentration. The large enhancements found at dilute ethanol concentration do suggest that salt augmented liquid extraction may be an attractive process alternative for ethanol product recovery.

9 Multicomponent Equilibrium Modelling

9.1 The UNIQUAC model for multicomponent equilibrium

Ethanol/water separation design will frequently require evaluation of multicomponent vapor/liquid equilibria. At ordinary pressures the ethanol/water system forms an azeotrope and an additional component must be added to alter the equilibrium, breaking the azeotrope to produce anhydrous ethanol (168). In liquid/liquid extraction processes, an additional chemical agent (the extractant) must be added to effect the ethanol/water separation (103). Fermentation beer contains fermentation by-products (aldehydes, glycerol, acids and fusel oils) which must be considered in the separation design (169).
The UNIQUAC model is especially valuable for separation process design as multicomponent equilibria can be computed using only parameters for the separate binaries which make up the complete multicomponent system.

The activity coefficient for each component in a multicomponent system is given by:

$$\ln \gamma_i = \ln \frac{\phi_i}{x_i} + (\frac{Z}{2}) q_i \ln \frac{\theta_i}{\phi_i} + \varepsilon_i - \frac{\phi_i}{x_i} \sum_j x_j \varepsilon_j \quad (9-1)$$

$$-q_i \ln(\sum_j \theta_j \tau_{ij}) + q_i' - q_i - \frac{\theta_i}{\sum_j \theta_k \tau_{kj}}$$

where:

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad \theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad \theta_i = \frac{q_i' x_i}{\sum_j q_j' x_j}$$

$$\varepsilon_j = \frac{Z}{2} (r_j - q_j) - (r_j - 1)$$

$$\tau_{ij} = \exp \left( \frac{-\Delta U_{ij}}{CRT} \right)$$

where all symbols have the same meaning as in section 6 equations 6-10 through 6-16. The pure component parameters \((r_i, q_i, q'_i)\) are determined from a knowledge of molecular structure and are tabulated for most common molecules (1), the binary parameters must be determined from vapor/liquid equilibrium data for all binaries in the system as was illustrated for the ethanol/water system in section 6.
The multicomponent UNIQUAC model is implemented for computer computation in the Prausnitz computer package described in Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria (1). Results for the system ethanol/water/benzene (a system used to break the ethanol/water azeotrope), are presented in Figure 45. The liquid/liquid ternary equilibrium was predicted based on the interaction parameters fit only to the binary vapor/liquid equilibrium data shown. Some improvement would be expected if the data for the binary systems and the predicted ternary were all at the same temperature.

9.2 Data sources for multicomponent equilibrium modeling

The binary parameters for ethanol and water should be found using the new temperature dependent model of Section 6. For other components of a multicomponent system, binary parameters can be fit to available data or new binary equilibrium data can be measured. A massive collection of equilibrium data compiled by Gmehling and Onken, with binary UNIQUAC parameters already computed in now available (75). Parameters for most components important to ethanol/water separation design are included in the Gmehling compilation. Some of these are summarized in Tables 27 through 29.

For preliminary equilibrium evaluations involving components for which no data is available, the UNIQUAC binary parameters can be estimated using the UNIFAC group equilibrium contribution method (92). This method is described in detail in the monograph Vapor-Liquid Equilibria Using UNIFAC (170). Using this method, a large number of separating agents can be rapidly screened and new separation methods compared.
Figure 45. UNIQUAC model for the ternary system ethanol/water/benzene.
### Table 27A

**UNIQUAC Binary Parameters for Beer Contaminants With Water**

<table>
<thead>
<tr>
<th>Component 1</th>
<th>Component 2</th>
<th>$\Delta U_{12}/R$</th>
<th>$\Delta U_{21}/R$</th>
<th>Equilibrium Conditions</th>
<th>Data Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>2,3-Butanediol</td>
<td>85.91</td>
<td>-54.82</td>
<td>4121 mmHg</td>
<td>171</td>
</tr>
<tr>
<td></td>
<td>Glycerol</td>
<td>-</td>
<td>-</td>
<td>760 mmHg</td>
<td>172</td>
</tr>
<tr>
<td></td>
<td>Acetaldehyde</td>
<td>-427.94</td>
<td>1198.40</td>
<td>763 mmHg</td>
<td>173</td>
</tr>
<tr>
<td></td>
<td>1-Propanol</td>
<td>493.90</td>
<td>69.95</td>
<td>760 mmHg</td>
<td>174</td>
</tr>
<tr>
<td></td>
<td>2-Propanol</td>
<td>-95.04</td>
<td>630.61</td>
<td>760 mmHg</td>
<td>175</td>
</tr>
<tr>
<td></td>
<td>Tert-Butanol</td>
<td>-10.85</td>
<td>553.26</td>
<td>760 mmHg</td>
<td>176</td>
</tr>
<tr>
<td></td>
<td>1-Butanol</td>
<td>477.23</td>
<td>181.72</td>
<td>760 mmHg</td>
<td>177</td>
</tr>
<tr>
<td></td>
<td>1-Pentanol</td>
<td>502.09</td>
<td>153.12</td>
<td>760 mmHg</td>
<td>178</td>
</tr>
<tr>
<td></td>
<td>3-Methylbutanol</td>
<td>819.62</td>
<td>-223.79</td>
<td>760 mmHg</td>
<td>179</td>
</tr>
<tr>
<td></td>
<td>2-Methyl-1-Propanol</td>
<td>283.07</td>
<td>299.94</td>
<td>35°C</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>Allyl Alcohol</td>
<td>217.67</td>
<td>78.00</td>
<td>760 mmHg</td>
<td>181</td>
</tr>
<tr>
<td></td>
<td>Acetic Acid</td>
<td>-251.69</td>
<td>407.01</td>
<td>760 mmHg</td>
<td>182</td>
</tr>
<tr>
<td></td>
<td>Formic Acid</td>
<td>-215.26</td>
<td>-111.50</td>
<td>760 mmHg</td>
<td>183</td>
</tr>
<tr>
<td></td>
<td>Furfural</td>
<td>537.73</td>
<td>-36.22</td>
<td>760 mmHg</td>
<td>191</td>
</tr>
<tr>
<td>Component 1</td>
<td>Component 2</td>
<td>$\Delta U_{12}/R$</td>
<td>$\Delta U_{21}/R$</td>
<td>Equilibrium Conditions</td>
<td>Data Source</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------------</td>
<td>-------------------</td>
<td>-------------------</td>
<td>------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Acetaldehyde</td>
<td>-593.73</td>
<td>-594.19</td>
<td>30°C</td>
<td>57</td>
</tr>
<tr>
<td>1-Propanol</td>
<td></td>
<td>-35.28</td>
<td>71.76</td>
<td>760 mmHg</td>
<td>184</td>
</tr>
<tr>
<td>2-Propanol</td>
<td></td>
<td>-350.68</td>
<td>480.80</td>
<td>760 mmHg</td>
<td>185</td>
</tr>
<tr>
<td>Tert-Butanol</td>
<td></td>
<td>-436.36</td>
<td>659.76</td>
<td>760 mmHg</td>
<td>186</td>
</tr>
<tr>
<td>1-Butanol</td>
<td></td>
<td>75.36</td>
<td>-38.71</td>
<td>760 mmHg</td>
<td>187</td>
</tr>
<tr>
<td>1-Pentanol</td>
<td></td>
<td>-280.94</td>
<td>508.22</td>
<td>760 mmHg</td>
<td>188</td>
</tr>
<tr>
<td>3-Methylbutanol</td>
<td></td>
<td>-166.42</td>
<td>316.35</td>
<td>70°C</td>
<td>189</td>
</tr>
<tr>
<td>2-Methyl-1-Propanol</td>
<td></td>
<td>-319.10</td>
<td>451.17</td>
<td>760 mmHg</td>
<td>186</td>
</tr>
<tr>
<td>Allyl Alcohol</td>
<td></td>
<td>391.45</td>
<td>-250.05</td>
<td>760 mmHg</td>
<td>181</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td></td>
<td>-162.72</td>
<td>122.36</td>
<td>706 mmHg</td>
<td>190</td>
</tr>
<tr>
<td>Furfural</td>
<td></td>
<td>125.45</td>
<td>403.43</td>
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<td>191</td>
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Table 28
UNIQUAC Binary Parameters for Ethanol/Water Separating Agents

<table>
<thead>
<tr>
<th>Component 1</th>
<th>Component 2</th>
<th>ΔU_{12}/R</th>
<th>ΔU_{21}/R</th>
<th>Equilibrium Conditions</th>
<th>Data Source</th>
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<tbody>
<tr>
<td>Water</td>
<td>Benzene</td>
<td>772.50</td>
<td>966.13</td>
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<td>192</td>
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<td></td>
<td>Diethyl Ether</td>
<td>102.27</td>
<td>1198.92</td>
<td>25°C</td>
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</tr>
<tr>
<td>Ethanol</td>
<td>Benzene</td>
<td>-293.47</td>
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<td>192</td>
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<tr>
<td></td>
<td>Trichloroethylene</td>
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<td>838.84</td>
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<td>Diethyl Ether</td>
<td>-173.48</td>
<td>665.42</td>
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Table 29A
UNIQUAC Pure Component Parameters

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<tr>
<th>Component</th>
<th>r</th>
<th>q</th>
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<td>2,3-Butanediol</td>
<td>3.756</td>
<td>3.320</td>
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<tr>
<td>Glycerol</td>
<td>3.586</td>
<td>3.060</td>
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<tr>
<td>Acetaldehyde</td>
<td>1.899</td>
<td>1.796</td>
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<tr>
<td>1-Propanol</td>
<td>2.780</td>
<td>2.512</td>
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<tr>
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<td>2.779</td>
<td>2.508</td>
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<tr>
<td>Tert-Butanol</td>
<td>3.453</td>
<td>3.128</td>
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<tr>
<td>1-Butanol</td>
<td>3.454</td>
<td>3.052</td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>4.129</td>
<td>3.592</td>
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<tr>
<td>3-Methylbutanol</td>
<td>4.128</td>
<td>3.588</td>
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<td>2-Methyl-1-Propanol</td>
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<td></td>
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<tr>
<td>Allyl Alcohol</td>
<td>2.550</td>
<td>2.300</td>
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<tr>
<td>Acetic Acid</td>
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<td>2.072</td>
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<td>Formic Acid</td>
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<td>1.532</td>
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<tr>
<td>Furfural</td>
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<tr>
<td>Benzene</td>
<td>3.188</td>
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<tr>
<td>Trichlorethylene</td>
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<td>3.395</td>
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Table 29B
UNIQUAC Modified Area Parameters

<table>
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<th>Component</th>
<th>$q'$ for Alcohols and Water</th>
<th>$q'$</th>
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<tr>
<td>Methanol</td>
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<tr>
<td>Ethanol</td>
<td></td>
<td>0.92</td>
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<tr>
<td>C3-OH</td>
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<td>0.89</td>
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<tr>
<td>C4-OH</td>
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<td>0.88</td>
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<tr>
<td>C5-OH</td>
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</tr>
<tr>
<td>C6-OH</td>
<td></td>
<td>1.78</td>
</tr>
</tbody>
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APPENDIX 1

ETOH COMPUTER EQUILIBRIUM PACKAGE PROGRAM AND DOCUMENTATION
Subroutine BDPTM

Purpose: Performs ethanol/water equilibrium bubble and dew point calculations

Usage: Call BDPTM (P, T, XETH, YETH, ITYPE)

Variables:

(In Call)
- Equilibrium pressure: P (mmHg)
- Equilibrium temperature: T (deg K)
- Equilibrium ethanol liquid mole fraction: XETH
- Equilibrium ethanol vapor mole fraction: YETH
- Control flag: ITYPE

(In Data Blocks)
- Equilibrium ratio, Y/X
- Print Control Flag: Mode(24)

Other needed routines
- PDEP, TDEP, TXDEP

Description:

This subroutine performs one of the following calculations:

For ITYPE = 1 or 2...
This subroutine calculates the bubble or dew temperature (deg K) for a given pressure (mmHg) and feed composition X(ITYPE=1) or Y(ITYPE=2). It returns T (K) and Y (ITYPE = 1) or X (ITYPE = 2). A guessed T must be supplied, but if it is LT. 200.0 or GT. 600.0, A guess of 325.0 will be supplied.

For ITYPE = 3 or 4...
This subroutine calculates the bubble or dew pressure (mmHg) for a given temperature (K) and feed composition X(ITYPE = 3) or Y(ITYPE = 4). It returns P (mmHg) and Y(ITYPE = 3) or X(ITYPE = 4). A guessed P must be supplied, but if it is LT. 1.OE-4 .OR .GT. 76000.0, a guess of 350.0 will be supplied.

Uses passed X and Y as initial guess for all cases.

A Newton-Raphson iteration is used based on the objective functions:

**Bubble point:**
\[ \sum_{i=1}^{2} K_i X_i = 1 \]

**Dew point:**
\[ \sum_{i=1}^{2} \frac{Y_i}{K_i} = 1 \]

where the equilibrium ratios "$K_i$" are calculated by PDEP, TDEP and TXDEP based on the new temperature dependent UNIQUAC equation.

**Variables used in subroutine BDPTM:**

<table>
<thead>
<tr>
<th>Name</th>
<th>Type</th>
<th>Main Use</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>ABS</td>
<td>R</td>
<td>standard</td>
<td>Dummy variable</td>
</tr>
<tr>
<td>ALOG</td>
<td>R</td>
<td>standard</td>
<td>Newton Raphson minimization variable</td>
</tr>
<tr>
<td>DUMMY</td>
<td>R</td>
<td>array</td>
<td>Newton Raphson minimization variable</td>
</tr>
<tr>
<td>F1</td>
<td>R</td>
<td>variable</td>
<td>Calculation index</td>
</tr>
<tr>
<td>F2</td>
<td>R</td>
<td>variable</td>
<td>Error flag</td>
</tr>
<tr>
<td>I</td>
<td>I</td>
<td>variable</td>
<td>Maximum allowable iterations</td>
</tr>
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<td>ITMAX</td>
<td>I</td>
<td>variable</td>
<td>Argument</td>
</tr>
<tr>
<td>ITYPE</td>
<td>I</td>
<td>variable</td>
<td>Calculation type flag</td>
</tr>
<tr>
<td>P</td>
<td>R</td>
<td>variable</td>
<td>Argument</td>
</tr>
<tr>
<td>PDEP</td>
<td>R</td>
<td>external</td>
<td>Sum of $KX$ (BP calculation) or $Y/X$ (DP calculation)</td>
</tr>
<tr>
<td>SS</td>
<td>R</td>
<td>variable</td>
<td>Sum of $KX$</td>
</tr>
<tr>
<td>T</td>
<td>R</td>
<td>variable</td>
<td>Liquid mole fractions used in iterative calculations</td>
</tr>
<tr>
<td>TDEP</td>
<td>R</td>
<td>external</td>
<td>Mole fraction ethanol in liquid--passed</td>
</tr>
<tr>
<td>TXDEP</td>
<td>R</td>
<td>external</td>
<td>Vapor mole fraction used in iterative calculations</td>
</tr>
<tr>
<td>X</td>
<td>R</td>
<td>array</td>
<td>Mole fraction ethanol in vapor--passed</td>
</tr>
<tr>
<td>XETH</td>
<td>R</td>
<td>variable</td>
<td>Mole fraction ethanol in liquid--passed</td>
</tr>
<tr>
<td>Y</td>
<td>R</td>
<td>array</td>
<td>Mole fraction ethanol in vapor--passed</td>
</tr>
<tr>
<td>YETH</td>
<td>R</td>
<td>variable</td>
<td>Mole fraction ethanol in vapor--passed</td>
</tr>
</tbody>
</table>
Subroutine PDEP

Purpose: Calculates ethanol/water equilibrium ratios: $K = Y/X$

Usage: Call PDEP (P, T, Y, K)

Input Variables:

(In Call)

- Equilibrium pressure $P$ [mmHg]
- Equilibrium temperature $T$ [deg K]
- Equilibrium vapor mole function $Y$
  $(1 = \text{EtOH}, 2 = \text{Water})$

(In Data Blocks)

- Liquid Molar Volumes $V_{\text{LIQ}}$
- Virial Coefficients $B$
- Activity Coefficients $\Gamma$

Output Variables:

- Equilibrium Ratio, $Y/X$
  $(1 = \text{EtOH}, 2 = \text{water})$
  $K$

Other Needed Routines

TDEP, TXDEP

Description

This subroutine calculates equilibrium ratios $Y/X$ as functions of $P$, $T$, $Y$. Vapor phase nonidealities are included as fugacity coefficients ($\phi_i$) based on virial coefficients calculated in TDEP. Liquid phase nonidealities are included as activity coefficients ($\gamma_i$) calculated in TXDEP based on the new temperature dependent UNIQUAC model.

$$K_i = \frac{\gamma_i \phi_{i,\text{ref, liquid}}}{\phi_i}$$

### Variables used in subroutine PDEP

<table>
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<tr>
<th>Name</th>
<th>Type</th>
<th>Main Use</th>
<th>Blocks</th>
<th>Description</th>
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<tbody>
<tr>
<td>B</td>
<td>R Array</td>
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<td>Virial coefficients (1=EtOH, 2=Cross, 3=Water)</td>
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<tr>
<td>BM</td>
<td>R Variable</td>
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<td></td>
<td>Mixture virial coefficient</td>
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<td>R standard</td>
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<td>F</td>
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<td>/SUBT/</td>
<td></td>
<td>Zero pressure reference fungacity</td>
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<tr>
<td>GAMMA</td>
<td>R Array</td>
<td>/SUBTX/</td>
<td></td>
<td>Activity coefficient (1=EtOH, 2=Water)</td>
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<td>I</td>
<td>I Variable</td>
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<td></td>
<td>Calculation index</td>
</tr>
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<td>K</td>
<td>R Array</td>
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<td>Argument</td>
<td>Equilibrium ratio Y/X (1=EtOH, 2=Water)</td>
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<td>P</td>
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<td></td>
<td>Argument</td>
<td>Pressure</td>
</tr>
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<td>R Array</td>
<td></td>
<td>Argument</td>
<td>Fugacity coefficient (1=EtOH, 2=Water)</td>
</tr>
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<td>PRT</td>
<td>R Variable</td>
<td></td>
<td>Argument</td>
<td>Pressure/(R x Temperature)</td>
</tr>
<tr>
<td>T</td>
<td>R Variable</td>
<td></td>
<td>Argument</td>
<td>Temperature (deg. K)</td>
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<td>VLIQ</td>
<td>R Array</td>
<td>/SÜBT/</td>
<td></td>
<td>Liquid specific volume (1=EtOH, 2=Water)</td>
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<td>Y</td>
<td>R Array</td>
<td></td>
<td>Argument</td>
<td>Mole fraction in vapor (1=EtOH, 2=Water)</td>
</tr>
</tbody>
</table>
Subroutine TDEP

Purpose: Calculates temperature dependent variables for the ethanol/water equilibrium system.
1) Liquid molar volumes;
2) Zero pressure reference fugacities;
3) Virial coefficients.

Usage: Call TDEP (T)

Input Variables:
(In Call)
Temperature T deg K

(In Data Blocks)
Initialization flag IFLAG1
(=0 on first call to initialize)

Output Variables:
Liquid molar volumes VLIQ
Zero pressure reference fugacities F
Virial Coefficients B

Other Needed Routines
None

Description

Calculates the temperature dependent equilibrium variables. Liquid molar volumes are calculated using the modified Rackett correlation. Zero pressure reference fugacities are calculated according to an empirical fit by Prausnitz. Virial coefficients are calculated using the Hayden-O'Connell method.

If this subroutine is used, IFLAG1 must be commoned to the main program. IFLAG1 = 0 when the subroutine is used for the first time.

### Variable used in Subroutine TDEP

<table>
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<tr>
<th>Name</th>
<th>Type</th>
<th>Main Use</th>
<th>Blocks</th>
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<tbody>
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<td>Virial coefficient intermediate calculation variable</td>
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<tr>
<td>ALOG</td>
<td>R Standard</td>
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<td>/SUBT/</td>
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<td>Virial coefficient intermediate calculation variable.</td>
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<td>Virial coefficient intermediate calculation variable.</td>
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<td>Virial coefficient intermediate calculation variable.</td>
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<td>Dipole moment intermediate calculation variable.</td>
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<tr>
<td>C1</td>
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<td>Reference fugacity equation constants (1=EtOH, 2=Water)</td>
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<td>Dipole moment (1=EtOH, 2=Water) (Debyes)</td>
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<td>Zero pressure reference fugacity (1=EtOH, 2=water)</td>
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<tr>
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<td>/SUBT/</td>
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<td>Calculation index</td>
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<td>I</td>
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<td>Control flag (=0, Initialize variables)</td>
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</tr>
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<td>I Variable</td>
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<td>Calculation index</td>
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<td>Critical Pressure (1=EtOH, 2=Water)</td>
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<td>R Variable</td>
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<td>Dipole moment intermediate calculation variable</td>
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<td>Dipole moment intermediate calculation variable</td>
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<td>P2</td>
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<td>Mean Radius of gyration (1=EtOH, 2=Water) (Angstroms)</td>
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<td>Modified reduced dipole moment</td>
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<td>R Array</td>
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<td>Effective nonpolar potential parameter</td>
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<td>Variable</td>
<td>Type</td>
<td>Role</td>
<td>Description</td>
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<td>----------</td>
<td>----------------------------------------------------------------------</td>
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</tr>
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<td>Argument</td>
<td>Temperature (deg K)</td>
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<td>Argument</td>
<td>Temperature (deg K)</td>
<td></td>
</tr>
<tr>
<td>TAU</td>
<td>R Variable</td>
<td>Molar volume intermediate calculation variable (1=EtOH, 2=Water)</td>
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<td>ZRA</td>
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<td>Rackett Parameters (1=EtOH, 2=Water)</td>
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</table>
Subroutine TXDEP

Purpose: Calculates temperature dependent activity coefficients for the ethanol/water equilibrium system.

Usage: Call TXDEP (T, X)

Input Variables:

(In Call)
- Temperature: T deg K
- Ethanol liquid mole fraction: X

(In Data Blocks)
- Initialization flag: IFLAG2
  (=0 on first call to initialize)
- Activity coefficient selector flag: NOP
  =1 2 parameter UNIQUAC
  =2 3 parameter UNIQUAC

Output Variables:
- Activity coefficients: GAMMA
  (1=EtOH, 2=Water)

Other Needed Routines
None

Description

This subroutine calculates activity coefficients for the ethanol/water equilibrium system. The new temperature dependent 2 or 3 parameter UNIQUAC equations are used.

If this subroutine is used, IFLAG2 and NOP must be commoned to the main program, IFLAG2=0 when the subroutine is called for the first time.

### Variables used in Subroutine TXDEP

<table>
<thead>
<tr>
<th>Name</th>
<th>Type</th>
<th>Main Use</th>
<th>Blocks</th>
<th>Description</th>
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<td>Argument: Mole fraction in liquid (1=EtOH,2=Water)</td>
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</table>
Program ETOH: Ethanol/Water Vapor/Liquid Equilibrium Model

DELETE,LGO,OUTPUT.
MNF4,T.
LINK,X.
EXIT.
DUMP,O.
GRUMP.

C
PROGRAM ETOH(TAPES=16,TAPE1=16,OUTPUT=TAPE6)
C
CONNECT FOR INTERACTIVE TERMINAL USE
C
CALL CONNECT(5)
CALL CONNECT(6)
C
******************************************************************************
C
ETOH IS A DRIVER PROGRAM USED TO GENERATE BUBBLE OR DEW POINT DATA LISTS FOR THE SYSTEM ETHANOL/WATER. THE MODIFIED TEMPERATURE DEPENDENT UNIQUAC METHOD IS USED.
C
C
NOP=1, SPECIFIES THE TWO PARAMETER UNIQUAC EQUATION.
C
NOP=2, SPECIFIES THE THREE PARAMETER UNIQUAC EQUATION.
C
C
RESULTS ARE VALID FOR THE PRESSURE RANGE FROM 50 TO 1000 MMHG.
C
C
COMMON /MAINT/ IFLAG1
COMMON /MAINTX/ IFLAG2,NOP
COMMON /DATA3/ LOOK,MODE(40)
NOP=1
MODE(24)=0
IFLAG1=0
IFLAG2=0
3 WRITE(6,1)
1 FORMAT(* IF YOU WISH DATA AT A CONSTANT TEMPERATURE, 1*,/* TYPE 00. IF YOU WISH DATA AT CONSTANT 2*,/* PRESSURE, TYPE A 01.*) READ(5,100)II
100 FORMAT(I2)
IF(II.GT.0) GO TO 110
WRITE(6,2)
2 FORMAT(* WHAT TEMPERATURE DO YOU WANT DATA AT? DEG(K)*) READ(5,4)T
4 FORMAT(F6.2)
WRITE(6,8)
8 FORMAT(* PRESSURE*,5X,*TEMP.*,12X,*XETH*,7X,*YETH*) ITYPE=3
P=55.0
XETH=0.0
YETH=0.0
GO TO 10
110 WRITE(6,20)
20 FORMAT(* WHAT PRESSURE DO YOU WANT DATA AT? (MMHG)*)
READ(5,120)P
120 FORMAT(F6.2)
WRITE(6,8)
ITYPE=1
T=325.
XETH=0.0
YETH=0.0
10 XETH=XETH+.01
   CALL BDPTM(P,T,XETH,YETH,ITYPE)
   WRITE(6,30) P,T,XETH,YETH
30 FORMAT(1X,F7.2,6X,F6.2,10X,F6.4,5X,F6.4)
   IF(XETH.GE.1.0) GO TO 40
   GO TO 10
40 WRITE(6,150)
150 FORMAT(*IF YOU WANT TO RE-RUN THE PROGRAM, TYPE A 00
1*,/,*IF YOU WANT TO STOP, TYPE A.01*)
   READ(5,160) IJ
160 FORMAT(I2)
   IF(IJ.LT.1) GO TO 3
STOP
END
SUBROUTINE BDPTM (P,T,XETH,YETH,ITYPE)

C
C THIS SUBROUTINE PERFORMS ONE OF THE FOLLOWING CALCULATIONS...
C
C ITYPE= 1-BUBBLE POINT TEMPERATURE (GIVEN P,X-FIND T,Y)
C ITYPE= 2-DEW POINT TEMPERATURE (GIVEN P,Y-FIND T,X)
C ITYPE= 3-BUBBLE POINT PRESSURE (GIVEN T,X-FIND P,Y)
C ITYPE= 4-DEW POINT PRESSURE (GIVEN T,Y-FIND P,X)

C FOR ITYPE=1 OR 2...
C THIS SUBROUTINE CALCULATES THE BUBBLE OR DEW TEMPERATURE (DEG K) FOR
C A GIVEN PRESSURE (MMHG) AND FEED COMPOSITION X (ITYPE=1) OR Y (ITYPE=2).
C IT RETURNS T (K) AND Y (ITYPE=1) OR X (ITYPE=2). A GUESSED T MUST BE
C SUPPLIED, BUT IF IT IS .LT. 200.0 OR .GT. 600.0, A GUESS OF 325.0
C WILL BE SUPPLIED. USES PASSED X AND Y AS INITIAL GUESS.
C
C FOR ITYPE=3 OR 4...
C THIS SUBROUTINE CALCULATES THE BUBBLE OR DEW PRESSURE (MMHG) FOR A
C GIVEN TEMPERATURE (K) AND FEED COMPOSITION X (ITYPE=3) OR Y (ITYPE=4).
C IT RETURNS P (MMHG) AND Y (ITYPE=3) OR X (ITYPE=4). A GUESSED P MUST BE
C SUPPLIED, BUT IF IT IS .LT. 1.0E-4 OR .GT. 76000.0, A GUESS OF 350.0
C WILL BE SUPPLIED. USES PASSED X AND Y AS INITIAL GUESS.
C
C SUBROUTINES TDEP, TXDEP, AND PDEP ARE CALLED.
C
C BDPTM IS BASED ON SUBROUTINES BUDT AND BUDEP,
C FOUND IN COMPUTER CALCULATIONS FOR MULTICOMPONENT VAPOR-LIQUID AND
C LIQUID-LIQUID EQUILIBRUM BY PRAUSNITZ, ANDERSON, GRENS, ECKERT, HSIEH, AND
C O, CONNELL, PRENTICE-HALL, 1980.
C
DIMENSION X(2), Y(2), DUMMY(2), E2(2), E6(3)
COMMON/DATA3/ LOOK, NODE40)
COMMON/SUBP/ PHI(2), BM
COMMON/SUBT/ VLIQ(2), F(2), B(3)
COMMON/SUBTX/ GAMMA(2)
REAL K(2)
DATA ITMAX /30/

C CHECK VALIDITY OF INPUT PARAMETERS.
C
IF (ITYPE .LT. 1 .OR. ITYPE .GT. 4) GO TO 510
IF (ITYPE .GT. 2) GO TO 10
C
C CHECK FOR VALIDITY OF GUESSED T.
C
IF (T .LT. 200.0 .OR. T .GT. 600.0) T=325.0
C
C CHECK FOR VALIDITY OF INPUT P.
IF (P.GT. 1.0E-4 .AND. P.LT. 76000.0) GO TO 20
IERRO=1
GO TO 300

C CHECK FOR VALIDITY OF GUESSED P.
C
10 IF (P.LT. 1.0E-4 .OR. P.GT. 76000.0) P=350.0
C
C CHECK FOR VALIDITY OF INPUT T.
C
IF (T.GT. 200.0 .AND. T.LT. 600.0) GO TO 20
IERRO=2
GO TO 300
20 IT=0
C
C INITIALIZE X
C
X(1)=XETH
X(2)=1.0-X(1)
C
C INITIALIZE Y
C
Y(1)=YETH
Y(2)=1.0-Y(1)
C
C TOP OF ITERATION LOOP
C
40 IT=IT+1
IF (IT.LT. ITMAX) GO TO 50
IERRO=3
GO TO 300
C
C GET K VALUES FOR P,T,X,Y
C
50 IF (ITYPE .EQ. 4 .AND. IT.GT. 1) GO TO 55
IF (ITYPE .EQ. 3 .AND. IT.GT. 1) GO TO 56
CALL TDEP (T)
55 CALL TXDEP (T,X)
56 CALL PDEP (P,T,Y,K)
C
C CALCULATE SUM OF KX (BP) OR Y/K (DP).
C
S=0.0
DO 80 I=1,2
   IF (ITYPE .EQ. 2 .OR. ITYPE .EQ. 4) GO TO 60
   DUMMY(I)=K(I)*X(I)
   GO TO 70
50 DUMMY(I)=Y(I)/K(I)
70 S=S+DUMMY(I)
80 CONTINUE
C
C BRANCH TO TWO METHODS OF CONVERGENCE FOR BUBDEUT AND BUBDEUP.
C
IF (ITYPE .GT. 2) GO TO 160
F1=ALOG(S)
C
C CHECK FOR CONVERGENCE.
C
IF (ABS(F1) .LT. 1.0E-8) GO TO 130
C
C FIND K VALUES AT T+1.0 FOR FINITE DIFFERENCE DERIVITIVE.
C
CALL TDEP (T+1.0)
CALL TXDEP (T+1.0,X)
CALL PDEP (P,T+1.0,Y,K)
SS=0.0
IF (ITYPE .EQ. 2) GO TO 100
C
C CALCULATE NEW VAPOR COMPOSITION FOR BP AND SUM OF KX AT T+1.0.
C
DO 90 I=1,2
   Y(I)=DUMMY(I)/S
   SS=SS+K(I)*X(I)
90 CONTINUE
GO TO 120
C
C CALCULATE NEW VAPOR COMPOSITION FOR DP AND SUM OF Y/K AT T+1.0.
C
100 DO 110 I=1,2
   X(I)=DUMMY(I)/S
   SS=SS+Y(I)/K(I)
110 CONTINUE
120 F2=ALOG(SS)
C
C CALCULATE NEW NEWTON-RAPHSON TEMPERATURE
C
T=(F2-F1)*T/(F2-F1/(T+1.0))
C
C BREAK LOOP IF T IS GETTING OUT OF RANGE.
C
IF (T .GT. 100.0 .AND. T .LT. 1000.0) GO TO 40
IERROR=4
GO TO 300
C
C NORMALIZE CONVERGED X OR Y.
C
130 DO 150 I=1,2
   IF (ITYPE .EQ. 2) GO TO 140
   Y(I)=DUMMY(I)/S
140 X(I)=DUMMY(I)/S
150 CONTINUE
GO TO 900
160 IF (I TYPE .EQ. 4) GO TO 180
   DO 170 I=1,2
      Y(I)=DUMMY(I)/S
170 CONTINUE
   GO TO 200
180 DO 190 I=1,2
      X(I)=DUMMY(I)/S
190 CONTINUE
200 IF (S .LT. 5.0 .AND. S .GT. 0.2) GO TO 220
   IF (S .LT. 1.0) GO TO 210
   S=5.0
   GO TO 220
210 S=0.2
220 IF (I TYPE .EQ. 4) GO TO 230
   P=P*S
   GO TO 240
230 P=P/S
240 IF (P .GT. 1.0E-4 .AND. P .LT. 76000.0) GO TO 250
   IERROR=5
   GO TO 300
250 IF (ABS(S-1.0) .LT. 1.0E-8) GO TO 900
   GO TO 40
C
C PRINT AN ERROR MESSAGE.
C
300 IF (I TYPE .GT. 2) GO TO 310
   E1=1HP
   E2(1)=4HM M 0
   E2(2)=4HF HG
   E5=4HTEMP
   GO TO 320
310 E1=1HT
   E2(1)=4HDEG
   E2(2)=1HK
   E5=4HPRES
320 IF (I TYPE .EQ. 2 .OR. I TYPE .EQ. 4) GO TO 330
   E3=1HX
   E4=3HBBL
   GO TO 340
330 E3=1HY
   E4=3HDEW
340 GO TO (350,360,370,380,390), IERROR
350 E6(1)=4HINPU
   E6(2)=4HT PR
   E6(3)=2HES
   GO TO 400
360 E6(1)=4HINPU
   E6(2)=4HT TE
   E6(3)=2HMP
   GO TO 400
370  E6(1)=4HNUMB
    E6(2)=4H. IT
    E6(3)=2HER
    GO TO 400
380  E6(1)=4HCALC
    E6(2)=4H. TE
    E6(3)=2HMP
    GO TO 400
390  E6(1)=4HCALC
    E6(2)=4H. PR
    E6(3)=2HES
400  GO TO (410,420,440,450), ITYPE
410  WRITE (6,470) E1,P,E2(1),E2(2),E3,X(1),E4,E5,(E6(I),I=1,3)
    GO TO 430
420  WRITE (6,470) E1,P,E2(1),E2(2),E3,Y(1),E4,E5,(E6(I),I=1,3)
430  T=0.0
    GO TO 1000
440  WRITE (6,470) E1,T,E2(1),E2(2),E3,X(1),E4,E5,(E6(I),I=1,3)
    GO TO 460
450  WRITE (6,470) E1,T,E2(1),E2(2),E3,Y(1),E4,E5,(E6(I),I=1,3)
460  P=0.0
    GO TO 1000
470  FORMAT (/1X,NAT #,A1,=#,F10.5,# =#,A1,=#,F8.5,# =#,A1,=#)
    2   A3,# A4,# has not been # calculated because #,
    2   A4,# exceeds its allowed range in subr. BDPHM./)
C
C ITYPE HAS NOT BEEN INPUT PROPERLY.
C
510  WRITE (6,520)
520  FORMAT (/1H,0,# SUBR. BDPHM ABORTED BECAUSE ITYPE WAS SET WRONG./)
    GO TO 1000
C
C STORE RESULTS IN PASSED ARGUMENTS
C
900  XETH=X(1)
    YETH=Y(1)
C
C PRINT COMPUTATIONAL DETAILS
C
    IF(MODE(24).NE.1) GO TO 1000
    WRITE(6,600) P,T,XETH,YETH
600  FORMAT(* P=*,F7.2,* MMHG. T=*,F6.2,* K XETH=*,F6.4,
      /* YETH=*,F6.4)
    WRITE(6,620)B(1),B(2),B(3),BM
620  FORMAT(* VIRIAL COEFS. B1=*,F7.2,*,B2=*,F7.2,*,B3=*
      /*F7.2,*,BM=*,F7.2)
    WRITE(6,640) PHI(1),PHI(2)
640  FORMAT(* FUGACITY COEFS. PHI1=*,F7.4,*,PHI2=*,F7.4)
182

WRITE(*,660) F(1),F(2)

660 FORMAT(* REFERENCE FUGACITY. F1=*,F7.2,* F2=*,F7.2)

WRITE(*,680) GAMMA(1),GAMMA(2)

680 FORMAT(* ACTIVITY COEFS. GAMMA1=*,F7.4,* GAMMA2=*,F7.4)

C

C EXIT

C

1000 RETURN

END
SUBROUTINE PDEP (P,T,Y,K)

C THIS SUBROUTINE CALCULATES K,S AS FUNCTIONS OF P,T,Y AND TDEP VARIABLES.
C THIS SUBROUTINE SHOULD BE CALLED ANYTIME P,T,X,OR Y ARE CHANGED, SINCE
C THE K VALUES ARE DEPENDENT ON GAMMA(T,X), P, AND T.
C T IS EXPRESSED IN DEGREES KELVIN, AND P IS EXPRESSED IN MHG.
C PDEP IS BASED ON SUBROUTINES PHIS2 AND VPLQK,
C FOUND IN -COMPUTER CALCULATIONS FOR MULTICOMPONENT VAPOR-LIQUID AND
C LIQUID-LIQUID EQUILIBRIA- BY PRAUSNITZ,ANDERSON,CRENS,ECKERT,HSIEH,AND
C O,CONNELL, PRENTICE-HALL, 1980.

DIMENSION PHI(2),Y(2)
COMMON/DATA3/ LOOK,MODE(40)
COMMON/SUBP/ PHI(2),BM
COMMON /SUBT/ VLIQ(2),F(2),B(3)
COMMON /SUBTX/ GAMMA(2)
REAL K(2)
C CONVERT P FROM MHG TO BARS, WHICH IS THE UNIT USED BY TDEP TO FIND
C ZERO PRESSURE REFERENCE FUGACITY.
P=P*1.01325/760.0
PRT=P/(T*83.1473)
BM=Y(1)*Y(1)*B(1)+Y(2)*Y(2)*B(3)+2.0*Y(1)*Y(2)*B(2)
PHI(1)=EXP((2.0*(Y(1)*B(1)+Y(2)*B(2))-BM)*PRT)
PHI(2)=EXP((2.0*(Y(2)*B(3)+Y(1)*B(2))-BM)*PRT)
DO 20 I=1,2
 K(I)=GAMMA(I)*F(I)*EXP(PRT*VLIQ(I))/(PHI(I)*P)
20 CONTINUE
C CONVERT P BACK TO MHG FROM BARS.
P=P*760.0/1.01325
RETURN
END
SUBROUTINE TDEP (T)

C
C THIS SUBROUTINE Calculates all the temperature dependent variables.
C THESE are: liquid molar volumes, zero pressure reference fugacities,
C and virial coefficients. Temperature is expressed in degrees Kelvin.
C THIS SUBROUTINE MUST be called each time a new T is used.
C IN addition, subroutine TDDEP should also be called, because activity
C coefficients are functions of T as well as X.
C IF THIS SUBROUTINE IS used, IFLAG1 MUST be commoned to the main
C program. IFLAG1 =0 when the subroutine is used for the first
C time to initialize fixed values.
C TDEP IS BASED ON subroutines MVOLM, REFUG, AND BIJS2,
C found in -computer calculations for multicomponent vapor-liquid and
C liquid-liquid equilibria- by Prausnitz, Anderson, Grens, Eckert, Hsieh, AND
C
DIMENSION C(2),C2(2),C3(2),C4(2),C5(2),PC(2),TC(2),ZRA(2),
2 RD(2),DM(2),ETA(3),W(3),SGM(3),EOK(3),RDP(3),A(3),DH(3),
3 E(3),B0(3),BD(3)
COMMON /MAINT/ IFLAG1
COMMON/DATA3/ LOOK,MODE(40)
COMMON /SUBT/ VLIQ(2),F(2),B(3)
IF (IFLAG1 .GT. 0) GO TO 100
C INITIALIZE constants for ethanol (1) and water (2).
C CRITICAL temperatures (deg K) and pressures (bars).
    TC(1)=516.26
    TC(2)=647.37
    PC(1)=63.80
    PC(2)=221.20
C ZERO PRESS. REF. Fugacity (bars) equation constants for ethanol.
    C1(1)=-90.9091889355
    C2(1)=-3465.873483496
    C3(1)=-0.062301397140768
    C4(1)=20.486492956207
    C5(1)=0.000020664221042773
C ZERO PRESS. REF. Fugacity (bars) equation constants for water.
    C1(2)=57.041587918252
    C2(2)=-7004. 8416152596
    C3(2)=0.003588844369749
    C4(2)=-6.669387843423
    C5(2)=0.00000365054287344029
C DIPOLE MOMENT (debyes).
    DM(1)=1.69
    DM(2)=1.83
C MEAN radius of gyration (angstroms).
    RD(1)=2.25
    RD(2)=0.615
C RACKETT parameters for saturated-liquid molar volume correlation.
    ZRA(1)=0.2520
    ZRA(2)=0.2380
C ASSOCIATION parameter for ethanol.
    ETA(1)=1.40
C SOLVATION parameter for ethanol-water binary.
ETA(2)=1.55
C ASSOCIATION PARAMETER FOR WATER.
ETA(3)=1.70
EX=0.28571429
C CALCULATE TEMP. DEPENDENT PURE-COMPONENT PARAMETERS (SUB. BIJS2).
DO 10 I=1,2
    J=(I+1)*I/2
    W(J)=RD(I)*RD(I)*(-0.001366*RD(I)+0.02096)+0.006026
    EDK(J)=TC(I)*(0.748+0.91*W(J))
    EDK(J)=EDK(J)-TC(I)*0.4*ETA(J)/(2.0+20.0*W(J))
    SGM(J)=(2.4507-W(J))*3*TC(I)/PC(I)
C ANGLE AVERAGING IS USED TO ACCOUNT FOR THE EFFECT OF POLARITY DUE TO
C A LARGE DIPOLE ON THE ENERGY AND SIZE PARAMETERS.
    PN=16.0+400.0*W(J)
    P1=PN/(PN-6.0)
    P2=3.0/(PN-6.0)
    CONT=2.882-1.882*W(J)/(0.03+W(J))
    XI=1.7941E07*DH(I)**4/(CONT*EDK(J)*SGM(J)**2+TC(I))
    EDK(J)=EDK(J)*(1.0-XI*P1+P1*(1.0+P1)*XI*XI/2.0)
    SGM(J)=SGM(J)*(1.0+XI*P2)
    RDP(J)=7243.8*DM(I)**2/(EDK(J)*SGM(J))
10 CONTINUE
C CALCULATE TEMPERATURE INDEPENDENT CROSS PARAMETERS.
I,J=2
I=1
J=3
W(I,J)=0.5*(W(I)+W(J))
EDK(I,J)=0.7*SQRT(EDK(I)*EDK(J))+0.6/(1.0/EDK(I)+1.0/EDK(J))
SGM(I,J)=SQRT(SGM(I)*SGM(J))
RDP(I,J)=7243.8*DM(I)*DM(2)/(EDK(I,J)*SGM(I,J))
C CALCULATE REMAINDER OF TEMPERATURE INDEPENDENT PARAMETERS.
DO 40 I=1,3
    B0(I)=1.2618*SGM(I)
    A(I)=-0.3-0.05*RDP(I)
    DH(I)=1.99+0.2*RDP(I)**2
C CALCULATE THE MODIFIED REDUCED DIPOLE TO BE USED IN CALCULATING THE
C FREE-POLAR CONTRIBUTION TO THE VIRIAL COEFFICIENT.
    IF (RDP(I) .LT. 0.25) GO TO 20
    RDP(I)=RDP(I)-0.25
    GO TO 30
20    IF (RDP(I) .LT. 0.04) GO TO 30
    RDP(I)=0.0
C CALCULATE E(IJ) VALUES FOR EACH ETA(IJ).
30    E(I)=ETA(I)*((650.0/(EDK(I)+300.0))-4.27)
40 CONTINUE
IFLAGT=1
100 CONTINUE
C CALCULATE LIQUID MOLAR VOLUMES (FROM SUB. MVOLM).
DO 130 I=1,2
    TR=T/TC(I)
    IF (TR .GT. 0.75) GO TO 110
    TAU=1.0+(1.0-TR)**EX
    GO TO 120
110    TAU=1.6+6.93026E-3/(TR-0.655)
120    VLIQ(I)=83.1473*TC(I)*ZRA(I)**TAU/PC(I)
130 CONTINUE
C CALCULATE ZERO PRESSURE REFERENCE FUGACITIES (FROM SUB. REFUG).
   DO 140 I=1,2
      F(I)=EXP(C1(I)+C2(I)/T+C3(I)*T+C4(I)*ALOG(T)+C5(I)*T**2)
   140 CONTINUE
C CALCULATE THE SECOND VIRIAL COEFFICIENTS (FROM SUB. BIJS2).
   DO 160 I=1,3
   TSP=1.0/TS-1.6*W(I)
   160 CONTINUE
C CALCULATE THE FREE CONTRIBUTION TO THE SECOND VIRIAL COEFFICIENT.
   B(I)=0.94-1.47*TSP-0.85*TSP**2+1.015*TSP**3
   IF (RDP(I) .LT. 1.0E-19) GO TO 150
   B(I)=B(I)-RDP(I)*(0.75-3.0*TSP+2.1*TSP**2+2.1*TSP**3)
   150 B(I)=B0(I)*B(I)
C CALCULATE THE METASTABLE, BOUND, AND CHEMICAL CONTRIBUTIONS.
   BD(I)=BD(I)*EXP((H(I)-T*I)/T)
   BD(I)=BD(I)+EXP((E(I)-T*I)/T)+1500.0*ETA(I)/T*E(I))
   B(I)=B(I)+BD(I)
160 CONTINUE
RETURN
END
SUBROUTINE TXDEP (T,X)

C THIS SUBROUTINE CALCULATES THE ACTIVITY COEFFICIENTS, WHICH ARE
C FUNCTIONS OF T AND X. IT SHOULD BE CALLED ANYTIME T OR X ARE CHANGED.
C
C T IS EXPRESSED IN DEGREES KELVIN. TXDEP IS PARTIALLY BASED ON ACTIV2,
C FOUND IN COMPUTER CALCULATIONS FOR MULTICOMPONENT VAPOR-LIQUID AND
C LIQUID-LIQUID EQUILIBRIA BY PRAUSNITZ, ANDERSON, GRENS, ECKERT, HSIEH, AND
C O, CONNELL, PRENTICE-HALL, 1980.
C
C IF THIS SUBROUTINE IS USED, IFLAG2 AND NOP MUST BE COMMONED TO THE
C MAIN PROGRAM. IFLAG2=0 WHEN THE SUBROUTINE IS CALLED FOR THE FIRST
C TIME. NOP=1 FOR THE 2-PARAMETER UNIQUAC
C =2 FOR THE 3-PARAMETER UNIQUAC
C FIT OF ACTIVITY COEFFICIENTS.
C
DIMENSION R(2), Q(2), GP(2), X(2)
COMMON /MAINTX/ IFLAG2, NOP
COMMON/DATA3/ LOOK, MODE(40)
COMMON /SUBTX/ GAMMA(2)
COMMON /PARMS/ PAR(3)
REAL LG1, LG2

   IF (IFLAG2.GT. 0) GO TO 10
C INITIALIZE CONSTANTS FOR ETHANOL (1) AND WATER (2).
C STRUCTURAL VOLUME PARAMETERS FOR UNIQUAC EQUATION.
   R(1)=2.1
   R(2)=0.92
C STRUCTURAL AREA PARAMETERS FOR UNIQUAC EQUATION.
   Q(1)=1.97
   Q(2)=1.40
C MODIFIED STRUCTURAL AREA PARAMETERS FOR UNIQUAC EQUATION.
   QP(1)=0.92
   QP(2)=1.00
   IFLAG2=1
10 CONTINUE
C CALCULATE PARAMETERS AND ACTIVITY COEFFICIENTS (FROM SUB. ACTIV2).
C IF (NOP .GT. 1) GO TO 20
C EQUATIONS FOR PARAMETERS OF 2-PARAMETER UNIQUAC FIT.
C INSERT FUNCTION FOR PARAMETER 1 HERE
   PAR(1)=-10845.0108153+144.454638358*T-0.6925389046*T**2+
       0.0014345962512*T**3-1.096233611E-6*T**4
   PAR(2)=38765.541722-475.052110708*T+2.14108540923*T**2-
       0.00420316593674*T**3+3.054583612E-6*T**4
C INSERT FUNCTION FOR PARAMETER 2 HERE
10 IF (NOP .GT. 2) GO TO 40
C COEFFICIENTS FOR 3-PARAHETER UNIOUAC FIT

DATA CTH0,CTH1 /-16.03058823E0, 0.04705882353E0/
DATA CP10,CP11,CP12,CP13,CP14,CP15
1 /-89.32844525E0, 24.27541863E0, 68.698815592E0,
2 14.59371360E0, -10.42198857E0, -4.522048302E0/
DATA CP20,CP21,CP22,CP23,CP24,CP25,CP26
1 /327.3816357E0, 198.6002199E0, 152.9937678E0, -8.512191087E0,
2 -58.2073705E0, 0.754751981E0, 7.061925131E0/
DATA CP30,CP31,CP32,CP33,CP34,CP35,CP36
1 /1.332501106E0, -0.7627075015E0, -0.3210071756E0,
2 0.2267275941E0, 0.1384721276E0, -0.0313666795E0,
3 -0.0170849291E0/

C EQUATIONS FOR PARAMETERS OF 3-PARAHETER UNIOUAC FIT.
THETA=CTHO+CTH1*T

C INSERT FUNCTION FOR PARAMETER 1 HERE
PAR(1)=CP10+THETA*(CP11+THETA*(CP12+THETA*(CP13+THETA*(CP14
1 +THETA*(CP15))))))

C INSERT FUNCTION FOR PARAMETER 2 HERE
PAR(2)=CP20+THETA*(CP21+THETA*(CP22+THETA*(CP23+THETA*(CP24
1 +THETA*(CP25+THETA*(CP26))))))

C INSERT FUNCTION FOR PARAMETER 3 HERE
PAR(3)=CP30+THETA*(CP31+THETA*(CP32+THETA*(CP33+THETA*(CP34
1 +THETA*(CP35+THETA*(CP36))))))

C NOW CALCULATE ACTIVITY COEFFICIENTS FOR UNIOUAC FIT.
30 T12=EXP(-PAR(1)/T)
T21=EXP(-PAR(2)/T)
EL1=5.0*(R(1)-Q(1))-(R(1)-1.0)
EL2=5.0*(R(2)-Q(2))-(R(2)-1.0)
PHS=X(1)*R(1)+X(2)*R(2)
PH1=X(1)*R(1)/PHS
PH2=1.0-PH1
THS=X(1)*Q(1)+X(2)*Q(2)
THP1=X(1)*QP(1)/(X(1)*QP(1)+X(2)*QP(2))
THP2=1.0-THP1
S1=THP2*THP1*T12
S2=THP1+THP2*T21
LG1=ALOG(R(1)/PHS)+5.0*Q(1)*ALOG(Q(1))PHS/R(1)/THS+
2 PH2*(EL1-EL2*R(1)/R(2))
LG1=LG1+PAR(3)*QP(1)*(ALOG(S2)+THP2*(T21/S2-T12/S1))
LG2=ALOG(R(2)/PHS)+5.0*Q(2)*ALOG(Q(2))PHS/R(2)/THS+
2 PH1*(EL2-EL1*R(2)/R(1))
LG2=LG2+PAR(3)*QP(2)*(-ALOG(S1)+THP1*(T12/S1-T21/S2))
GO TO 100
40 CONTINUE
100 GAMMA(1)=EXP(LG1)
GAMMA(2)=EXP(LG2)
RETURN
END
Program ETOH—Sample Output

IF YOU WISH DATA AT A CONSTANT TEMPERATURE, TYPE 00. IF YOU WISH DATA AT CONSTANT PRESSURE, TYPE A 01.

WHAT TEMPERATURE DO YOU WANT DATA AT? DEG(K)

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If you want to stop, type A 01

If you wish data at a constant temperature, type CO. If you wish data at constant pressure, type A 01.

What pressure do you want data at? (1200 C)

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If you want to re-run the program, type A 00
If you want to stop, type A 01
01
APPENDIX 2

PROGRAM CONTEST

Vapor/Liquid Equilibrium Data,
Thermodynamic Consistency Test
Program Contest: Vapor/Liquid Equilibrium Data, Thermodynamic Consistency Test

1PW=POS
ROUTF=USERB
AID=

PROGRAM CONTEST (INPUT, OUTPUT)

C THIS PROGRAM DOES AN AREA THERMODYNAMIC CONSISTENCY TEST FOR THE
C ETHANOL-WATER SYSTEM. DATA IS TO BE INPUT AS A DUMMY CARD, SOURCE
C CARD (SPACES 1-70) WITH NUMBER OF DATA SETS IN SPACES 78,79,80.
C ALL DATA SETS, DUMMY CARD, NEXT BATCH, AND 2 BLANKS TO END RUN.
C DATA MUST BE ISOTHERMAL AND IN FIG. 5 FORMAT. THE ORDER MUST BE
C P,T,x,y, WITH P IN MMHG, AND T IN DEGREES K.
C ALL DATA MUST BE IN ORDER OF INCREASING X.
C VARIABLES:
A- AREA FOR INTEGRAL OF LN(ACT1/ACT2) VERSUS X
ACT1- ACTIVITY COEFFICIENT FOR ETHANOL
ACT2- ACTIVITY COEFFICIENT FOR WATER
F01- ZERO PRESSURE REFERENCE FUGACITY FOR ETHANOL
F02- ZERO PRESSURE REFERENCE FUGACITY FOR WATER
G- LN(ACT1/ACT2)
N- NUMBER OF DATA SETS
P- SYSTEM PRESSURE IN MMHG
SOURCE- DATA SOURCE
T- SYSTEM TEMPERATURE IN DEGREES KELVIN
X- MOLE FRACTION OF ETHANOL IN LIQUID
Y- MOLE FRACTION OF ETHANOL IN VAPOR

DIMENSION ACT1(150), ACT2(150), G(150), P(150), SOURCE(17), T(150),
2 X(150), Y(150)

READ 10, DUMMY, SOURCE, N
10 FORMAT (4F10.5)
IF IN *EGO 0) GO TO 1000
DO 30 I=1,N
READ 20, P(I), T(I), X(I), Y(I)
20 FORMAT (4F10.5)
30 CONTINUE
40 FORMAT (A10)
FD1=EXP(-90.909918893555-3465.8734683496/T(I))
FD2=EXP(57.041597918252-704.8416152967/T(I))
FD1=FD1*760.0/1.01325
FD2=FD2*760.0/1.01325
DO 50 I=1,N
IF (X(I) .EQ. 0.0) GO TO 45
IF (X(I) .EQ. 1.0) GO TO 46
ACT1(I)=(1.0-P(I))/X(I)*FD1
ACT2(I)=(1.0-Y(I))*P(I)/(1.0-X(I))*FD2
G(I)=ALOG(ACT1(I)/ACT2(I))
GO TO 50
45 ACT2(I)=1.0
GO TO 50
46 ACT1(I)=1.0
50 CONTINUE
GO TO 0
GO TO 5
IF (X(N) .GT. 0.0) GO TO 50
ACT2(N) = ACT2(N-1) + (1.0 - X(N-1)) * (ACT2(N-1) - ACT2(N-2)) / (X(N-1) - X(N-2)) + ACT2(N-1) / (X(N-1) - X(N-3)) / 2.0
G(N) = ALOG(ACT1(N) / ACT2(N))
G1 = G(N)
50 A = 0.0
DC 70 I = 2 + N
A = A + (X(I) - X(I-1)) * (G(I) + G(I-1)) / 2.0
CONTINUE
IF (G1 .GT. 0.0) GO TO 75
A2 = ACT2(N-1) / (X(N-1) - X(N)) + ACT2(N-2) / (X(N-2) - X(N)) + ACT2(N-2) / (X(N-2) - X(N-3)) / 2.0
G1 = ALOG(A1 / A2)
A = A + (G1 + C(N)) * (X(N) - X(N-1)) / 2.0
CONTINUE
IF (G1 .GT. 0.0) GO TO 75
A2 = ACT2(N-1) / (X(N-1) - X(N)) + ACT2(N-2) / (X(N-2) - X(N)) + ACT2(N-2) / (X(N-2) - X(N-3)) / 2.0
G1 = ALOG(A1 / A2)
A = A + (G1 + C(N)) * (X(N) - X(N-1)) / 2.0
75 CONTINUE
PRINT 80, SOURCE + T(1), FC01, FC02
80 FORMAT (1H1, *T(A10), *NUMBER OF SETS=,'#13,A#, TEMPERATURE=#F8.3, # DEG
7K=/* 1H0=ZERO PRESSURE REFERENCE FUGACITY FOR ETHANOL=#F7.2,
3=MMHG/#1H=ZERO PRESSURE REFERENCE FUGACITY FOR WATER #F7.2,
4=MMHG/#1H=5X*ACT1*8X*ACT2*3X*LN(ACT1/ACT2)*6X*XX*11X*Y
5=6X*XX*4X*5X*XX*(T(K)+1)
DC 10C I = 1 + N
PRINT 90, ACT1(I), ACT2(I), G(I) * X(I) * Y(I) * D(I) * T(I)
CONTINUE
PRINT 100, GC, G1, A
100 FORMAT (1H, *HC05, *LN(ACT1/ACT2) AT X=0 /* F10.5/1H, *LN(ACT1/ACT2) AT X=0 /* F10.5/1H, *AREA= /* F10.5)
GO TO 5
STOP
Program Contest--Sample Output

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<th>T (K)</th>
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LN(ACT1/ACT2) AT x=0 1.90734
LN(ACT1/ACT2) AT #1.0 1.95652

AREA 0.00244792
APPENDIX 3

PROGRAM HMIXING

Ethanol/Water Heat of Mixing Model
Program HMIXING: Ethanol/Water Heat of Mixing Model

ROUTE:USERB
*PW=RUT
PUN*
LGO*

PROGRAM HMIXING (INPUT, OUTPUT)

WRITTEN BY BRIAN MAIORELLA, SUMMER 1981

PROGRAM HMIXING IS A DRIVER PROGRAM FOR THE SUBROUTINE HMIX.

HMIXING READS IN UP TO 20 TEMPERATURES AT WHICH HEAT OF MIXING
OF ETHANOL/WATER MIXTURES ARE TO BE FOUND. HEAT OF MIXING
RESULTS ARE COMPUTED AT .05 MOLAR INTERVALS FOR THE SELECTED
TEMPERATURES. VALUES OF THE UNIQUAC MIXING PARAMETERS (THETA1 AND
THETA2) AND INTERACTION ENERGIES (TAU12, TAU21, DELU12, DELU21)
ARE ALSO PRINTED. UNITS FOR HEAT OF MIXING AND DELU CORRESPOND
TO THE UNITS OF R (SET AS J/MOL*DEG K) AND CAN BE CHANGED BY
SPECIFYING R IN ANOTHER UNIT SYSTEM.

DIMENSION A12(5), A21(5), TEMP(20)
REAL NTLP
COMMON /UNIPAR/ A12, A21, TAU12, TAU21, G1, G2*
/THETA1, THETA2, DELU12, DELU21

IDEAL GAS CONSTANT (J/MOL*DEG K)
R = 8.3144
IFLAG = 1
READ 3*N
FORMAT (12)
DO 7 I = 1, N
PRINT 5, TEMP(I)
7 FORMAT (F9.3)
DO 20 I = 1, N
T = TEMP(I)
PRINT 10, T
10 FORMAT (141.5X, *TEMP = **FB.3*(DEG K) */*//)
PRINT 20
20 FORMAT (1HC+12*X*;5*7*5*7*X*7*10*X*F6.4*5*X*F8.4*10*X*F12.5)
/HEATING (J/MOL) *//
DO 150 J = 1, 21
X1 = (G0.05*FLOAT(J)-1.05
CALL HMIX(X1), P, NTLP, IFLAG)
IFLAG = 1 + IFLAG
X2 = 1.0 - X1
PRINT 30, X1, X2, THETA1, THETA2, NTLP
30 FORMAT (1HC+12*X*F6.4*5*X*F3.3*10*X*F8.4*5*X*F8.4*10*X*F12.5)
150 CONTINUE
PRINT 90, TAU12, TAU21, DELU12, DELU21
90 FORMAT (1HC+12*X*F7.3*3*X*F7.3*10*X*F3.3*5*X*F8.3)
200 CONTINUE
END

SUBROUTINE HMIX(T, X1, P, NTLP, IFLAG)

WRITTEN BY B. MAIORELLA, SUMMER 1981.

SUBROUTINE HMIX CALCULATES THE HEAT OF MIXING OF AN ETHANOL/
WATER SOLUTION (MOLE FRACTION ETHANOL = X1) AT TEMPERATURE
T (DEG K) BASED ON A TEMPERATURE DEPENDENT UNIQUAC EQUATION.

DIMENSION A12(5), A21(5)
REAL NTLP
COMMON /UNIPAR/ A12, A21, TAU12, TAU21, Q1, Q2,  
/THETA1, THETA2, DELU12, DELU21  
IF (IFLAG .NE. 1) GO TO 70  
C UNIQUAC ETHANOL AND WATER MODIFIED STRUCTURAL AREA PARAMETERS.  
Q1 = 0.92  
Q2 = 1.00  
C TEMPERATURE DEPENDENT UNIQUAC PARAMETERS.  
A12(1) = -10845.010853  
A12(2) = 144.454638358  
A12(3) = -0.69328910466  
A12(4) = 0.00143459625212  
A12(5) = -1.09233611E-6  
A21(1) = 38765.547777  
A21(2) = -475.05210708  
A21(3) = 2.14108540933  
A21(4) = -3.00229316593674  
A21(5) = 3.054823612E-6  
T LAST = -1.0  
XLAST = -1.0  
70 IF (T EQ T LAST) GO TO 100  
DELU12 = A12(1) + A12(2) + (A12(3) * (T ** 2 + 0.1)  
/ = (A12(4) * (T ** 3 + 0.1) + (A12(5) * (T ** 4 + 0.1)  
DELU21 = A21(1) + A21(2) + (A21(3) * (T ** 2 + 0.1)  
/ = (A21(4) * (T ** 3 + 0.1) + (A21(5) * (T ** 4 + 0.1)  
THETA12 = EXP(-DELU12/T)  
THETA21 = EXP(-DELU21/T)  
DELU12 = R * DELU12  
DELU21 = R * DELU21  
DELU12 = -A12(1) + A12(3) * (T ** 2 + 0.1) - (2.0 * A12(4) * (T ** 3 + 0.1)  
/ = (3.0 * A12(5) * (T ** 4 + 0.1)  
DELU21 = -A21(1) + A21(3) * (T ** 2 + 0.1) - (2.0 * A21(4) * (T ** 3 + 0.1)  
/ = (3.0 * A21(5) * (T ** 4 + 0.1)  
100 IF (X1 * EC * XLAST) GO TO 150  
X2 = 1.0 - X1  
THETA1 = (Q1 * X1) / (Q1 * X1) + (Q2 * X2)  
THETA2 = 1.0 - THETA1  
150 G1 = (THETA2 * TAU21 * DELU21) / (THETA1 * (THETA2 * TAU21))  
G2 = (THETA1 * TAU12 * DELU12) / ((THETA1 * TAU12) * THETA2)  
NTLP = -R * ((Q1 * X1 * G1) + (Q2 * X2 * G2))  
T LAST = T  
XLAST = X1  
RETURN  
END
Program HMIXING--Sample Output

TEMP = 343.150 (DEG K)

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