A THEORETICAL AND EXPERIMENTAL INVESTIGATION
OF VAPOR- LIQUID EQUILIBRIA IN THE BINARY
SYSTEMS FORMED AMONG THE CONSTITUENTS
NORMAL HEXANE, METHYLCYCLOHEXANE,
AND TOLUENE

By

ROBERT LOUIS ROBINSON, JR.

Bachelor of Science
Oklahoma State University
Stillwater, Oklahoma
August, 1959

Submitted to the faculty of the Graduate School of the
Oklahoma State University of Agriculture and
Applied Sciences in partial fulfillment
of the requirements for the degree
of MASTER OF SCIENCE
May, 1962
A THEORETICAL AND EXPERIMENTAL INVESTIGATION
OF VAPOR-LIQUID EQUILIBRIA IN THE BINARY
SYSTEMS FORMED AMONG THE CONSTITUENTS
NORMAL HEXANE, METHYLCYCLOHEXANE,
AND TOLUENE

Thesis Approved

Wayne Edmister
Thesis Adviser

Joseph M. Marchello

Dean of the Graduate School

505221
PREFACE

New vapor-liquid equilibria data at atmospheric pressure have been determined for the binary systems formed among the constituents normal hexane, methylcyclohexane, and toluene. A review of the subject of thermodynamic consistency of experimental data and a check of the applicability of two equations of state to the prediction of vapor phase behavior are also presented.

I am indebted to Professor Wayne C. Edmister for his counseling and guidance during this study; the aid of the entire staff of the School of Chemical Engineering has been appreciated. Special gratitude is also due Mr. R. E. Thompson for his suggestions and Mr. R. S. Joyner for programing the Benedict-Webb-Rubin equation of state for the IBM 650 computer.

The hydrocarbons used in this work were generously donated by Phillips Petroleum Company.

Financial aid for these past two years has been gratefully received from the National Science Foundation.

By far the greatest thanks is due my wife, Gayle, whose unfailing encouragement, aid, and patience have made my graduate studies possible.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. THERMODYNAMIC CONSISTENCY OF VAPOR-LIQUID EQUILIBRIA DATA</td>
<td>5</td>
</tr>
<tr>
<td>The Value of Thermodynamic Consistency Tests</td>
<td>5</td>
</tr>
<tr>
<td>Need for a Review of Thermodynamic Consistency Tests</td>
<td>6</td>
</tr>
<tr>
<td>Derivation of the Gibbs-Duhem Equation</td>
<td>6</td>
</tr>
<tr>
<td>Activity Coefficients</td>
<td>14</td>
</tr>
<tr>
<td>Standard States for Activity Coefficients</td>
<td>15</td>
</tr>
<tr>
<td>Calculation of Activity Coefficients from Experimental Data</td>
<td>16</td>
</tr>
<tr>
<td>III. TESTS FOR THERMODYNAMIC CONSISTENCY OF VAPOR-LIQUID EQUILIBRIA DATA</td>
<td>23</td>
</tr>
<tr>
<td>A Rigorous Equation for Testing Isothermal Data in Terms of Activity Coefficients</td>
<td>23</td>
</tr>
<tr>
<td>A Rigorous Equation for Testing Isobaric Data in Terms of Activity Coefficients</td>
<td>27</td>
</tr>
<tr>
<td>A Rigorous Test for Thermodynamic Consistency in Terms of K Values</td>
<td>30</td>
</tr>
<tr>
<td>Frequently Used Consistency Tests Involving Approximations</td>
<td>35</td>
</tr>
<tr>
<td>The Gibbs-Duhem Equation at Constant Temperature and Pressure</td>
<td>35</td>
</tr>
<tr>
<td>The Redlich-Kister Test</td>
<td>38</td>
</tr>
<tr>
<td>Particular Integrated Solutions to the Gibbs-Duhem Equation</td>
<td>39</td>
</tr>
<tr>
<td>Herington's Test for Isobaric Data</td>
<td>41</td>
</tr>
<tr>
<td>Summary</td>
<td>44</td>
</tr>
<tr>
<td>IV. APPARATUS AND EXPERIMENTAL PROCEDURE</td>
<td>54</td>
</tr>
<tr>
<td>Apparatus</td>
<td>54</td>
</tr>
<tr>
<td>Equilibrium Still</td>
<td>54</td>
</tr>
<tr>
<td>Temperature Measurement</td>
<td>55</td>
</tr>
<tr>
<td>Pressure Control</td>
<td>56</td>
</tr>
<tr>
<td>Sampling</td>
<td>56</td>
</tr>
<tr>
<td>Analysis of Samples</td>
<td>57</td>
</tr>
<tr>
<td>Stopcock Lubricant</td>
<td>57</td>
</tr>
</tbody>
</table>
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>Test for Consistency of Data on Acetone-Water System at 100°C.</td>
<td>46</td>
</tr>
<tr>
<td>II.</td>
<td>Z Factors for Benzene and Normal Heptane</td>
<td>47</td>
</tr>
<tr>
<td>III.</td>
<td>Test for Consistency of Data on Benzene-Normal Heptane System at One Atmosphere</td>
<td>48</td>
</tr>
<tr>
<td>IV.</td>
<td>Binary Refractive Index-Composition Relations at 25°C.</td>
<td>62</td>
</tr>
<tr>
<td>V.</td>
<td>Vapor-Liquid Equilibria Data: System: n-Hexane-Methylcyclohexane at One Atmosphere</td>
<td>63</td>
</tr>
<tr>
<td>VI.</td>
<td>Vapor-Liquid Equilibria Data: System: n-Hexane-Toluene at One Atmosphere</td>
<td>64</td>
</tr>
<tr>
<td>VII.</td>
<td>Vapor-Liquid Equilibria Data: System: Methylcyclohexane-Toluene at One Atmosphere</td>
<td>65</td>
</tr>
<tr>
<td>VIII.</td>
<td>Results of Herington's Test for Consistency of Binary Data</td>
<td>80</td>
</tr>
<tr>
<td>IX.</td>
<td>Comparison of Experimental Data on MCH-Toluene System</td>
<td>81</td>
</tr>
<tr>
<td>X.</td>
<td>Test for Consistency of Data on MCH-Toluene System at One Atmosphere (This Work)</td>
<td>82</td>
</tr>
<tr>
<td>XI.</td>
<td>Activity Coefficient-Composition Relations for MCH-Toluene System at One Atmosphere (Quiggle and Fenske)</td>
<td>83</td>
</tr>
<tr>
<td>XII.</td>
<td>Activity Coefficient-Composition Relations for MCH-Toluene System at One Atmosphere (Garner and Hall)</td>
<td>84</td>
</tr>
<tr>
<td>XIII.</td>
<td>Comparison of Experimental Data on n-Hexane-MCH System</td>
<td>85</td>
</tr>
</tbody>
</table>
XIV. Activity Coefficient-Composition Relations for n-Hexane-Methylcyclohexane System at One Atmosphere (This Work) 86

XV. Activity Coefficient-Composition Relations for n-Hexane-Methylcyclohexane System at One Atmosphere (Myers) 87

XVI. Comparison of Experimental Data on n-Hexane-Toluene System 88

XVII. Activity Coefficient-Composition Relations for n-Hexane-Toluene System at One Atmosphere (This Work) 89

XVIII. Activity Coefficient-Composition Relations for n-Hexane-Toluene System at One Atmosphere (Sieg) 90

XIX. Z Factors for n-Hexane, Methylcyclohexane, and Toluene 91

XX. Comparison of Calculated and Experimental Vapor Fugacity Coefficients 105
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Graphical Integration for Acetone-Water Consistency Test.</td>
<td>50</td>
</tr>
<tr>
<td>2.</td>
<td>Z Factor for Calculating Activity Coefficients.</td>
<td>51</td>
</tr>
<tr>
<td>3.</td>
<td>Graphical Integration for Benzene-n-Heptane Consistency Test.</td>
<td>52</td>
</tr>
<tr>
<td>4.</td>
<td>Graphical Integration of Heat of Mixing Term for Benzene-n-Heptane Consistency Test.</td>
<td>53</td>
</tr>
<tr>
<td>5.</td>
<td>Modified Gillespie Vapor-Liquid Equilibrium Still.</td>
<td>66</td>
</tr>
<tr>
<td>6.</td>
<td>Binary Composition-Refractive Index Relations.</td>
<td>67</td>
</tr>
<tr>
<td>7.</td>
<td>x-y Data for n-Hexane-Benzene System.</td>
<td>68</td>
</tr>
<tr>
<td>8.</td>
<td>x-y Data for n-Hexane-Methylcyclohexane System.</td>
<td>69</td>
</tr>
<tr>
<td>9.</td>
<td>x-y Data for n-Hexane-Toluene System.</td>
<td>70</td>
</tr>
<tr>
<td>10.</td>
<td>x-y Data for Methylcyclohexane-Toluene System.</td>
<td>71</td>
</tr>
<tr>
<td>11.</td>
<td>T-x Relations for Binary Equilibria Data.</td>
<td>72</td>
</tr>
<tr>
<td>12.</td>
<td>Graphical Integration for MCH-Toluene Consistency Test.</td>
<td>92</td>
</tr>
<tr>
<td>13.</td>
<td>$\gamma'$-x Relation for MCH-Toluene System.</td>
<td>93</td>
</tr>
<tr>
<td>14.</td>
<td>$\gamma$-x Relation for MCH-Toluene System.</td>
<td>94</td>
</tr>
<tr>
<td>15.</td>
<td>$\gamma'$-x Relation for n-Hexane-MCH System.</td>
<td>95</td>
</tr>
<tr>
<td>16.</td>
<td>$\gamma$-x Relation for n-Hexane-MCH System.</td>
<td>96</td>
</tr>
<tr>
<td>17.</td>
<td>$\gamma'$-x Relation for n-Hexane-Toluene System.</td>
<td>97</td>
</tr>
<tr>
<td>18.</td>
<td>$\gamma$-x Relation for n-Hexane-Toluene System.</td>
<td>98</td>
</tr>
<tr>
<td>19.</td>
<td>Z Factor for Calculating Activity Coefficients.</td>
<td>99</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>20.</td>
<td>Comparison of Calculated and Experimental Vapor Fugacity Coefficients of Propane in Methane.</td>
<td>106</td>
</tr>
<tr>
<td>21.</td>
<td>Comparison of Calculated and Experimental Vapor Fugacity Coefficients of n-Butane in Methane.</td>
<td>107</td>
</tr>
<tr>
<td>22.</td>
<td>Comparison of Calculated and Experimental Vapor Fugacity Coefficients of n-Pentane in Propane.</td>
<td>108</td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

Vapor-liquid equilibria data have become extremely important in the chemical and related industries. With the advent of high-pressure technology as applied to multiphase contact operations such as distillation and absorption, accurate vapor-liquid equilibria data are essential. No longer will simple approximation rules, i.e., Raoult's law, Dalton's law, etc., suffice to describe equilibria at high pressures and among exotic chemical species. Any inaccuracies in equilibria data will be reflected in equipment design and ultimately in process economics.

The complete description of the vapor-liquid equilibria in a system requires an accurate knowledge of the relation among the pressure, temperature, and compositions of the equilibrium vapor and liquid phases. Innumerable methods for obtaining such data have been proposed and used; the fact remains that the experimental determination of vapor-liquid equilibria data is a difficult, time-consuming, and expensive undertaking. In addition, the number of technically important chemical substances is so large that the experimental investigation of all possible combinations of the substances is a physical impossibility.

In view of the above considerations, much attention is currently being directed toward the theoretical prediction of vapor-liquid equilibria data. The ultimate goal of these "solution theory"
studies is the prediction of mixture properties from data on the pure components. Methods are presently available for predicting the properties of multicomponent vapor-liquid equilibria mixtures from data on binary systems (9, 35, 46, 60) or even from pure-component data (17, 26). The value of such methods is obvious, providing the methods are demonstrated to be applicable.

In a recent study, Huang (29) attempted to test the applicability of two prediction techniques, namely

1. The method of Wohl (60) for predicting data on multicomponent systems from data on the constituent binary systems.
2. The method of Hildebrand-Scatchard (26) for predicting data on multicomponent systems from pure-component data.

(See Appendix A for a discussion of these methods.)

In order to test the above correlation schemes, Huang experimentally investigated the vapor-liquid equilibria relationships for the ternary system normal hexane-methylcyclohexane-toluene at atmospheric pressure. He then compared the above correlation techniques with his experimental data. In applying Wohl's correlation, Huang employed data from the literature on the binary systems normal hexane-methylcyclohexane (37), normal hexane-toluene (54), and methylcyclohexane-toluene (44). From his study, Huang reached the conclusion that

1. Neither of the above prediction techniques were in agreement with the experimental data.
2. The literature data on the binary systems were
incorrect (thermodynamically inconsistent) and probably accounted for the failure of Wohl’s method to fit the ternary data.

3. The ternary data of Huang are thermodynamically consistent (as tested by a method proposed by Huang).

In view of the work of Huang, the present study was undertaken to determine thermodynamically consistent vapor-liquid equilibria data for the binary systems which Huang had reported as being incorrect in the literature. The correct data could then be used to re-evaluate Wohl’s prediction method.

In the course of this study, the thermodynamic consistency tests applied by Huang to his ternary data (29) and the literature binary data (25) came under suspicion. These suspicions eventually led to a comprehensive review of the general subject of thermodynamic consistency of vapor-liquid equilibria data, and this review is included herein.

Prior to entering on the study mentioned above, the author had worked on the subject of the correlation and prediction of vapor-liquid equilibria data. In such work, equations of state are often employed to represent vapor-phase behavior. The Redlich-Kwong (R-K) equation of state (47) has been used in this connection in several recent studies (12, 39, 40, 43). The R-K equation was recommended by its authors as being applicable in the gaseous region, i.e., at temperatures above the critical temperature; the applicability of this equation in the vapor region had never been satisfactorily demonstrated. Thus, a direct comparison of the R-K
equation, as well as the Benedict-Webb-Rubin (BWR) equation (7), with experimental data in the prediction of thermodynamic properties in the vapor region was made. The results are presented in this thesis. (See Appendix B for a discussion of the above equations of state.)

The major goals of this thesis may now be stated:

1. Determination of thermodynamically consistent equilibria data at atmospheric pressure for the three binary systems formed among the constituents normal hexane, methylcyclohexane, and toluene.

2. Evaluation of the conclusions in the work of Huang.

3. A review of the subject of thermodynamic consistency of vapor-liquid equilibria data.

4. A check of the applicability of the Redlich-Kwong and the Benedict-Webb-Rubin equations of state to the prediction of vapor-phase properties.
CHAPTER II

THERMODYNAMIC CONSISTENCY OF VAPOR-LIQUID EQUILIBRIA DATA

The discussion of the thermodynamic consistency of vapor-liquid equilibria data is presented in these first sections since an understanding of the subject is necessary to the developments of later sections.

The Value of Thermodynamic Consistency Tests

The purpose of experimental vapor-liquid equilibria studies is to gather accurate data for use in (a) design calculations or (b) development of new methods and theories for describing the data. However, inaccuracies may appear in experimental data through human or mechanical errors; such incorrect data are not only of no positive value but are detrimental in that they may lead to incorrect conclusions regarding a design or theory. A means for establishing the accuracy of experimental data is needed.

No method exists which will permit experimental data to be termed as unquestionably correct, but means are available for detection of much of the incorrect data. Thermodynamic considerations may be employed to derive relations which data must obey if the data are correct. One such relation is the "Gibbs-Duhem"
equation, which will be derived and discussed below. Compliance with the Gibbs-Duhem equation is a necessary, but not sufficient, condition for data to be correct, and data which do not obey the equation are definitely inaccurate. Various tests have been based on the Gibbs-Duhem equation and are specifically designed for use in the analysis of experimental data. A survey of the conflicting data reported on many systems in the literature readily attests to the worth of thermodynamic consistency tests, which will often allow systematic selection of the best possible data.

Need for a Review of Thermodynamic Consistency Tests

The applicability of the Gibbs-Duhem equation to testing equilibria data has long been realized. Considerable attention has been devoted to the subject in the literature (2, 25, 30, 36, 46, 57). However, confusion is evident in the literature regarding the application of the Gibbs-Duhem equation. The use of incorrect forms of the equation, insufficient discussion of simplifying assumptions, and invalid assumptions are often found. The general lack of a thorough understanding of consistency tests, in view of their importance, led to this review of the subject.

Derivation of the Gibbs-Duhem Equation

Consider any closed system. The "First Law of Thermodynamics" may be written for such a system as

\[ dU = Q + W \]  

(II-1)

where \( dU \) = change in internal energy of the system, in units of energy.
\[ \delta Q = \text{infinitesimal quantity of heat added to the system, energy.} \]

\[ \delta W = \text{infinitesimal amount of work performed on the system, energy.} \]

The \( \delta \) in front of the \( Q \) and \( W \) terms is used to signify that these quantities are not exact differentials, i.e., not properties of the state of the system. The internal energy, \( U \), is an exact differential and a state property, the value of the internal energy being fixed for a given state of the system.

For a reversible process in which pressure is the only force acting on the system, the work term in Equation II-1 may be written

\[ \delta W = -PdV \]  \hspace{1cm} (II-2)

where \( P = \text{total pressure exerted on the system, force/area.} \)

\( V = \text{volume of the system.} \)

Also, for this reversible process, the "Second Law of Thermo-dynamics" states that

\[ \delta Q = TdS \] \hspace{1cm} (II-3)

where \( T = \text{absolute temperature of the system, degrees absolute.} \)

\( S = \text{entropy of the system, energy/degree.} \)

Combining Equations II-1, II-2, and II-3,

\[ dU = TdS - PdV \] \hspace{1cm} (II-4)

The "enthalpy", \( H \), of the system is defined as

\[ H = U + PV \] \hspace{1cm} (II-5)
Thus,
\[ dH = dU + PdV + VdP \]  \hspace{1cm} (II-6)

Substituting Equation II-4 into Equation II-6,
\[ dH = TdS + VdP \]  \hspace{1cm} (II-7)

The "Gibbs free energy" of the system is defined by
\[ G = H - TS \]  \hspace{1cm} (II-8)
so that
\[ dG = dH - TdS - SdT \]  \hspace{1cm} (II-9)

In view of Equation II-7, Equation II-9 may be written
\[ dG = VdP - SdT \]  \hspace{1cm} (II-10)

Now consider an "open" system, i.e., a system in which the mass is variable. The Gibbs free energy of such a system will be a function of temperature, pressure, and the amount of each constituent present; formally
\[ G = G(T,P,n_1,\ldots,n_N) \]  \hspace{1cm} (II-11)

where \( n_1,\ldots,n_N \) = number of moles of component \( 1,\ldots,N \), respectively.
\[ N = \text{total number of constituents in the system.} \]

From Equation II-11,
\[ dG = \left( \frac{\partial G}{\partial T} \right)_P,n_i dT + \left( \frac{\partial G}{\partial P} \right)_{T,n_i} dP + \sum_{i=1}^{N} \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_i} dn_i \]  \hspace{1cm} (II-12)
where \( \sum_{i=1}^{N} = \) summation over all components in system, i.e., from 1 to N. Hereafter, the symbol \( \sum \) will be used for simplicity.

From Equation II-10, the following relations are obvious;

\[
\left( \frac{\partial G}{\partial P} \right)_{T,n_i} = V \tag{II-13}
\]

\[
\left( \frac{\partial G}{\partial T} \right)_{P,n_i} = -S \tag{II-14}
\]

and Equation II-12 may be written

\[
dG = -SdT + VdP + \sum \left( \frac{\partial G}{\partial n_i} \right)_{T,P} dn_i \tag{II-15}
\]

Using the method described by Guggenheim (24), consider the system at constant \( T \) and \( P \). Equation II-15 becomes

\[
dG = \sum \left( \frac{\partial G}{\partial n_i} \right)_{T,P} dn_i \tag{II-16}
\]

Allow the quantity of each component in the system to change by an amount proportional to itself, i.e.,

\[
dP = dT = 0 \quad ; \quad dn_i = n_i d\xi \tag{II-17}
\]

where \( \xi = \) the fractional change in the mass of the system.

The Gibbs free energy will also change by an amount

\[
dG = Gd\xi \tag{II-18}
\]

and Equation II-16 becomes
Integrating Equation II-19 from $\xi = 0$ to $\xi = 1.0$ (or dividing by $d\xi$)

$$G = \sum \left( \frac{\partial G}{\partial n_i} \right) T_i P_i n_i d\xi$$  \hspace{1cm} (II-20)

The term $\left( \frac{\partial G}{\partial n_i} \right) T_i P_i$ is given the name "chemical potential" and represented by $\mu_i$. Thus,

$$G = \sum \mu_i n_i$$  \hspace{1cm} (II-21)

Equation II-21 was obtained by a special integration but is generally valid (it may be derived in another manner using Euler's theorem (40)).

Differentiating Equation II-21,

$$dG = \sum \mu_i d n_i + \sum n_i d\mu_i$$  \hspace{1cm} (II-22)

Comparing Equations II-15 and II-22,

$$\sum n_i d\mu_i = -S dT + V dP$$  \hspace{1cm} (II-23)

Equation II-23 is the Gibbs-Duhem equation in its most general form. Dividing Equation II-23 by the total number of moles in the system, $\sum n_i$, and recalling that $x_i = n_i / \sum n_i$

$$\sum x_i d\mu_i = -S dT + V dP$$  \hspace{1cm} (II-24)

where the subscript _ indicates the value of the property per
mole of the system. Equation II-24 is equally applicable to the vapor phase, where \( y_i \) would be used in place of \( x_i \).

Although Equation II-23 (or II-24) is the basis for thermodynamic consistency tests, the form of the equation is not convenient for practical application. Fugacities or activity coefficients are usually introduced to replace the chemical potential, so a few relations involving fugacity and the activity coefficient will now be developed for future use.

G. N. Lewis (34) originally postulated the use of fugacity. For a pure component, he defined the fugacity, \( f \), as

\[
dG = RT \, d \ln f \quad (T \, \text{constant}) \quad (\text{II-25})
\]

\[
\lim_{P \to 0} \left( \frac{f}{P} \right) = 1.0 \quad (\text{II-26})
\]

The fugacity of a component in a solution may be defined similarly (15) by

\[
d\mu_i = RT \, d \ln \bar{f}_i \quad (T \, \text{constant}) \quad (\text{II-27})
\]

where \( \bar{f}_i \) = fugacity of component "i" in solution, force/area. The definition may be completed by requiring that \( \bar{f}_i \) be equal to the partial pressure of component "i" when the solution is in the ideal gas state, i.e.,

\[
\bar{f}_i^* = x_i P^* \quad (\text{II-28})
\]

where the superscript * denotes the ideal gas state. (For a thorough discussion of fugacity refer to the work of Tunell (59)).
Lewis also defined "activity", $a_i$, as

$$a_i = \frac{\bar{f}_i}{\bar{f}_i^0}$$

(II-29)

where $\bar{f}_i^0$ = fugacity of component "i" in some arbitrary reference state.

Integrating Equation II-27 at constant $T$ from the reference state to some other state,

$$\mu_i - \mu_i^0 = RT \ln \frac{\bar{f}_i}{\bar{f}_i^0} = RT \ln a_i$$

(II-30)

The "activity coefficient" for the liquid phase, $\gamma_i$, has been defined as

$$\gamma_i = \frac{a_i}{x_i} = \frac{\bar{f}_i}{x_i \bar{f}_i^0}$$

(II-31)

In future developments, the dependence of the fugacity on pressure must be known. From Equation II-27,

$$\left(\frac{\partial u_i}{\partial P}\right)_T = RT \left(\frac{\partial \ln \bar{f}_i}{\partial P}\right)_T$$

(II-32)

The left side of Equation II-32 may be replaced as follows.

Differentiating Equation II-13 with respect to $n_i$,

$$\left[\frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial P}\right)_{T,P}\right]_{T,P} = \frac{\partial V}{\partial n_i} = \bar{v}_i$$

(II-33)

where $\bar{v}_i$ = partial molal volume of component "i", volume/mole.

The function $G$ is considered to possess the mathematical
properties requisite for a change in the order of differentiation (25) of Equation II-33. Thus,

\[
\left. \frac{\partial}{\partial P} \left( \frac{\partial G}{\partial n_i} \right) \right|_{T,P,n_j} = \left( \frac{\partial \mu_i}{\partial P} \right)_{T,n_j} = \bar{V}_i \tag{II-34}
\]

Combining Equations II-32 and II-34,

\[
\left( \frac{\partial \ln \bar{f}_i}{\partial P} \right)_T = \frac{\bar{V}_i}{RT} \tag{II-35}
\]

Equation II-35 gives the dependence of fugacity on pressure.

The effect of temperature on fugacity may be seen by differentiating Equation II-30 with respect to \( T \),

\[
\left( \frac{\partial \mu_i}{\partial T} \right)_P - \left( \frac{\partial \mu_i^o}{\partial T} \right)_P = RT \left[ \left( \frac{\partial \ln \bar{f}_i}{\partial T} \right)_P - \left( \frac{\partial \ln \bar{f}_i^o}{\partial T} \right)_P \right] + R \ln \frac{\bar{f}_i}{\bar{f}_i^o} \tag{II-36}
\]

Since the reference state for \( \mu_i^o \) is arbitrary, choose it such that Equation II-28 is applicable, and thus,

\[
\left( \frac{\partial \ln \bar{f}_i^o}{\partial T} \right)_P = 0 \tag{II-37}
\]

Note that if Equation II-14 is differentiated with respect to \( n_i \) and the order of differentiation reversed,

\[
\left. \frac{\partial}{\partial T} \left( \frac{\partial G}{\partial n_i} \right) \right|_{T,P,n_j} = \left( \frac{\partial \mu_i}{\partial T} \right)_{P,n_j} = -\bar{S}_i \tag{II-38}
\]

where \( \bar{S}_i \) = partial molal entropy of component "i", energy/degree mole.
If Equation II-8 is differentiated with respect to \( n_i \),

\[
\mu_i = \bar{H}_i - T\bar{S}_i 
\]  

(II-39)

or

\[
-S_i = \frac{\mu_i}{T} - \frac{\bar{H}_i}{T} 
\]  

(II-40)

where \( \bar{H}_i \) = partial molal enthalpy of component "i", energy/mole.

Substituting Equations II-30, II-37, II-38, and II-40 into Equation II-36,

\[
\frac{\mu_i}{T} - \frac{\bar{H}_i}{T} - \frac{\mu_i}{T} + \frac{\bar{H}_i}{T} = RT \left[ \frac{\partial \ln f_i}{\partial T} \right]_p - 0 + \frac{\mu_i}{T} - \frac{\mu_i}{T} 
\]  

(II-41)

or, since \( \bar{H}_i^0 = \bar{H}_i^* = \bar{H}_i^* \),

\[
\frac{\partial \ln f_i}{\partial T} \bigg|_p = \frac{H_i^* - \bar{H}_i}{RT^2} 
\]  

(II-42)

Equation II-42 gives the dependence of fugacity on temperature.

**Activity Coefficients**

Most tests for thermodynamic consistency are performed in terms of activity coefficients, which are used to replace the chemical potentials in the Gibbs-Duhem equation. Care must be taken to use properly determined activity coefficients if the consistency test is to be meaningful. This section is designed to serve as a guide for calculating correct activity coefficients.
from experimental data.

Standard States for Activity Coefficients

The activity coefficient defined by Equation II-31 has no meaning until the "standard state", the conditions at which $\overline{f}_i^0$ is evaluated, is specified. Several standard states are used in vapor-liquid equilibria calculations (3). However, the most widely used and intuitively satisfying standard state is that of the pure component at the same conditions as the system and in the same physical state. If this standard state is used, $\overline{f}_i^0$ becomes $f_i^0$, and any difference between $\overline{f}_i^0$ and $f_i^0$ is due to the effect of composition on fugacity. Pipkin (40) pointed out that this definition is in harmony with the goal of solution theory, i.e., the prediction of mixture properties from pure-component data. The above definition of standard state will be adhered to in this thesis, and the definition of activity coefficient may be rewritten

$$\gamma_i = \frac{\overline{f}_i}{x_i f_i^0} \quad (II-43)$$

The pure component standard state is not without drawbacks. Consider a component in a liquid phase at a temperature above the boiling point of that component; the standard state for the component in this instance is a purely hypothetical one, since the pure component could not exist as a liquid at the system conditions. In such instances, extrapolation procedures must be employed to calculate the standard state fugacities. Recent
discussions of such procedures have been presented by Prausnitz (42) and Edmister (18) and will not be repeated here.

Calculation of Activity Coefficients
from Experimental Data

The liquid phase activity coefficient may be written as a single function of all the vapor-liquid equilibria variables. The most commonly seen expression of this relationship, valid only when the vapor phase is an ideal gas and the liquid forms an ideal solution, is

\[ Y'_i = \frac{P_i y_i}{p_i x_i} \]  

(II-44)

where \( y_i \) = mole fraction of component "i" in the vapor phase.

\( p_i \) = vapor pressure of component "i" at the existing conditions.

\( Y'_i \) = activity coefficient, superscript indicates an approximate relation.

Note that Equation II-44 combines all the experimental variables (a) pressure, \( P \), (b) equilibrium phase compositions, \( x_i \) and \( y_i \), and (c) temperature, \( T \), indirectly through the vapor pressure, which is a function of temperature.

More often than not, Equation II-44 is not applicable due to the highly restrictive assumptions involved in its derivation. A completely general expression for \( Y'_i \), is needed and will now be derived.

A few preliminary equations must first be developed. From Equation II-34,
Combining Equations II-34 and II-27,

\[ RT \ln \bar{f}_i = \bar{V}_i dP \quad \text{(T constant)} \quad (II-46) \]

Integrating Equation II-46, where the lower limit is such that Equation II-28 is valid, yields

\[ \ln \bar{f}_i = \frac{1}{RT} \int_{P^*}^{P} \bar{V}_i dP + \ln x_i + \ln P^* \quad \text{(II-47)} \]

For a pure component, Equations II-25 and II-13 may be combined and integrated to yield

\[ \ln \frac{f_2}{f_1} = \frac{1}{RT} \int_{P_1}^{P_2} \bar{V} dP \quad \text{(II-48)} \]

where \( \bar{V} \) = the molar volume of the pure component.

Equation II-47 and II-48 are equally applicable to the liquid and vapor phases.

From the above equations, a relation between \( \gamma_i \) and the experimental data may be established. By definition, the liquid phase activity coefficient is

\[ \gamma_i = \frac{\frac{f_i}{x_i f_i^0L}}{f_i} \quad \text{(II-49)} \]

where the superscript \( L \) denotes the liquid phase. Likewise, the superscript \( V \) will be used to denote the vapor phase. At
equilibrium, the fugacity of a component is the same in all phases,

$$f_i^L = f_i^V$$  \hspace{1cm} (II-50)

and Equation II-49 may be written

$$\gamma_i = \frac{f_i^V}{f_i^L}$$  \hspace{1cm} (II-51)

and $f_i^V$ may be represented by Equation II-47 as

$$\ln f_i^V = \frac{1}{RT} \int_{p_i}^P \bar{V}_i^V dP + \ln \gamma_i + \ln P^*$$  \hspace{1cm} (II-52)

For a pure component at its vapor pressure, $p_i$,

$$\frac{f_i^L}{p_i} = \frac{f_i^V}{p_i}$$  \hspace{1cm} (II-53)

From equation II-48 and II-53,

$$\ln f_i^{oL} = \frac{1}{RT} \int_{p_i}^P \bar{V}_i^{oL} dP + \ln \frac{f_i^V}{p_i}$$  \hspace{1cm} (II-54)

Expressing $\frac{f_i^V}{p_i}$ in terms of Equation II-47 and substituting into Equation II-54

$$\ln f_i^{oL} = \frac{1}{RT} \int_{p_i}^P \bar{V}_i^{oL} dP + \frac{1}{RT} \int_{p_i}^{P^*} \frac{p_i}{\bar{V}_i} \bar{V}_i^V dP + \ln P^*$$  \hspace{1cm} (II-55)

Now, $\gamma_i$, as defined by Equation II-51, may be expressed in terms of Equations II-52 and II-55, after first taking the logarithm
of Equation II-51,

\[ \ln \gamma_i = \frac{1}{RT} \int_{p_i}^{p} \frac{V_i^V}{p*} dP + \ln \frac{V_i^L}{x_i} - \frac{1}{RT} \int_{p_i}^{P*} \frac{V_i^L}{p*} dP - \frac{1}{RT} \int_{p_i}^{P*} \frac{V_i^V}{p*} dP \]  

(II-56)

Equation II-56 is generally valid and may be used to calculate \( \gamma_i \) under all conditions (let \( P^* = 0 \)) at which the individual terms of Equation II-56 can be evaluated. Unfortunately, all the volumetric data necessary to apply Equation II-56 are seldom available. Under certain conditions the equation may be simplified.

Assume that the following approximations are valid:

1. There is no volume change on mixing of the vapors, i.e., \( \bar{V}_i^V = V_i^V \). (This is equivalent to the Lewis and Randall rule which has been variously recommended as being valid up to 0.6 of the critical pressure of the component in question (22) or to 0.8 of the pseudo-critical pressure of the mixture (28)).

2. The vapor volume may be represented by the truncated virial equation

\[ \bar{V}_i^V = \frac{RT}{P} + B_i \]

where \( R = \) universal gas constant.

\( B_i = \) 2nd virial coefficient of component \( "i" \), volume/mole.

(This equation generally holds when the vapor
density is less than 1/4 the critical density (41).

3. The effect of pressure on the liquid volume is negligible between \( p_i \) and \( P \). (This is usually true except near the critical region.)

Using the above approximations, Equation II-56 becomes

\[
\ln \gamma_i = \frac{1}{RT} \ln \frac{\gamma_i}{x_i} - \frac{V_i L}{RT} (P - p_i) - \frac{1}{RT} \int_{p_i}^{p} \left( \frac{RT}{P} + B_i \right) dP
\]

or

\[
\ln \gamma_i = \frac{1}{RT} \ln \frac{\gamma_i}{x_i} - \frac{V_i L}{RT} (P - p_i)
\]

(II-57)

or

\[
\ln \gamma_i = \ln \frac{P \gamma_i}{p_i x_i} + \left[ \frac{(B_i - V_i L)}{RT} (P - p_i) \right]
\]

(II-58)

(II-59)

Thus

\[
\gamma_i = \left( \frac{P \gamma_i}{p_i x_i} \right) \exp \left( \frac{1}{RT} (B_i - V_i L) (P - p_i) \right) = \gamma'_i Z
\]

(II-60)

\[
Z = \exp \left[ \frac{1}{RT} (B_i - V_i L) (P - p_i) \right]
\]

(II-61)

Note the similarity of Equations II-44 and II-60. The factor \( Z \) may be considered a correction to Equation II-44 to account for non-ideal gas vapors and non-ideal liquid solution.

To apply Equation II-60 requires data which may be obtained as follows:
1. Virial coefficients - These data should be taken from the literature if experimental data are available, but approximate methods may be required. Berthelot's equation (27), Wohl's equation (20), or Pitzer and Curl's correlation (14) for $B_i$ may provide suitable estimations. The virial coefficients are not functions of pressure, so experimental data at pressures other than the system pressure may be used.

2. Liquid volumes - Experimental data are usually available in literature compilations (31, 49). If the liquid state is hypothetical, data at higher pressure may be employed.

3. Vapor pressures - These data are also usually in the literature (31, 49). However, if a component is above its critical temperature, both vapor pressure and liquid volume are meaningless, and methods other than the use of activity coefficients may be employed. These methods will be discussed later.

Equation II-56 may be used at all conditions below the critical to calculate $Y$, while Equation II-60 is usually applicable at moderate pressures, and Equation II-44 may be suitable at very low pressures. Note that all these equations require data other than vapor-liquid equilibria data, i.e., vapor pressures, virial coefficients, etc. Thus, accurate
activity coefficients always require accurate auxiliary data in addition to the P-T-x-y data.

Equation II-60 is by no means the only approximate method for calculating $\gamma(6,22)$ but is among the most satisfactory and easily applicable methods.
CHAPTER III

TESTS FOR THERMODYNAMIC CONSISTENCY OF
VAPOR-LIQUID EQUILIBRIA DATA

In this chapter, several tests for thermodynamic consistency of vapor-liquid equilibria data are developed and discussed. Both rigorous and approximate tests are considered.

A Rigorous Equation for Testing Isothermal Data

in Terms of Activity Coefficients

At constant temperature, Equation II-24 may be written for the liquid phase as

\[ \frac{V^L}{L} dP = \sum x_i d\mu_i \]  \hspace{1cm} (III-1)

Combining Equations III-1 and II-27,

\[ \frac{V^L}{L} dP = \sum x_i RT d\ln \bar{f}_i \]  \hspace{1cm} (III-2)

For the remainder of this chapter, the discussion will be restricted to binary systems. Under this restriction, Equation III-2 becomes

\[ \frac{V^L}{RT} dP = x_1 d\ln \bar{f}_1 + x_2 d\ln \bar{f}_2 \]  \hspace{1cm} (III-3)

Differentiating Equation III-3 with respect to \( x_1 \), and noting that \( dx_1 = -dx_2 \) for a binary system,
\[
\frac{V^L}{RT} \frac{dP}{dx_1} = \frac{d\ln \bar{f}_1}{d\ln x_1} - \frac{d\ln \bar{f}_2}{d\ln x_2} \quad (III-4)
\]

To change Equation III-4 into an expression in terms of activity coefficients, note that from Equation II-43

\[
\frac{d\ln \gamma_i}{d\ln x_i} = \frac{d\ln \bar{f}_i}{d\ln x_i} - \frac{d\ln \gamma_i}{d\ln x_i} - \frac{d\ln f_i^0}{d\ln x_i} \quad (III-5)
\]

or in view of Equation II-35

\[
\frac{d\ln \bar{f}_i}{d\ln x_i} = \frac{d\ln \gamma_i}{d\ln x_i} + x_i \frac{d\ln f_i^0}{dP} + 1 = \frac{d\ln \gamma_i}{d\ln x_i} + \frac{x_i V^L}{RT} \frac{dP}{dx_1} + 1 \quad (III-6)
\]

Equation III-4 becomes

\[
\frac{V^L}{RT} \frac{dP}{dx_1} = \frac{d\ln \gamma_1}{d\ln x_1} + x_1 \frac{V^L}{RT} \frac{dP}{dx_1} - \frac{d\ln \gamma_2}{d\ln x_2} - \frac{x_2 V^L}{RT} \frac{dP}{dx_2} \quad (III-7)
\]

Rearranging, recalling that \(dP/dx_1 = -dP/dx_2\),

\[
\frac{1}{RT} \left[ V^L - x_1 V^L_{-1} - x_2 V^L_{-2} \right] \frac{dP}{dx_1} = \frac{\Delta V^L_{\text{mix}}}{RT} \frac{dP}{dx_1} = \frac{d\ln \gamma_1}{d\ln x_1} - \frac{d\ln \gamma_2}{d\ln x_2} \quad (III-8)
\]

where \(\Delta V^L_{\text{mix}} = \text{volume change on mixing of the liquid solution, volume/mole}\).

Either Equation III-4 or III-8 is suitable for consistency tests, but their differential form is inconvenient (slopes are difficult to determine accurately). Equation III-8 will now be transformed into a more easily applicable integral form.
Equation III-8 may be written in the form

\[
\frac{x_1 \ln \gamma_1}{dx_1} + (1 - x_1) \frac{\ln \gamma_2}{dx_1} = \frac{\ln (\gamma_1/\gamma_2)}{dx_1} = \frac{\Delta V^L_{\text{mix}}}{RT} \frac{dP}{dx_1} \tag{III-9}
\]

Integrating Equation III-9,

\[
\int_{x_1=0}^{x_1=1} \left[ x_1 \ln (\gamma_1/\gamma_2) + \ln \gamma_2 \right] = \int_{0}^{1} \left( \frac{\Delta V^L_{\text{mix}}}{RT} \frac{dP}{dx_1} \right) dx_1 = \int_{p_1}^{p_2} \left( \frac{\Delta V^L_{\text{mix}}}{RT} \right) dP \tag{III-10}
\]

The first term on the left of Equation III-10 is considered to have the mathematical properties requisite for integration by parts, i.e., \( x_1 \) is a continuous function of \( \ln (\gamma_1/\gamma_2) \) from \( x_1 = 0 \) to \( x_1 = 1 \).

Thus,

\[
\int_{x_1=0}^{x_1=1} x_1 \ln (\gamma_1/\gamma_2) = x_1 \ln (\gamma_1/\gamma_2) \bigg|_{x_1=0}^{x_1=1} - \int_{0}^{1} \ln (\gamma_1/\gamma_2) dx_1
\]

\[
= -\ln \gamma_2(x_1=1) - \int_{0}^{1} \ln (\gamma_1/\gamma_2) dx_1 \tag{III-11}
\]

Also,

\[
\int_{x_1=0}^{x_1=1} \ln \gamma_2 = \ln \gamma_2(x_1=1) \tag{III-12}
\]

Substituting Equations III-11 and III-12 into III-10 and simplifying
\[
\int_0^1 \ln \left( \frac{Y_1}{Y_2} \right) dx_1 = - \int_0^1 \left( \frac{\Delta V_{\text{mix}}^L}{RT} \frac{dP}{dx_1} \right) dx_1 = \int_{p_1}^{p_2} \frac{\Delta V_{\text{mix}}^L}{RT} dP \quad (\text{III-13})
\]

Equation III-13 is a rigorous expression of the Gibbs-Duhem equation at constant temperature in a conveniently applicable form.

The use of Equation III-13 requires data on volume changes on mixing of the liquid phase, which limits the utility of the equation; volumetric data are seldom available, and most of the available data are at 25°C. However, the right side of Equation III-13 is often negligible at moderate pressures, and

\[
\int_0^1 \ln \left( \frac{Y_1}{Y_2} \right) dx_1 = 0 \quad (\text{III-14})
\]

if often permissible. The use of Equation III-13 is illustrated in Table I and Figure 1 where atmospheric data on acetone-water at 100°C are tested for consistency by the author. (Tables and figures are presented at the end of each chapter.) Notice that the volumetric term in Equation III-13 is negligible, as shown in note at bottom of Table I, and Equation III-14 is applicable. The data are obviously consistent. The inherent random errors in experimental data will usually cause the two sides of Equation III-13 to differ slightly, and some judgment must be used to determine if the inequality is significant.
A Rigorous Equation for Testing Isobaric Data

in Terms of Activity Coefficients

The fugacity of a component in a mixture is a function of temperature, pressure, and composition, i.e., for a binary mixture

$$f_i = f_i(T, P, x_i)$$ \hspace{1cm} (III-15)

and

$$\ln f_i = \frac{\partial \ln f_i}{\partial T} \frac{\partial T}{P, x_i} + \frac{\partial \ln f_i}{\partial P} \frac{\partial P}{T, x_i} + \frac{\partial \ln f_i}{\partial \ln x_i} \frac{\partial \ln x_i}{T, P}$$ \hspace{1cm} (III-16)

At constant pressure ($dP = 0$), combining Equations II-42 and III-16,

$$\ln f_i = \frac{H_i^* - H_i}{RT^2} dT + \frac{\partial \ln f_i}{\partial \ln x_i} \frac{\partial \ln x_i}{T, P}$$ \hspace{1cm} (III-17)

Writing Equation III-17 for components 1 and 2 separately, multiplying by their respective mole fractions, and adding

$$x_1 \ln f_1 + x_2 \ln f_2 = \frac{1}{RT^2} \left( x_1 H_1^* + x_2 H_2^* - x_1 H_1 - x_2 H_2 \right) dT$$

$$+ \frac{\partial \ln f_1}{\partial \ln x_1} \frac{\partial \ln x_1}{T, P} dx_1 + \frac{\partial \ln f_2}{\partial \ln x_2} \frac{\partial \ln x_2}{T, P} dx_2$$ \hspace{1cm} (III-18)

But from Equation III-3, note that at constant $T, P$

$$\frac{\partial \ln f_1}{\partial \ln x_1} \frac{\partial \ln x_1}{T, P} dx_1 + \frac{\partial \ln f_2}{\partial \ln x_2} \frac{\partial \ln x_2}{T, P} dx_2 = 0$$ \hspace{1cm} (III-19)
and Equation III-18 becomes

\[ x_1 \frac{d \ln \bar{f}_1}{d \ln x_1} + x_2 \frac{d \ln \bar{f}_2}{d \ln x_2} = \frac{1}{RT^2} (x_1 \bar{H}_1^* + x_2 \bar{H}_2^* - x_1 \bar{H}_1 - x_2 \bar{H}_2) \frac{dT}{dx_1} \]

\[ = \frac{\Delta H_{vap}}{RT^2} \frac{dT}{dx_1} \quad (III-20) \]

where \( \Delta H_{vap} \) = heat of vaporization of mixture to ideal gas state, energy/mole.

Differentiating Equation III-20 with respect to composition

\[ \frac{d \ln \bar{f}_1}{d \ln x_1} - \frac{d \ln \bar{f}_2}{d \ln x_2} = \frac{\Delta H_{vap}^{\text{mix}}}{RT^2} \frac{dT}{dx_1} \quad (III-21) \]

This is a rigorous equation at constant pressure. To introduce activity coefficients into Equation III-21, rewrite Equation III-5 as

\[ \frac{d \ln Y_i}{d \ln x_i} = \frac{d \ln \bar{f}_i}{d \ln x_i} - x_i \frac{\Delta H_i^{\text{mix}} - \Delta H_i}{RT^2} \frac{dT}{dx_i} - 1 \quad (III-22) \]

Rearranging Equation III-22 and introducing Equation II-42 (written for a pure component),

\[ \frac{d \ln \bar{f}_i}{d \ln x_i} = \frac{d \ln Y_i}{d \ln x_i} + x_i \frac{\Delta H_i^{\text{mix}} - \Delta H_i}{RT^2} \frac{dT}{dx_i} + 1 \quad (III-23) \]

Thus, Equation III-21 becomes

\[ \frac{d \ln Y_1}{d \ln x_1} - \frac{d \ln Y_2}{d \ln x_2} = \frac{1}{RT^2} (x_1 \bar{H}_1 + x_2 \bar{H}_2 - x_1 \bar{H}_1 - x_2 \bar{H}_2) \frac{dT}{dx_1} = - \frac{\Delta H_{mix}^{\text{L}}}{RT^2} \frac{dT}{dx_1} \quad (III-24) \]
where \( \frac{\Delta H^L_{\text{mix}}}{\text{mole}} \) = integral heat of mixing of the liquid mixture, energy/mole.

Note the similarity between Equations III-8 and III-24. Equation III-24 may be integrated in a manner analogous to that performed on Equation III-8 to yield

\[
\int_0^1 \ln \left( \frac{\gamma_1}{\gamma_2} \right) \, dx_1 = \int_0^1 \left( \frac{\Delta H^L_{\text{mix}}}{RT^2} \right) \, dx_1 = \int_{T_1}^{T_2} \frac{\Delta H^L_{\text{mix}}}{RT^2} \, dT \quad (\text{III-25})
\]

where \( T_1, T_2 \) = boiling points of components 1 and 2, respectively.

Equation III-25 is in a form convenient for testing isobaric data. (Thijssen (57) previously derived Equation III-25 from different considerations.) The equation is applied in a manner analogous to that for Equation III-13. Again, some tolerance for the inequality of the two sides of Equation III-25 must be allowed due to unavoidable experimental errors.

Heat of mixing data are seldom available, and the data available are usually at 25°C. However, Ibl and Dodge (30) suggest that such room temperature data will often suffice to permit a meaningful check of the equilibria data (the same applies for volumes of mixing).

In contrast to the volumetric term of Equation III-13, the heat of mixing term in Equation III-25 is frequently significant and should always be evaluated, at least approximately. The method of applying Equation III-25 is illustrated in Tables II and III and Figures 2, 3, and 4 for the system benzene-normal heptane at atmospheric pressure. This system was chosen at random for testing by the author and illustrates a "border line"
case in which the difference in the value of the two sides of Equation III-25 borders on being sufficiently large to invalidate the data. In this case, the use of 25°C heat of mixing data might cause the inequality. The method of application of Equation III-25 is illustrated by this example, however.

In both cases where volume change on mixing or heat of mixing data are needed, these quantities should theoretically be evaluated at the conditions of the equilibria data. An inspection of the individual terms in these expressions will reveal that a hypothetical state will be encountered at the system conditions, the more volatile component being a hypothetical liquid. In these cases, little error will be involved in using volumetric and enthalpy data taken at pressures sufficiently high that the hypothetical state is avoided.

**A Rigorous Test for Thermodynamic Consistency in Terms of K Values**

In cases where extension or correlation of data is not involved, no particular advantage is gained by using activity coefficients in the consistency tests. In such instances, the vapor-liquid equilibrium phase distribution ratio, or K value, is much more convenient to use, where

\[ K_i = \frac{y_i}{x_i} \]  

(III-26)

Consistency tests in terms of K values will now be derived using the method of Adler, et al (2).

First, consider the case of constant temperature. From
Equation II-35,

\[ RT \ln \frac{\bar{f}_{i2}}{\bar{f}_{i1}} = \int_{P_1}^{P_2} \bar{V}_1 dP \quad (T \text{ constant}) \quad (III-27) \]

If state "1" is chosen such that \[ \bar{f}_1 = P y_1, \]

\[ RT \ln \frac{\bar{f}_{i2}}{P y_1} = \int_{P_1}^{P_2} \bar{V}_1 dP = \int_{P_1}^{P_2} \left( \frac{RT}{P} - \bar{\alpha}_i \right) dP \quad (III-28) \]

where

\[ \bar{\alpha}_i = \frac{RT}{P} - \bar{V}_i \quad (III-29) \]

Thus, from Equation III-28

\[ RT \ln \frac{\bar{f}_{i2}}{P y_1} = RT \ln P_1 - RT \ln y_1 = RT \ln P_2 - RT \ln P_1 - \int_{P_1}^{P_2} \frac{\bar{\alpha}_i}{P} dP \quad (III-30) \]

or

\[ RT \ln \frac{\bar{f}_i}{P y_1} = - \int_{P_1}^{P_2} \frac{\bar{\alpha}_i}{P} dP \quad (III-31) \]

Letting \[ P_1 \to 0, \]

\[ RT \ln \frac{\bar{f}_i}{P y_1} = - \int_{0}^{P} \frac{\bar{\alpha}_i}{P} dP \quad (III-32) \]

or finally, by rearranging Equation III-32,
\[
\ln \frac{f_i}{P_i} = \left( \frac{PV_i}{RT} - 1 \right) d\ln P \tag{III-33}
\]

From the above equation

\[
d\ln f_i = d\ln P_i + \left( \frac{PV_i}{RT} - 1 \right) d\ln P \tag{III-34}
\]

Equation III-3 may be written

\[
x_1 d\ln f_1 + x_2 d\ln f_2 = \frac{PV}{RT} d\ln P \quad (T \text{ constant}) \tag{III-35}
\]

Substituting Equation III-34 into Equation III-35, defining \(z_i = \frac{PV_i}{RT}\), and recalling that \(\frac{y_i}{K_i} = x_i\),

\[
x_1 d\ln P_i + \frac{y_1}{K_1} \left( z_i - 1 \right) d\ln P + x_2 d\ln P + \frac{y_2}{K_2} \left( z_2 - 1 \right) d\ln P
\]

\[
= \frac{PV}{RT} d\ln P \tag{III-36}
\]

Note that

\[
V^V = y_1 V_1^V + y_2 V_2^V \tag{III-37}
\]

or

\[
V_2^V = \frac{1}{y_2} V^V - \frac{y_1}{y_2} V_1^V \tag{III-38}
\]

Thus

\[
z_2^V = \frac{1}{y_2} z^V - \frac{y_1}{y_2} z_1^V \tag{III-39}
\]
Introducing Equation III-39 into Equation III-36

\[ x_1 \ln y_1 + x_2 \ln y_2 + \left[ \frac{y_1}{K_1} z_1 - \frac{y_1}{K_1} + 1 + \frac{y_2}{K_2} \left( \frac{1}{y_2} z_1 - \frac{y_1}{y_2} z_2 + 1 \right) \right] \ln P = 0 \]  

(III-40)

Note that inside the brackets

\[ \frac{y_1}{K_1} - \frac{y_2}{K_2} + 1 = -(x_1 + x_2) + 1 = 0 \]  

(III-41)

Combining Equation III-41 and the relation

\[ x_1 \ln x_1 + x_2 \ln x_2 = 0 \]  

(III-42)

with Equation III-40

\[ x_1 \ln K_1 + x_2 \ln K_2 = \left[ z^L + z_1^V y_1 \left( \frac{1}{K_2} - \frac{1}{K_1} \right) - \frac{z^V}{K_2} \right] \ln P \]  

(III-43)

Integrating Equation III-43 from \( x_1 = 0 \) to \( x_1 = x_1' \),

\[ \begin{align*}
K_1(x_1) & \quad K_2(1-x_1) & \quad P(x_1) \\
x_1 \ln K_1 & + x_2 \ln K_2 = \int \left[ z^L + z_1^V y_1 \left( \frac{1}{K_2} - \frac{1}{K_1} \right) - \frac{z^V}{K_2} \right] \ln P \\
K_1(0) & + K_2(1) & + P(0) 
\end{align*} \]  

(III-44)

Equation III-44 is a thermodynamically rigorous expression for an isothermal system. This equation has an advantage over tests previously derived in terms of activity coefficients; all terms in Equation III-44 may be obtained from data in stable regions, i.e., the problem of hypothetical states is avoided.

The equation is especially useful in cases where the more volatile
component is above its critical temperature (in such cases vapor pressure is undefined and activity coefficients cannot be determined accurately).

Adler, et al (2) seem to imply that Equation III-44 is dependent on the Lewis and Randall rule. This is so only if the z factors are estimated from molar rather than partial molar volumes; when partial volumes are used, Equation III-44 is generally valid. More often than not, however, molar volumes or even generalized compressibility charts must be used to obtain the z factors, placing the restriction of the Lewis and Randall rule and of the generalized charts on the equation. Even in cases where molal volumes must be used, the problem of hypothetical states may be avoided by use of Equation III-39 to calculate $V_i^z_2$. Clear examples of the use of Equation III-44 have recently been given elsewhere (2, 40) and will not be repeated here.

Adler, et al also presented an approximate equation for testing isobaric data. If the Lewis and Randall rule is applicable,

$$\frac{V_i}{f_i} = y_i f_i^V = K_i x_i P \gamma_i$$  \hspace{1cm} (III-45)

where $\gamma_i$ = fugacity coefficient of pure component "i", $f_i^V$/P.

Substitution of Equation III-45 into Equation III-20 and simplification yields

$$x_1 \ln K_1 \gamma_1 + x_2 \ln K_2 \gamma_2 = \frac{\Delta H_{vap}}{RT} dT$$  \hspace{1cm} (III-46)

This equation may be in a manner similar to Equation III-44. The
use of Equation III-46 requires enthalpy and fugacity coefficient data. Adler, et al point out methods for estimating the $z$ factors in Equation III-44 and $\gamma$ and $\Delta H_{vap}$ in Equation III-46; estimation procedures are almost always required, and care must be taken to assure that inaccuracies in the estimation methods do not obscure the original purpose of the consistency tests.

**Frequently Used Consistency Tests Involving Approximations**

The consistency tests which have been discussed above (with the exception of Equation III-46) are in rigorous agreement with the Gibbs-Duhem equation. All these tests, however, require the use of volumetric or enthalpy data. Since such data are seldom available, many approximate forms of the Gibbs-Duhem equation are used to test data. Some of the more commonly employed approximate tests will now be discussed, with emphasis on their limitations. All too often, approximate equations are presented without descriptions of their limitations and/or are used in cases where they are invalid.

**The Gibbs-Duhem Equation at Constant Temperature and Pressure**

At constant temperature and pressure, the Gibbs-Duhem equation (Equation II-24) reduces to

\[ \sum x_i \, du_i = \sum x_i \, RT \, d\ln f_i = \sum x_i \, d\ln \bar{f}_i = 0 \]  

(III-47)

For a binary system
\[ x_1 \, d\ln \bar{f}_1 + x_2 \, d\ln \bar{f}_2 = 0 \]  \hspace{1cm} (III-48)

Equivalent expressions are

\[ \left( \frac{\partial \ln \bar{f}_1}{\partial \ln x_1} \right)_{T,P} = \left( \frac{\partial \ln \bar{f}_2}{\partial \ln x_2} \right)_{T,P} \]  \hspace{1cm} (III-49)

or

\[ \left( \frac{\partial \ln \gamma_1}{\partial \ln x_1} \right)_{T,P} = \left( \frac{\partial \ln \gamma_2}{\partial \ln x_2} \right)_{T,P} \]  \hspace{1cm} (III-50)

The above equations are the most frequently seen forms of the
Gibbs-Duhem equation and are used to test both isobaric and
isothermal data.

Equations III-48 to III-50 may never be rigorously applied
to vapor-liquid equilibria data. Consider the Gibbs phase rule

\[ P + F = C + 2 \]  \hspace{1cm} (III-51)

where \( P \) = number of phases in the system.

\( F = \) number of variables which must be
specified to fix the state of the
system.

\( C = \) number of components in the system.

For a binary system

\[ 2 + F = 2 + 2 \text{ or } F = 2 \]  \hspace{1cm} (III-52)

If the temperature and pressure are specified as being constant,
\( F = 0 \), and the state of the system is fixed. Thus, the com-
position of the system is invariant, and only one vapor-liquid
equilibrium composition is possible.

The assumptions required to permit use of Equations III-49 and III-50 are easily determined. For isothermal equilibria data, compare Equations III-49 and III-50 with Equations III-4 and III-8, respectively. Use of Equation III-49 assumes that \( \frac{V^L dP}{RT dx_1} \) is negligible, and Equation III-50 assumes that \( \frac{V^L_{mix} dP}{RT dx_1} \), negligible.

Fortunately, the terms can often be neglected. Note that

\[
\frac{V^L dP}{RT dx_1} = \frac{P y^L_1 d\ln P}{RT} = \frac{V^L d\ln P}{V_1 dx_1} \quad (\text{III-53})
\]

where \( V_1 \) = ideal gas volume.

The ratio of the liquid volume to ideal gas volume is often negligible, and at moderate conditions \( \frac{d\ln P}{dx_1} \) is of the same order of magnitude as \( \frac{d\ln f_1}{dx_1} \). Equations III-49 and III-50 are usually applicable to a high degree of accuracy to isothermal data at moderate pressures (note the data on acetone-water tested in Table I).

For isobaric data, Equations III-21 and III-24 indicate that the use of Equation III-49 requires the neglect of \( \frac{\Delta H_{\text{vap}} dT}{RT^2 dx_1} \), and Equation III-50 the neglect of \( \frac{\Delta H_{\text{mix}}^L dT}{RT^2 dx_1} \). The terms are frequently significant, and may be important in some concentration ranges and negligible in others. Ibl and Dodge point out that for the system carbon disulfide-acetone at atmospheric pressure, the use
of Equation III-49 results in an error of 0.7% at $x_A = 0.5$, but 13% at $x_A = 0.1$, and 7% at $x_A = 0.9$.

In summation, Equations III-49 and III-50 may usually be employed to isothermal data at moderate conditions, but the equations are often in error for isobaric data, particularly if the boiling range is more than a few degrees.

The Redlich-Kister Test

The consistency test of Redlich and Kister (46) is given by the following relation

\[
\int_0^1 \ln \left( \frac{y_1}{y_2} \right) dx_1 = 0 \quad (III-54)
\]

Equation III-54 is widely used for testing isothermal and isobaric data. (Equations III-54 and III-14 are identical.) Redlich and Kister derived Equation III-54 from excess free energy considerations, starting with

\[
G^E = RT \sum x_i \ln y_i \quad (III-55)
\]

where $G^E$ = excess free energy (above an ideal solution) of mixture, energy/mole.

From Equation III-55, for a binary system

\[
\frac{d \left( \frac{G^E}{RT} \right)}{dx_1} = \ln \left( \frac{y_1}{y_2} \right) + x_1 \frac{d \ln y_1}{dx_1} - x_2 \frac{d \ln y_2}{dx_2} \quad (III-56)
\]

If the last two terms of Equation III-56 are neglected,
which is the Redlich-Kister test. However, note that the assumption involved in neglecting the last terms of Equation III-56 is equivalent to

$$\int_{x_1=0}^{x_1=1} \frac{d\frac{G^E}{RT}}{x_1} = 0 - 0 = \int_0^1 \ln \left( \frac{\gamma_1}{\gamma_2} \right) dx_1$$  \hspace{1cm} (III-57)

Compare this equation with Equation III-50; thus, the use of the Redlich-Kister test is equivalent to the use of the constant temperature-pressure Gibbs-Duhem equation. The assumptions involved in using Equation III-54 are identical to those discussed for use of Equation III-50. (Equation III-54 may be obtained from Equation III-50 by integration by parts.) However, Equation III-54 is more convenient than Equation III-50 since it is in integral rather than differential form.

Comparison of Equations III-54 with Equation III-13 and III-25 yields a clear picture of the terms neglected by the Redlich-Kister test.

Particular Integrated Solutions
to the Gibbs-Duhem Equation

Much attention has been directed toward the use of mathematical functions to describe activity coefficients. The two most widely used such expressions are the van Laar equation, one form of which is
\[
\ln Y_1 = \frac{A}{\left( \frac{A x_1}{B x_2 + 1} \right)^2} ; \quad \ln Y_2 = \frac{B}{\left( \frac{B x_2}{A x_1 + 1} \right)^2} \quad (III-59)
\]

where \( A, B \) = constants at a given temperature.

and the Margules equation, one form of which is

\[
\ln Y_1 = b x_2^2 + c x_2^3 ; \quad \ln Y_2 = b x_1^2 + \frac{3}{2} c x_1^2 - c x_1^3 \quad (III-60)
\]

where \( b, c \) = constants at a given temperature.

Both of the above equations are particular solutions of the constant \( T, P \) Gibbs-Duhem equation. The van Laar equation is based on semi-theoretical considerations, and the Margules equation is empirical; both equations are thoroughly discussed elsewhere (11,48).

Particular solutions of the Gibbs-Duhem equation, such as Equations III-59 and III-60, are often employed to determine whether or not experimental equilibria data, both isothermal and isobaric, are consistent. Such tests consist of attempts to fit the mathematical equations to the experimental activity coefficients. The data are judged according to whether or not they may be fitted to the particular equation selected. Recent applications of such tests are available (1, 37).

The range of applicability of the tests described above is severely limited. First, the constant \( T, P \) Gibbs-Duhem equation must be applicable. If this condition is met, and if the data conform to the particular equation chosen, the data are consistent. However, since there are innumerable particular
solutions to the constant $T$, $P$ Gibbs-Duhem equation, the failure of the data to conform to any one particular solution is not evidence that the data are inconsistent.

The use of the above tests does not seem advisable unless the user is able to recognize from experience when a particular solution is apt to fit a given set of data (and provided that the conditions for applicability of the constant $T$, $P$ Gibbs-Duhem equation are met).

Herington's Test for Isobaric Data

Herington (25), realizing that the approximate tests discussed previously are usually not applicable to isobaric data, attempted to derive a test for isobaric data which indirectly accounts for the heat of mixing term in the rigorous tests. Herington's derivation follows.

Consider the right side of Equation III-25. Obviously

$$
\left| \frac{\Delta H_{\text{mix}}^L}{RT^2} \right| dT < \frac{1}{R} \left( \frac{|\Delta H_{\text{mix}}^L|^M}{T_i^2} \right) \theta
$$

where $|\Delta H_{\text{mix}}^L|^M = \text{maximum value of absolute value of } \Delta H_{\text{mix}}^L \text{ in range } x_1 = 0 \text{ to } x_1 = 1$.

$\theta = T_{\text{max}} - T_{\text{min}}.$

$T_i = T_{\text{min}}$

At constant temperature, Equation III-56 becomes
If the volumetric term of Equation III-8 is negligible, Equation III-56a becomes

$$\frac{d(G^E)}{dx_1} \bigg|_T = \ln \left( \frac{\gamma_1}{\gamma_2} \right) + x_1 \left( \frac{d\ln \gamma_1}{dx_1} \right)_T - x_2 \left( \frac{d\ln \gamma_2}{dx_2} \right)_T \quad \text{(III-56a)}$$

Herington then states that

$$\ln \left( \frac{\gamma_1}{\gamma_2} \right) = \ln \left( \frac{\gamma_1}{\gamma_2} \right) \bigg|_{T_1} = \ln \left( \frac{\gamma_1}{\gamma_2} \right) \bigg|_{T_2}$$

(III-62)

Herington then states that

$$\int_0^1 \left| \ln \left( \frac{\gamma_1}{\gamma_2} \right) \right| \, dx_1 \approx \frac{2}{RT} \frac{|G^E|}{|E|^M} \quad \text{(III-63)}$$

where $|G^E| = \text{maximum value of } |G^E|$ from $x_1 = 0$ to $x_1 = 1$.

with no accompanying derivation. From Herington's statements, the author concluded that Herington obtained Equation III-63 as follows.

Let $\omega$ be the value of $x_1$ where $|G^E|^M$ occurs. Thus, from Equation III-57,

$$\int_0^1 \left| \ln \left( \frac{\gamma_1}{\gamma_2} \right) \right| \, dx_1 = \int_0^\omega \left| \ln \left( \frac{\gamma_1}{\gamma_2} \right) \right| \, dx_1 + \int_\omega^1 \left| \ln \left( \frac{\gamma_1}{\gamma_2} \right) \right| \, dx_1$$

$$= \left( \int_{x_1=0}^{x_1=\omega} \frac{dG^E}{RT} \right) + \left( \int_{x_1=1}^{x_1=\omega} \frac{dG^E}{RT} \right) \quad \text{(III-64)}$$

Integrating the right side of Equation III-64 by parts,

$$\int_0^1 \left| \ln \left( \frac{\gamma_1}{\gamma_2} \right) \right| \, dx_1 = \left[ \frac{|G^E|}{RT} \right]_0^\omega + \left[ \frac{|G^E|}{RT^2} \right]_0^T \omega + \left[ \frac{|G^E|}{RT} \right]_T^\omega + \left[ \frac{|G^E|}{RT^2} \right]_T^\omega \quad \text{(III-65)}$$
Inspection of Equation III-65 will reveal that the terms under the integral signs on the right will often be negligible with respect to the other terms. Thus,

\[
\int_0^1 \left| \ln \left( \frac{Y_1}{Y_2} \right) \right| \, dx_1 \approx \frac{2 \left| \frac{G}{M} \right|}{RT_\omega} \approx \frac{2 \left| \frac{G}{M} \right|}{RT_i} \quad \text{(III-63a)}
\]

Herington defined

\[
I = \int_0^1 \log \left( \frac{Y_1}{Y_2} \right) \, dx_1 \quad \text{(III-66)}
\]

\[
\sum' = \int_0^1 \left| \log \left( \frac{Y_1}{Y_2} \right) \right| \, dx_1
\]

Combining Equations III-25, III-61, and III-63,

\[
\frac{|I|}{\sum'} < \frac{1}{2} \left( \frac{\Delta H_{\text{mix}}^L}{\frac{G}{E} |M|} \right) \frac{\theta}{T_i} \quad \text{(III-67)}
\]

From an analysis of considerable data on polar and non-polar mixtures, Herington concluded that a safe approximation is

\[
\frac{\Delta H_{\text{mix}}^L}{\frac{G}{E} |M|} < 3.0 \quad \text{(III-68)}
\]

Combining Equations III-67 and III-68 and multiplying by a factor of 100,

\[
\frac{100 |I|}{\sum'} < \frac{1500 \theta}{T_i} \quad \text{(III-69)}
\]

or by defining

\[
D = 100 |I| / \sum' \quad ; \quad J = \frac{1500 \theta}{T_i} \quad \text{(III-70)}
\]
Equation III-69 becomes

$$D < J$$ for consistent data \hspace{1cm} (III-71)

Herington suggests that from experience some tolerance should be included in Equation III-71; he suggests

$$D - J < 10$$ implies consistent data. \hspace{1cm} (III-72)

This is the final form of Herington's test.

Obvious limitations to Herington's test are Equations III-63 and III-68, which must be applicable for the test to be of value. Note that if Herington arrived at Equation III-63 via the steps presented in Equation III-64 and III-65, then Equation III-63 is based on Equation III-62. But Equation III-62 is the same relation on which the Redlich-Kister test is based (see Equation III-57). Thus, Herington's test, as well as the Redlich-Kister test, rests upon the applicability of the constant $T$, $P$ Gibbs-Duhem equation to isobaric equilibria. Herington's test is, in this case, little or no improvement on the other approximate tests.

There are many approximate consistency tests other than those mentioned above, but the above are among the most frequently employed. Tests based on such highly restrictive assumptions as validity of the ideal gas law are frequently encountered, but their inclusion would have added little to the discussion. Also, special phenomena such as multiple liquid phases and association in the vapor or liquid phase have not been considered.

**Summary**

The main ideas presented in this chapter will now be
summarized.

The value of thermodynamic consistency tests is to permit detection of inaccurate experimental data; inconsistent data are incorrect, but consistent data are not necessarily correct. No rigorous method for positively identifying data as correct is known.

In applying thermodynamic consistency tests, the following points should be remembered:

1. To perform a rigorous test for consistency of experimental data requires volumetric data (for isothermal equilibria) or calorimetric data (for isobaric equilibria). Equations III-13 and III-44 for isothermal data and Equation III-25 for isobaric data are rigorous equations in convenient forms.

2. If activity coefficients are employed, use the proper relation. Equation II-56, II-60, or II-44 may be used depending on the components and conditions under study. Equation II-56 is always preferable. Before one uses Equation II-44, at least an approximate check of its validity by use of Equation II-60 is advisable.

3. If approximate tests must be employed, carefully check all assumptions to assure their validity.

4. If a test indicates the data are inconsistent, recheck to determine if the auxiliary data or testing method could be at fault.
TABLE I: TEST FOR CONSISTENCY OF DATA ON ACETONE-WATER SYSTEM AT 100 °C

<table>
<thead>
<tr>
<th>Pressure, psia</th>
<th>Mol % Acetone Vapor</th>
<th>Mol % Acetone Liquid</th>
<th>$\gamma_A^I$</th>
<th>$\gamma_W^I$</th>
<th>$Z_A$</th>
<th>$Z_W$</th>
<th>$\gamma_A$</th>
<th>$\gamma_W$</th>
<th>$\log (\gamma_A/\gamma_W)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.1</td>
<td>9.02</td>
<td>0.33</td>
<td>8.961</td>
<td>1.000</td>
<td>1.049</td>
<td>0.999</td>
<td>9.400</td>
<td>0.999</td>
<td>0.974</td>
</tr>
<tr>
<td>16.4</td>
<td>10.9</td>
<td>0.40</td>
<td>8.187</td>
<td>0.998</td>
<td>1.049</td>
<td>0.999</td>
<td>8.588</td>
<td>0.997</td>
<td>0.935</td>
</tr>
<tr>
<td>17.0</td>
<td>11.8</td>
<td>0.45</td>
<td>8.270</td>
<td>1.025</td>
<td>1.048</td>
<td>0.999</td>
<td>8.667</td>
<td>1.024</td>
<td>0.928</td>
</tr>
<tr>
<td>18.9</td>
<td>20.7</td>
<td>0.80</td>
<td>9.073</td>
<td>1.028</td>
<td>1.045</td>
<td>0.998</td>
<td>9.841</td>
<td>1.026</td>
<td>0.982</td>
</tr>
<tr>
<td>32.5</td>
<td>54.5</td>
<td>4.8</td>
<td>6.864</td>
<td>1.057</td>
<td>1.029</td>
<td>0.992</td>
<td>7.044</td>
<td>1.048</td>
<td>0.827</td>
</tr>
<tr>
<td>35.5</td>
<td>61.3</td>
<td>8.2</td>
<td>4.924</td>
<td>1.018</td>
<td>1.024</td>
<td>0.991</td>
<td>5.042</td>
<td>1.009</td>
<td>0.699</td>
</tr>
<tr>
<td>40.4</td>
<td>63.2</td>
<td>10.8</td>
<td>4.386</td>
<td>1.113</td>
<td>1.018</td>
<td>1.024</td>
<td>0.991</td>
<td>5.042</td>
<td>0.707</td>
</tr>
<tr>
<td>43.7</td>
<td>65.7</td>
<td>9.8</td>
<td>4.667</td>
<td>1.059</td>
<td>1.020</td>
<td>0.989</td>
<td>4.465</td>
<td>1.120</td>
<td>0.601</td>
</tr>
<tr>
<td>44.5</td>
<td>70.5</td>
<td>22.0</td>
<td>2.646</td>
<td>1.145</td>
<td>1.013</td>
<td>0.987</td>
<td>2.680</td>
<td>1.130</td>
<td>0.375</td>
</tr>
<tr>
<td>46.4</td>
<td>71.5</td>
<td>30.8</td>
<td>1.998</td>
<td>1.300</td>
<td>1.010</td>
<td>0.986</td>
<td>2.018</td>
<td>1.282</td>
<td>0.197</td>
</tr>
<tr>
<td>46.5</td>
<td>71.9</td>
<td>31.6</td>
<td>1.963</td>
<td>1.300</td>
<td>1.010</td>
<td>0.986</td>
<td>1.983</td>
<td>1.282</td>
<td>0.189</td>
</tr>
<tr>
<td>48.4</td>
<td>72.7</td>
<td>39.7</td>
<td>1.644</td>
<td>1.491</td>
<td>1.008</td>
<td>0.985</td>
<td>1.657</td>
<td>1.469</td>
<td>0.052</td>
</tr>
<tr>
<td>49.7</td>
<td>74.2</td>
<td>52.6</td>
<td>1.308</td>
<td>1.812</td>
<td>1.006</td>
<td>0.985</td>
<td>1.316</td>
<td>1.785</td>
<td>-0.133</td>
</tr>
<tr>
<td>50.4</td>
<td>74.7</td>
<td>48.0</td>
<td>1.455</td>
<td>1.668</td>
<td>1.005</td>
<td>0.984</td>
<td>1.462</td>
<td>1.641</td>
<td>-0.050</td>
</tr>
<tr>
<td>51.8</td>
<td>80.1</td>
<td>69.5</td>
<td>1.108</td>
<td>2.299</td>
<td>1.004</td>
<td>0.984</td>
<td>1.112</td>
<td>2.262</td>
<td>-0.308</td>
</tr>
<tr>
<td>50.7</td>
<td>81.4</td>
<td>71.5</td>
<td>1.071</td>
<td>2.251</td>
<td>1.005</td>
<td>0.984</td>
<td>1.076</td>
<td>2.215</td>
<td>-0.314</td>
</tr>
<tr>
<td>52.2</td>
<td>82.3</td>
<td>74.2</td>
<td>1.074</td>
<td>2.436</td>
<td>1.003</td>
<td>0.984</td>
<td>1.077</td>
<td>2.397</td>
<td>-0.348</td>
</tr>
<tr>
<td>52.6</td>
<td>83.7</td>
<td>77.1</td>
<td>1.059</td>
<td>2.547</td>
<td>1.003</td>
<td>0.983</td>
<td>1.062</td>
<td>2.504</td>
<td>-0.373</td>
</tr>
<tr>
<td>53.3</td>
<td>87.8</td>
<td>85.4</td>
<td>1.017</td>
<td>3.030</td>
<td>1.001</td>
<td>0.983</td>
<td>1.018</td>
<td>2.978</td>
<td>-0.466</td>
</tr>
<tr>
<td>53.5</td>
<td>94.6</td>
<td>94.4</td>
<td>0.995</td>
<td>3.509</td>
<td>1.001</td>
<td>0.983</td>
<td>0.996</td>
<td>3.449</td>
<td>-0.539</td>
</tr>
<tr>
<td>53.4</td>
<td>97.2</td>
<td>97.1</td>
<td>0.992</td>
<td>3.507</td>
<td>1.001</td>
<td>0.983</td>
<td>0.993</td>
<td>3.447</td>
<td>-0.541</td>
</tr>
<tr>
<td>53.5</td>
<td>97.8</td>
<td>97.7</td>
<td>0.994</td>
<td>3.481</td>
<td>1.001</td>
<td>0.983</td>
<td>0.995</td>
<td>3.422</td>
<td>-0.536</td>
</tr>
</tbody>
</table>

* Equilibria data, $\gamma^I$ and $\gamma$ values, and Z factors are from reference 23.

From Figure 1, \[ \int_0^1 \log \left( \frac{\gamma_A}{\gamma_W} \right) dx = 0.181 - 0.181 = 0.000. \]

From data at 30°C (58), maximum $\Delta V_{mix}^L < -2.0$ cc/gmol. Thus, \[ \int_{P_1}^{P_2} \frac{\Delta V_{mix}^L}{RT} dP < 0.0002 \]

In view of Equation III-13, the data are thermodynamically consistent.
### TABLE II
Z FACTORS FOR BENZENE AND NORMAL HEPTANE

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>80</th>
<th>85</th>
<th>90</th>
<th>95</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Vapor Pressure, mm Hg (49)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>757.6</td>
<td>881.7</td>
<td>1,020.9</td>
<td>1,176.8</td>
<td>1,350.5</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>427.8</td>
<td>503.5</td>
<td>589.4</td>
<td>686.4</td>
<td>795.8</td>
</tr>
<tr>
<td><strong>2nd Virial Coefficient, cc/gmol</strong>*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Liquid Molal Volume, cc/gmol</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene (38)</td>
<td>89.6</td>
<td>89.9</td>
<td>90.2</td>
<td>90.5</td>
<td>90.8</td>
</tr>
<tr>
<td>n-Heptane (31)</td>
<td>158.4</td>
<td>159.6</td>
<td>160.8</td>
<td>162.0</td>
<td>163.2</td>
</tr>
<tr>
<td><strong>Z Factor</strong>**</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>0.999</td>
<td>1.005</td>
<td>1.011</td>
<td>1.018</td>
<td>1.024</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>0.976</td>
<td>0.982</td>
<td>0.988</td>
<td>0.995</td>
<td>1.002</td>
</tr>
</tbody>
</table>

* Estimated using the Berthelot equation.

** Calculated from Equation II-61.
TABLE III: TEST FOR CONSISTENCY OF DATA ON BENZENE-NORMAL HEPTANE SYSTEM AT ONE ATMOSPHERE

<table>
<thead>
<tr>
<th>T, °C</th>
<th>Mol % Benzene</th>
<th>Y_B **</th>
<th>Y_H **</th>
<th>Z_B ***</th>
<th>Z_H</th>
<th>Y_B</th>
<th>Y_H</th>
<th>log (Y_B/Y_H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>98.5</td>
<td>0.0</td>
<td>0.0</td>
<td>0.998</td>
<td>1.022</td>
<td>1.000</td>
<td>-</td>
<td>0.988</td>
<td>-</td>
</tr>
<tr>
<td>96.8</td>
<td>5.0</td>
<td>10.0</td>
<td>1.228</td>
<td>0.994</td>
<td>1.020</td>
<td>0.998</td>
<td>1.253</td>
<td>0.992</td>
</tr>
<tr>
<td>95.1</td>
<td>10.0</td>
<td>18.8</td>
<td>1.211</td>
<td>0.996</td>
<td>1.018</td>
<td>0.995</td>
<td>1.233</td>
<td>0.991</td>
</tr>
<tr>
<td>92.0</td>
<td>20.0</td>
<td>34.0</td>
<td>1.195</td>
<td>1.000</td>
<td>1.014</td>
<td>0.991</td>
<td>1.212</td>
<td>0.991</td>
</tr>
<tr>
<td>89.2</td>
<td>30.0</td>
<td>46.0</td>
<td>1.168</td>
<td>1.020</td>
<td>1.010</td>
<td>0.987</td>
<td>1.180</td>
<td>1.007</td>
</tr>
<tr>
<td>86.9</td>
<td>40.0</td>
<td>55.3</td>
<td>1.126</td>
<td>1.059</td>
<td>1.008</td>
<td>0.984</td>
<td>1.135</td>
<td>1.042</td>
</tr>
<tr>
<td>85.1</td>
<td>50.0</td>
<td>63.5</td>
<td>1.091</td>
<td>0.998</td>
<td>1.005</td>
<td>0.982</td>
<td>1.096</td>
<td>1.078</td>
</tr>
<tr>
<td>83.6</td>
<td>60.0</td>
<td>71.1</td>
<td>1.065</td>
<td>1.141</td>
<td>1.004</td>
<td>0.980</td>
<td>1.069</td>
<td>1.118</td>
</tr>
<tr>
<td>82.3</td>
<td>70.0</td>
<td>78.0</td>
<td>1.042</td>
<td>1.208</td>
<td>1.002</td>
<td>0.978</td>
<td>1.044</td>
<td>1.181</td>
</tr>
<tr>
<td>81.3</td>
<td>80.0</td>
<td>84.8</td>
<td>1.022</td>
<td>1.294</td>
<td>1.001</td>
<td>0.977</td>
<td>1.023</td>
<td>1.264</td>
</tr>
<tr>
<td>80.5</td>
<td>90.0</td>
<td>92.2</td>
<td>1.012</td>
<td>1.363</td>
<td>1.000</td>
<td>0.977</td>
<td>1.012</td>
<td>1.332</td>
</tr>
<tr>
<td>80.3</td>
<td>95.0</td>
<td>95.9</td>
<td>1.003</td>
<td>1.443</td>
<td>1.000</td>
<td>0.977</td>
<td>1.003</td>
<td>1.410</td>
</tr>
<tr>
<td>80.1</td>
<td>100.0</td>
<td>100.0</td>
<td>1.000</td>
<td>-</td>
<td>1.000</td>
<td>0.976</td>
<td>1.000</td>
<td>-</td>
</tr>
</tbody>
</table>

* The equilibria data are from smoothed curves of data presented by Chu (13).
** Calculated using API 44 (49) vapor pressures.
*** From Table II.

From Figure 3,

\[
\int_0^1 \ln \left( \frac{Y_B}{Y_H} \right) \, dx_B = 2.303 \int_0^1 \log \left( \frac{Y_B}{Y_H} \right) \, dx_B = 0.0811 - 0.0829 = -0.0018
\]


**TABLE III, (continued)**

Evaluation of Heat of Mixing Term

<table>
<thead>
<tr>
<th>(x_B)</th>
<th>(T^\circ)</th>
<th>(\Delta H^L_{\text{mix}})</th>
<th>(\frac{\Delta H^L_{\text{mix}}}{RT^2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>93.5</td>
<td>436</td>
<td>0.000389</td>
</tr>
<tr>
<td>0.21</td>
<td>91.7</td>
<td>546</td>
<td>0.000457</td>
</tr>
<tr>
<td>0.22</td>
<td>91.4</td>
<td>584</td>
<td>0.000530</td>
</tr>
<tr>
<td>0.30</td>
<td>89.2</td>
<td>742</td>
<td>0.000678</td>
</tr>
<tr>
<td>0.324</td>
<td>88.7</td>
<td>772</td>
<td>0.000707</td>
</tr>
<tr>
<td>0.376</td>
<td>86.4</td>
<td>823</td>
<td>0.000762</td>
</tr>
<tr>
<td>0.441</td>
<td>86.1</td>
<td>902</td>
<td>0.000838</td>
</tr>
<tr>
<td>0.511</td>
<td>84.9</td>
<td>945</td>
<td>0.000887</td>
</tr>
<tr>
<td>0.588</td>
<td>83.7</td>
<td>948</td>
<td>0.000893</td>
</tr>
<tr>
<td>0.650</td>
<td>82.9</td>
<td>928</td>
<td>0.000881</td>
</tr>
<tr>
<td>0.715</td>
<td>82.2</td>
<td>857</td>
<td>0.000817</td>
</tr>
<tr>
<td>0.828</td>
<td>81.1</td>
<td>629</td>
<td>0.000601</td>
</tr>
<tr>
<td>0.878</td>
<td>80.7</td>
<td>511</td>
<td>0.000490</td>
</tr>
</tbody>
</table>

* Temperature from equilibria data.

** Heats of mixing are from reference (10) and are at 20\(^\circ\)C. These data will be used to give an approximate consistency check.

From Figure 4,

\[
\int_{\frac{T_1}{T_2}} \frac{\Delta H^L_{\text{mix}}}{RT^2} \, dT = -0.0103
\]

Thus, the two sides of Equation III-25 differ by

\[-0.0103 + 0.0018 = -0.0085\]

The 0.0085 is approximately 5\% of the absolute area of Figure 3. This magnitude of error borders on being sufficiently large to declare the data inconsistent. However, the use of 30\(^\circ\)C heats of mixing could account for part of this error. No conclusive decision may be reached regarding the consistency of the equilibria data in this case.
Figure 1
Graphical Integration for Acetone-Water Consistency Test

System: Acetone-Water, 100°C

Log ($Y_A/Y_W$)

Mol Fraction Acetone in Liquid
Figure 2

Z Factor for Calculating Activity Coefficients

\[ Z = \exp \left( \frac{1}{RT} \left( \frac{V_i}{V_i^L} \right) (P - P_i) \right) \]
Figure 3
Graphical Integration for Benzene-n-Heptane Consistency Test

System: Benzene-n-Heptane, 1 Atm.
Figure 4

Graphical Evaluation of

\[ \int_{T_1}^{T_2} \frac{\Delta H_{\text{mix}}}{RT^2} \, dT \]

System: Benzene-n-Heptane, 1 A tm.
CHAPTER IV

APPARATUS AND EXPERIMENTAL PROCEDURE

Huang, in his recent investigation of the ternary system normal hexane-methylcyclohexane-toluene, concluded that the literature data on the binary systems normal hexane-methylcyclohexane (37), normal hexane-toluene (54), and methylcyclohexane-toluene (44) are thermodynamically inconsistent. He used Herington's test for isobaric data (25) to show this inconsistency. Huang cited the inconsistent binary data as the probable cause for the failure of Wohl's (60) method to predict ternary data (from the binary data) that would agree with the experimental data of Huang.

In order to permit a meaningful test of Wohl's method, the author undertook an investigation to redetermine experimental data for the three binary systems mentioned above. The experimental apparatus and procedure will be discussed below.

Apparatus

Equilibrium Still

The still used in the investigation was of the Gillespie (21) type as modified by Drehman (16). This still (see Figure 5) was selected since it was the same still used by Drehman and Huang, both of whom reported success with its use.
The Gillespie still is of the recirculating type and employs a Cottrell pump to carry an intimate mixture of vapor and liquid from the boiling chamber (reboiler) to the disengagement chamber. After disengaging, the liquid flows past a sampling port and back into the reboiler. The vapor is totally condensed in an external condenser, flows past a sampling port, and is mixed with the returning liquid phase before entering the reboiler. This mixing eliminates concentration gradients in the reboiler.

The sample ports are simply small openings covered with rubber hypodermic bottle caps, through which samples can be drawn with a hypodermic syringe. This sampling technique reduces sample hold-up to a minimum and allows a small charge to be used in the still.

The Cottrell pump and disengagement chamber were coated with insulation to minimize the possibility of partial condensation of the vapors.

Temperature Measurement

The temperature of the equilibrium mixture was measured in the disengagement zone using an ASTM Petrolatum melting point thermometer, 79 mm immersion, 32-127°C, with 0.2°C divisions. The thermometer was read to the nearest 0.05°C with an expected precision of 0.03°C. The thermometer was standardized by measuring the boiling points of the following substances:
<table>
<thead>
<tr>
<th>Substance</th>
<th>Temperature, °C</th>
<th>Pressure, mm Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>Measured 99.15</td>
<td>Accepted Value 99.17</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>68.75</td>
<td>68.74 (49)</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>100.95</td>
<td>100.934 (38)</td>
</tr>
<tr>
<td>Toluene</td>
<td>110.65</td>
<td>110.625 (49)</td>
</tr>
</tbody>
</table>

The boiling point of water was measured in a hypsometer without pressure regulation; the accepted boiling point was read from an NBS calibrated thermometer. The hydrocarbon boiling points were measured in the equilibrium still, with pressure regulated at 760 mm Hg. From the above measurements, the thermometer was assumed to be sufficiently accurate for this investigation. A reasonable estimation of the accuracy of temperature measurements is ± 0.1 °C.

Pressure Control

Pressure on the system was maintained at 760 ± 0.5 mm Hg by use of a nitrogen cap and dip-tube arrangement. A slow bleed of nitrogen was continuously fed to the system at the condenser.

The pressure imposed by the nitrogen was regulated with a dip-tube similar to that used by Steinhauser (55). A dip-tube is simply a piece of glass tubing attached to the system which may be immersed to a variable level in a water reservoir. When the pressure in the system is sufficiently high to overcome this head of water, the nitrogen bleeds from the dip-tube and the pressure on the system remains constant. This regulation method required changes in the dip-tube level with barometric changes.

Sampling
Sampling was done with two 0.25 cc hypodermic syringes. Samples were taken by insertion of the syringes in the sample ports.

Analysis of Samples

All samples were analyzed using a four-place American Optical refractometer on which readings can be made to four decimal places (X.XXXX). The readings were reproducible to ± 0.0002. The refractometer plates were maintained at 25.00 ± 0.05°C using a water bath with an Arthur S. LaPine and Company "Tecam" temperature regulator.

Stopcock Lubricant

Both stopcocks were lubricated with "Non-Aq" stopcock lubricant, which is hydrocarbon insoluble.

Heat Input

Heat was supplied to the reboiler by a Glas-Col heating mantle and controlled by a Variac.

Chemicals

The chemicals employed were research grade hydrocarbons from Phillips Petroleum Company. The manufacturers specifications were:

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Purity, Mole %</th>
<th>Major Impurity</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>99.96</td>
<td>Methylcyclopentane</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>99.72</td>
<td>Toluene</td>
</tr>
<tr>
<td>Toluene</td>
<td>99.96</td>
<td>2,2,4 Trimethyl-pentene-2</td>
</tr>
</tbody>
</table>
No further purification of the hydrocarbons was attempted.

Experimental Procedure

Prior to the equilibria investigation, the relationship between composition and refractive index for the binaries was established. This was done by making up known mixtures and determining their refractive indices. The known samples were prepared in 2 cc hypodermic vials using analytical balances to determine the weight of each component in the vials. The refractive index of each sample was determined twice to insure accuracy. From the weight fractions, mole fractions were calculated, and the composition-refractive index relation was established. Table IV and Figure 6 present these relations.

Operation of the Still

Prior to charging the still, the nitrogen bleed was opened and the dip-tube was set such that the pressure on the system was 760 mm Hg. The ambient pressure was read from an accurate barometer and the difference between the ambient pressure and 760 mm Hg was imposed on the system using the dip-tube and a manometer attached to the system.

The system was then closed, evacuated, and filled through a sample port, using a 10 cc syringe. Approximately 110-115 cc of a pure component was charged to begin a run. Heat was then supplied to the system, and the condenser was turned on. When the pressure in the still neared 760 mm Hg, the nitrogen bleed was opened. The heat was then adjusted so that a ring of reflux
was maintained in the condenser. Care was taken to see that the reflux never entered the nitrogen exit line, i.e., a nitrogen cap was maintained above the vapors in the condenser.

The still containing the pure first component was allowed to run for approximately one hour with the pressure checked at 15 minute intervals. At the end of the hour, the boiling point of the pure component was read, a measured quantity of the charge removed from the still, and an equal quantity of the second component added. The still was again allowed to operate for one hour as before, then 0.05 cc samples were withdrawn from vapor and liquid sample ports and analyzed. Operation was allowed to continue for another 20 minutes, and duplicate samples were taken and analyzed. If for some reason the analyses of the second samples did not agree with the first to within the accuracy of the refractometer, another 20 minute period was allowed and a third set of samples was taken.

When agreement between samples was found (almost always from the first two samples), a measured quantity of the mixture was removed from the still and replaced by an equal amount of the second component. This procedure was repeated until the liquid sample became an almost equimolar mixture. The still was then shut down, cleaned, recharged with the pure second component, and the above procedure repeated, adding the first component to the still as samples were removed. Operations were again stopped when the liquid sample became approximately equimolar.

Sample analysis by refractometry was very rapid. After sampling, the samples were transferred directly from the syringe
to the refractometer. Between samples, the refractometer plates were wiped dry, rinsed with acetone, wiped again, and allowed to dry.

Operation of the still was quite sensitive to the amount of sample charged. The optimum point for smooth operation seemed to occur when the height of condensed vapor in the vapor return leg was midway between the bottom of the condenser cold finger and the top of the stopcock at the base of the condenser. At lower charges, considerable pulsing in the return legs occurred, and with charges less than 70 cc, the Cottrell pump ceased to function properly (liquid ceased to be pumped up the tube).

Satisfactory operation was obtained over a wide range of vapor flow rates. Although no quantitative measurement of flow rates was made, the rate at which condensate dripped from the cold finger gave a qualitative estimate of the vapor rate. A trial run on the normal hexane-benzene system showed no effect of flow rate on the vapor or liquid compositions over the range tested. In actual operations, the heat input was adjusted to give a moderate rate of vapor flow (about 30 drops per minute from the cold finger).

In all systems studied, the temperature reached steady-state in approximately 15 minutes. Drehman found that equilibrium was reached within 30 minutes for the six-carbon-hydrocarbons of his study, but the author allowed one hour for safety.
The first system run was normal hexane-benzene. Drehman had previously investigated this system, and the author used the system to check his operating technique. The x-y data of Drehman and of this work are presented in Figure 7 for the normal hexane-benzene system. The author's data agree with the data of Drehman to within experimental limits; the benzene-rich half of the binary was not investigated by the author. Temperature measurements, not included here, also agreed with those of Drehman. From these data, the author concluded that his pressure control, temperature measurement, and operational technique were satisfactory.

The binary systems of interest were investigated next. The order of investigation was normal hexane-methylcyclohexane, normal hexane-toluene, and methylcyclohexane (MCH)-toluene. The experimental results are presented in Tables V, VI, and VII, and Figures 8, 9, 10, and 11.
<table>
<thead>
<tr>
<th>Mol % n-Hexane</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.4202</td>
</tr>
<tr>
<td>5.0</td>
<td>1.4180</td>
</tr>
<tr>
<td>14.1</td>
<td>1.4138</td>
</tr>
<tr>
<td>24.3</td>
<td>1.4087</td>
</tr>
<tr>
<td>34.4</td>
<td>1.4039</td>
</tr>
<tr>
<td>44.6</td>
<td>1.3988</td>
</tr>
<tr>
<td>54.0</td>
<td>1.3947</td>
</tr>
<tr>
<td>66.8</td>
<td>1.3880</td>
</tr>
<tr>
<td>74.9</td>
<td>1.3842</td>
</tr>
<tr>
<td>84.5</td>
<td>1.3798</td>
</tr>
<tr>
<td>91.2</td>
<td>1.3761</td>
</tr>
<tr>
<td>100.0</td>
<td>1.3719</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mol % n-Hexane</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.4938</td>
</tr>
<tr>
<td>6.0</td>
<td>1.4850</td>
</tr>
<tr>
<td>11.9</td>
<td>1.4762</td>
</tr>
<tr>
<td>21.5</td>
<td>1.4630</td>
</tr>
<tr>
<td>29.7</td>
<td>1.4519</td>
</tr>
<tr>
<td>40.9</td>
<td>1.4374</td>
</tr>
<tr>
<td>51.9</td>
<td>1.4236</td>
</tr>
<tr>
<td>59.5</td>
<td>1.4150</td>
</tr>
<tr>
<td>71.9</td>
<td>1.4008</td>
</tr>
<tr>
<td>80.7</td>
<td>1.3913</td>
</tr>
<tr>
<td>90.7</td>
<td>1.3812</td>
</tr>
<tr>
<td>100.0</td>
<td>1.3720</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mol % MCH</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.4938</td>
</tr>
<tr>
<td>5.2</td>
<td>1.4890</td>
</tr>
<tr>
<td>13.9</td>
<td>1.4810</td>
</tr>
<tr>
<td>22.7</td>
<td>1.4731</td>
</tr>
<tr>
<td>30.3</td>
<td>1.4670</td>
</tr>
<tr>
<td>39.2</td>
<td>1.4597</td>
</tr>
<tr>
<td>50.1</td>
<td>1.4516</td>
</tr>
<tr>
<td>58.6</td>
<td>1.4457</td>
</tr>
<tr>
<td>68.9</td>
<td>1.4385</td>
</tr>
<tr>
<td>84.1</td>
<td>1.4291</td>
</tr>
<tr>
<td>91.8</td>
<td>1.4249</td>
</tr>
<tr>
<td>100.0</td>
<td>1.4202</td>
</tr>
</tbody>
</table>
### TABLE V

**VAPOR-LIQUID EQUILIBRIA DATA:**

**SYSTEM:** n-HEXANE-METHYLCYCLOHEXANE

**AT ONE ATMOSPHERE PRESSURE**

<table>
<thead>
<tr>
<th>T, °C</th>
<th>Mol % n-Hexane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Liquid</td>
</tr>
<tr>
<td>68.75</td>
<td>100.0</td>
</tr>
<tr>
<td>68.90</td>
<td>99.2</td>
</tr>
<tr>
<td>69.05</td>
<td>97.9</td>
</tr>
<tr>
<td>69.25</td>
<td>97.5</td>
</tr>
<tr>
<td>69.40</td>
<td>96.4</td>
</tr>
<tr>
<td>69.65</td>
<td>95.5</td>
</tr>
<tr>
<td>70.10</td>
<td>93.6</td>
</tr>
<tr>
<td>70.80</td>
<td>89.8</td>
</tr>
<tr>
<td>71.50</td>
<td>86.7</td>
</tr>
<tr>
<td>72.45</td>
<td>82.5</td>
</tr>
<tr>
<td>73.95</td>
<td>76.0</td>
</tr>
<tr>
<td>75.85</td>
<td>68.6</td>
</tr>
<tr>
<td>78.20</td>
<td>59.1</td>
</tr>
<tr>
<td>79.40</td>
<td>54.9</td>
</tr>
<tr>
<td>81.60</td>
<td>47.8</td>
</tr>
<tr>
<td>83.35</td>
<td>42.2</td>
</tr>
<tr>
<td>85.70</td>
<td>36.5</td>
</tr>
<tr>
<td>87.25</td>
<td>31.4</td>
</tr>
<tr>
<td>89.15</td>
<td>26.4</td>
</tr>
<tr>
<td>91.15</td>
<td>21.4</td>
</tr>
<tr>
<td>93.20</td>
<td>16.3</td>
</tr>
<tr>
<td>95.60</td>
<td>11.4</td>
</tr>
<tr>
<td>98.10</td>
<td>5.5</td>
</tr>
<tr>
<td>99.70</td>
<td>2.3</td>
</tr>
<tr>
<td>100.95</td>
<td>0.0</td>
</tr>
</tbody>
</table>
TABLE VI

VAPOR-LIQUID EQUILIBRIA DATA:

SYSTEM: n-HEXANE-TOLUENE

AT ONE ATMOSPHERE PRESSURE

<table>
<thead>
<tr>
<th>T, °C</th>
<th>Mol % n-Hexane Liquid</th>
<th>Mol % n-Hexane Vapor</th>
</tr>
</thead>
<tbody>
<tr>
<td>68.75</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>69.60</td>
<td>95.8</td>
<td>97.9</td>
</tr>
<tr>
<td>70.80</td>
<td>90.2</td>
<td>95.8</td>
</tr>
<tr>
<td>71.80</td>
<td>85.5</td>
<td>94.6</td>
</tr>
<tr>
<td>72.85</td>
<td>80.9</td>
<td>92.3</td>
</tr>
<tr>
<td>73.85</td>
<td>76.4</td>
<td>91.2</td>
</tr>
<tr>
<td>74.90</td>
<td>72.0</td>
<td>89.4</td>
</tr>
<tr>
<td>75.85</td>
<td>68.1</td>
<td>88.0</td>
</tr>
<tr>
<td>76.95</td>
<td>64.6</td>
<td>85.0</td>
</tr>
<tr>
<td>78.95</td>
<td>59.2</td>
<td>83.4</td>
</tr>
<tr>
<td>79.75</td>
<td>54.1</td>
<td>80.2</td>
</tr>
<tr>
<td>80.65</td>
<td>51.0</td>
<td>79.2</td>
</tr>
<tr>
<td>81.00</td>
<td>50.0</td>
<td>78.4</td>
</tr>
<tr>
<td>82.40</td>
<td>46.2</td>
<td>76.4</td>
</tr>
<tr>
<td>84.00</td>
<td>41.6</td>
<td>73.7</td>
</tr>
<tr>
<td>85.80</td>
<td>37.2</td>
<td>69.6</td>
</tr>
<tr>
<td>86.85</td>
<td>34.5</td>
<td>67.2</td>
</tr>
<tr>
<td>88.95</td>
<td>29.6</td>
<td>62.8</td>
</tr>
<tr>
<td>91.25</td>
<td>25.2</td>
<td>58.4</td>
</tr>
<tr>
<td>93.90</td>
<td>20.6</td>
<td>52.8</td>
</tr>
<tr>
<td>96.80</td>
<td>15.7</td>
<td>46.1</td>
</tr>
<tr>
<td>100.30</td>
<td>11.0</td>
<td>36.4</td>
</tr>
<tr>
<td>105.05</td>
<td>5.4</td>
<td>20.0</td>
</tr>
<tr>
<td>109.25</td>
<td>1.4</td>
<td>5.5</td>
</tr>
<tr>
<td>110.65</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
TABLE VII

VAPOR-LIQUID EQUILIBRIA DATA:

SYSTEM: METHYLCYCLOHEXANE-TOLUENE

AT ONE ATMOSPHERE PRESSURE

<table>
<thead>
<tr>
<th>T, °C</th>
<th>Mol % Methylcyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Liquid</td>
</tr>
<tr>
<td>100.95</td>
<td>100.0</td>
</tr>
<tr>
<td>101.20</td>
<td>94.7</td>
</tr>
<tr>
<td>101.35</td>
<td>89.9</td>
</tr>
<tr>
<td>101.50</td>
<td>85.3</td>
</tr>
<tr>
<td>101.70</td>
<td>80.8</td>
</tr>
<tr>
<td>101.90</td>
<td>75.9</td>
</tr>
<tr>
<td>102.15</td>
<td>71.2</td>
</tr>
<tr>
<td>102.40</td>
<td>66.0</td>
</tr>
<tr>
<td>102.80</td>
<td>61.9</td>
</tr>
<tr>
<td>103.15</td>
<td>56.8</td>
</tr>
<tr>
<td>103.50</td>
<td>52.3</td>
</tr>
<tr>
<td>104.20</td>
<td>42.4</td>
</tr>
<tr>
<td>104.75</td>
<td>32.0</td>
</tr>
<tr>
<td>105.35</td>
<td>32.4</td>
</tr>
<tr>
<td>105.80</td>
<td>28.6</td>
</tr>
<tr>
<td>106.35</td>
<td>24.2</td>
</tr>
<tr>
<td>107.00</td>
<td>20.2</td>
</tr>
<tr>
<td>107.70</td>
<td>15.8</td>
</tr>
<tr>
<td>108.55</td>
<td>10.7</td>
</tr>
<tr>
<td>109.90</td>
<td>3.6</td>
</tr>
<tr>
<td>110.65</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Figure 5

Modified Gillespie Vapor-Liquid Equilibrium Still
Figure 6

Binary Composition-Refractive Index Relations

Mol Fraction More Volatile Component
Pressure = 760 mm Hg

Figure 7

x-y Data for n-Hexane-Benzene System
Pressure = 760 ± 0.5 mm Hg

Figure 8

x-y Data for n-Hexane-Methylcyclohexane System
Pressure = 760 ± 0.5 mm Hg

Figure 9

x-y Data for n-Hexane-Toluene System
Figure 10

x-y Data for Methylcyclohexane-Toluene System

Pressure = 760 ± 0.5 mm Hg
Pressure = 760 ± 0.5 mm Hg

Figure 11
T-x Relations for Binary Equilibria Data
CHAPTER V

DISCUSSION OF RESULTS

In their surveys of the literature, both Huang and the author found only a single reference to data on each of the systems normal hexane-MCH (37), normal hexane-toluene (54), and MCH-toluene (44) at atmospheric pressure. Huang had checked each of these sets of data using Herington's test with activity coefficients defined as in Equation II-44. Huang found all these data to be thermodynamically inconsistent; the author rechecked the data by the same method, reached the same conclusions, and experimentally redetermined the vapor-liquid equilibria relations for these systems as described in Chapter IV. The new data passed Herington's test in each case.

Shortly after demonstrating the consistency of the new data (via Herington's test), the author read a statement by Sukkar (56) that one of the main causes for apparent inconsistencies in experimental data is the failure to correct the activity coefficients for vapor non-ideality. A review of the subject of thermodynamic consistency was then begun (as described in Chapters II and III), and Herington's test was reapplied with corrections for vapor non-ideality.

Using the corrected $\gamma$ values, the literature data on all three binaries passed Herington's test, while only the MCH-
toluene data of this work passed. Table VIII presents a résumé of Herington's test as applied to the systems of interest. However, further study revealed that Herington's test is not a suitable method for testing isobaric data in general. Each of the binary systems studied will now be discussed separately.

At the beginning of this study, only one set of literature data on MCH-toluene (44) was known to the author. However, in the course of a literature review of thermodynamic consistency, the author found two additional sets of data on the system. One set was determined by Garner and Hall (20) as part of their study of the ternary system MCH-toluene-furfural; another set was presented by Thijssen (57) in his paper on thermodynamic evaluation of binary data.

Thijssen tested both his data and that of Quiggle and Fenske using Equation III-25. He presented a figure containing a heat of mixing term for the MCH-toluene system without any reference to the source of the heat of mixing data. (The author was unable to find such data on any of the systems studied.) Using this rigorous test, Thijssen found the data of Quiggle and Fenske to be inconsistent and his own data to be consistent. The data presented by Thijssen were x-y only; he employed the T-x data of Quiggle and Fenske.

A comparison of all four sets of data on MCH-toluene is presented in Table IX. The data of Garner and Hall, Thijssen, and this work are in agreement to within the limits of experimental error. The x-y data of Quiggle and Fenske differ in several instances from the data of the other investigators by
an amount greater than the experimental errors.

The heat of mixing data from Thijsen were used to show that the data on MCH-toluene from this study are consistent, as shown in Table X and Figure 12. The data of all investigators of the MCH-toluene system, with the exception of the data of Quiggle and Fenske, are probably equally suitable from a practical standpoint.

Activity coefficient-composition relations for the MCH-toluene system are presented in Tables X, XI, and XII, and Figures 13 and 14 (the method of calculating the activity coefficients is discussed later). Note that the data of Quiggle and Fenske give rather "wavy" curves, while the other data yield smooth curves. Since Thijsen did not present T-x data, activity coefficients were not determined from his data. The MCH-toluene system exhibits moderate derivations from ideality (\(Y = 1.0\)).

The data of Myers (37) and of this work on the system normal hexane-MCH are compared in Table XIII. In the MCH-rich composition range of the system, both the x-y and T-x data of the two investigators differ by more than the expected experimental errors. Activity coefficient-composition relations for the system are presented in Tables XIV, and XV, and Figures 15 and 16. This system was the most nearly ideal of the three binaries studied.

Since no heat of mixing data were available on the normal-hexane-MCH system, no meaningful test for thermodynamic consistency could be employed to discriminate between the two sets of data. Some statements in favor of each set of data may be made.
Since the data of this work on the MCH-toluene system were found to be thermodynamically consistent, inconsistency of data on the other two binaries investigated in this work, being not too dissimilar in nature from the MCH-toluene system, would seem unlikely. However, the activity coefficients determined from the data of this work for the normal hexane-MCH system seem somewhat "unusual". The deviations of the MCH \( \gamma \) values from unity in both the positive and negative directions are uncommon; the author has not previously seen such trends in literature data on other hydrocarbon systems. This trend is much less pronounced in the data of Myers. However, such intuitive considerations cannot be regarded as sufficient grounds for selecting one set of data over another. No definite conclusion as to the superiority (or even consistency) of one of the sets of normal-hexane-MCH data is possible from the available information.

For the normal hexane-toluene data, Table XVI shows that the T-x data of Seig and of this work agree to within experimental limits. However, in the toluene-rich composition range, the x-y data of the investigators do not agree. As in the case for normal hexane-MCH, no definite conclusions may be drawn regarding which, if either, of the sets of data on normal hexane-toluene are consistent. No preference between the data is indicated. The same points may be made concerning these data as were made for the normal hexane-MCH data. The activity coefficient-composition relations (Tables XVII and XVIII, and Figures 17 and 18) again reveal that the \( \gamma \) for the heavier component exhibits both positive and negative deviations from unity when the
data of this work are employed. Of the three binaries studied, this system gave the largest deviations from unity for the activity coefficients.

Some explanation of the methods used to calculate the activity coefficients for the above binary systems seems advisable. All $x$ and $y$ values were read from visually smoothed $x$-$y$ plots prepared by the author, except for the data of Quiggle and Fenske, who presented only smoothed values. Equation III-60 was used to calculate the activity coefficients. The data employed for calculating the $Z$ factors (see Equation III-61) were as follows.

1. Vapor pressures - from API 44 (49) for both normal hexane and toluene.

2. Virial coefficients - from the Berthelot (27) equation for normal hexane and Wohl's (20) equation for toluene. These equations were used since they agreed with experimentally determined virial coefficients for normal hexane (33) and toluene (4) at their normal boiling points with less than 1% error.

3. Liquid volumes - from ICT (31) for both normal hexane and toluene.

The $Z$ factors for MCH were estimated from a nomograph by Scheibel (53). This was done since no experimental data on virial coefficients for MCH were found; also, the Scheibel method gave $Z$ factors for normal hexane and toluene which agreed with those from Equation II-60 to within 1%.
The Z factors for the components of interest are shown in Table XIX and Figure 19. Estimation of the accuracy of the Z factors is difficult since the accuracy of each of the individual terms comprising Z must be determined. The accuracy of these terms, particularly virial coefficients, is hard to access. Over the range of this study, the Z factors are probably accurate to about 1 or 2%.

The accuracy of the γ values is a function of the composition of the mixture. Since errors in analysis of samples are usually absolute rather than percentage errors, the percent error increases in dilute regions. For this reason, no weight was given to activity coefficients in composition ranges where \( x_i \leq 0.1 \) in constructing the γ-x plots. The accuracy of the γ-x plots is no better than ± 2% in the middle concentration ranges.

One original goal of this thesis was to re-evaluate, in the light of consistent binary data, the conclusions of Huang concerning Wohl's prediction method for ternary data. Such a re-evaluation now seems unadvisable for reasons which follow.

First, consistency of the ternary data and two of the sets of binary data has not been demonstrated. For the ternary data, Huang devised a new test for consistency. His test involved assuming that the van Laar equation could be applied to ternary data by combining two of the components to form a pseudo-component, giving a pseudo-binary mixture. The ternary experimental data were fitted to this van Laar type equation and then tested for consistency using a Redlich-Kister type test. Such a test has no value since the van Laar equation always satisfies the Redlich-
Kister equation. Also, the Redlich-Kister test is not applicable to the system under study.

Second, Huang's data were not taken at one atmosphere, but at pressures ranging from 739 to 745 mm Hg. He also used sample charges as small as 35 cc. The author found that even at considerably higher charges the Cottrell pump did not function, only vapor ascending the Cottrell tube.

In view of these factors, the author feels that no further investigations based on the data of Huang are merited until thermodynamic consistency of the data has been demonstrated. The same statement applies to the binary data of this work on the systems normal hexane-MCH and normal hexane-toluene.
### TABLE VIII

RESULTS OF HERINGTON'S TEST FOR CONSISTENCY OF BINARY DATA

<table>
<thead>
<tr>
<th>System</th>
<th>Author</th>
<th>Activity Coefficient Used</th>
<th>I</th>
<th>$\sum'$</th>
<th>$\theta_0$</th>
<th>$T_i^0$</th>
<th>D</th>
<th>J</th>
<th>D-J</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane-</td>
<td>Robinson</td>
<td>$Y'$</td>
<td>-0.0099</td>
<td>0.0465</td>
<td>32.2</td>
<td>341.9</td>
<td>21.3</td>
<td>14.1</td>
<td>7.2</td>
</tr>
<tr>
<td>MCH</td>
<td></td>
<td></td>
<td>0.0156</td>
<td>0.0300</td>
<td>32.2</td>
<td>341.9</td>
<td>52.0</td>
<td>14.1</td>
<td>37.9*</td>
</tr>
<tr>
<td>Myers</td>
<td></td>
<td>$Y'$</td>
<td>-0.0153</td>
<td>0.0189</td>
<td>32.2</td>
<td>341.9</td>
<td>80.9</td>
<td>14.1</td>
<td>66.8*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-0.0012</td>
<td>0.0209</td>
<td>32.2</td>
<td>341.9</td>
<td>5.7</td>
<td>14.1</td>
<td>-8.4</td>
</tr>
<tr>
<td>n-Hexane-</td>
<td>Robinson</td>
<td>$Y'$</td>
<td>-0.0044</td>
<td>0.0814</td>
<td>41.9</td>
<td>341.9</td>
<td>5.4</td>
<td>18.4</td>
<td>-13.0</td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
<td></td>
<td>0.0248</td>
<td>0.0832</td>
<td>41.9</td>
<td>341.9</td>
<td>29.8</td>
<td>18.4</td>
<td>11.4*</td>
</tr>
<tr>
<td>Sieg</td>
<td></td>
<td>$Y'$</td>
<td>-0.0295</td>
<td>0.0775</td>
<td>41.9</td>
<td>341.9</td>
<td>38.1</td>
<td>18.4</td>
<td>19.7*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-0.0078</td>
<td>0.0754</td>
<td>41.9</td>
<td>341.9</td>
<td>10.4</td>
<td>18.4</td>
<td>-8.1</td>
</tr>
<tr>
<td>MCH-</td>
<td>Robinson</td>
<td>$Y'$</td>
<td>-0.0020</td>
<td>0.0504</td>
<td>9.7</td>
<td>374.1</td>
<td>4.0</td>
<td>3.9</td>
<td>0.1</td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
<td></td>
<td>0.0026</td>
<td>0.0514</td>
<td>9.7</td>
<td>374.1</td>
<td>5.1</td>
<td>3.9</td>
<td>1.2</td>
</tr>
<tr>
<td>Quiggle &amp;</td>
<td></td>
<td>$Y'$</td>
<td>-0.0104</td>
<td>0.0484</td>
<td>9.7</td>
<td>374.1</td>
<td>21.5</td>
<td>3.9</td>
<td>17.6*</td>
</tr>
<tr>
<td>Fenske</td>
<td></td>
<td></td>
<td>-0.0068</td>
<td>0.0498</td>
<td>9.7</td>
<td>374.1</td>
<td>13.7</td>
<td>3.9</td>
<td>9.7</td>
</tr>
<tr>
<td>Garner &amp;</td>
<td></td>
<td></td>
<td>0.0000</td>
<td>0.049</td>
<td>9.7</td>
<td>374.1</td>
<td>0.0</td>
<td>3.9</td>
<td>3.9</td>
</tr>
<tr>
<td>Hall</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Indicates inconsistent data according to Herington's test.
### Table IX

**Comparison of Experimental Data on MCH-Toluene System**

#### Comparison of x-y Data

<table>
<thead>
<tr>
<th>$x_{MCH}$</th>
<th>Difference in $y_{MCH}$ Values Among Investigators</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R-Q*</td>
</tr>
<tr>
<td>0.1</td>
<td>0.004</td>
</tr>
<tr>
<td>0.2</td>
<td>0.002</td>
</tr>
<tr>
<td>0.3</td>
<td>0.003</td>
</tr>
<tr>
<td>0.4</td>
<td>0.008</td>
</tr>
<tr>
<td>0.5</td>
<td>0.007</td>
</tr>
<tr>
<td>0.6</td>
<td>0.003</td>
</tr>
<tr>
<td>0.7</td>
<td>-0.002</td>
</tr>
<tr>
<td>0.8</td>
<td>0.004</td>
</tr>
<tr>
<td>0.9</td>
<td>0.003</td>
</tr>
</tbody>
</table>

#### Comparison of T-x Data**

<table>
<thead>
<tr>
<th>$x_{MCH}$</th>
<th>Difference in Temperature Values Among Investigators, °C</th>
<th>R-Q</th>
<th>R-G</th>
<th>Q-G</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.2</td>
<td>0.15</td>
<td>-0.05</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.15</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.05</td>
<td>0.00</td>
<td>-0.05</td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>0.15</td>
<td>0.10</td>
<td>-0.05</td>
<td></td>
</tr>
<tr>
<td>0.7</td>
<td>0.10</td>
<td>0.05</td>
<td>-0.05</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>0.10</td>
<td>0.15</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>0.9</td>
<td>0.15</td>
<td>0.15</td>
<td>0.00</td>
<td></td>
</tr>
</tbody>
</table>

#### Estimated Accuracy of Data by Investigators

<table>
<thead>
<tr>
<th>Investigator</th>
<th>x-y Data</th>
<th>T, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>± 0.002</td>
<td>± 0.1</td>
</tr>
<tr>
<td>Q</td>
<td>± 0.002</td>
<td>± 0.1</td>
</tr>
<tr>
<td>T</td>
<td>No estimate</td>
<td>-----</td>
</tr>
<tr>
<td>G</td>
<td>No estimate</td>
<td>± 0.2</td>
</tr>
</tbody>
</table>

* R = Robinson; Q = Quiggle & Fenske; T = Thijssen; G = Garner and Hall

** Thijssen did not present T-x data.
## TABLE X: TEST FOR CONSISTENCY OF DATA ON MCH-TOLUENE SYSTEM AT ONE ATMOSPHERE
(Data of This Work)

<table>
<thead>
<tr>
<th>T, °C</th>
<th>Mol % MCH</th>
<th>Y_M</th>
<th>Y_T</th>
<th>Z_M</th>
<th>Z_T</th>
<th>Y_M</th>
<th>Y_T</th>
<th>log (Y_M/Y_T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>109.65</td>
<td>5.0</td>
<td>7.7</td>
<td>1.212</td>
<td>0.999</td>
<td>1.013</td>
<td>0.998</td>
<td>1.228</td>
<td>0.997</td>
</tr>
<tr>
<td>108.75</td>
<td>10.0</td>
<td>14.7</td>
<td>1.187</td>
<td>1.000</td>
<td>1.012</td>
<td>0.997</td>
<td>1.201</td>
<td>0.997</td>
</tr>
<tr>
<td>107.85</td>
<td>15.0</td>
<td>21.3</td>
<td>1.174</td>
<td>1.002</td>
<td>1.010</td>
<td>0.996</td>
<td>1.186</td>
<td>0.998</td>
</tr>
<tr>
<td>107.05</td>
<td>20.0</td>
<td>27.2</td>
<td>1.150</td>
<td>1.007</td>
<td>1.009</td>
<td>0.995</td>
<td>1.160</td>
<td>1.002</td>
</tr>
<tr>
<td>106.25</td>
<td>25.0</td>
<td>32.9</td>
<td>1.136</td>
<td>1.014</td>
<td>1.008</td>
<td>0.994</td>
<td>1.145</td>
<td>1.008</td>
</tr>
<tr>
<td>105.60</td>
<td>30.0</td>
<td>38.1</td>
<td>1.116</td>
<td>1.022</td>
<td>1.007</td>
<td>0.993</td>
<td>1.124</td>
<td>1.015</td>
</tr>
<tr>
<td>105.00</td>
<td>35.0</td>
<td>43.1</td>
<td>1.100</td>
<td>1.030</td>
<td>1.006</td>
<td>0.992</td>
<td>1.107</td>
<td>1.022</td>
</tr>
<tr>
<td>104.50</td>
<td>40.0</td>
<td>47.8</td>
<td>1.082</td>
<td>1.038</td>
<td>1.005</td>
<td>0.992</td>
<td>1.087</td>
<td>1.030</td>
</tr>
<tr>
<td>104.05</td>
<td>45.0</td>
<td>52.4</td>
<td>1.067</td>
<td>1.046</td>
<td>1.005</td>
<td>0.991</td>
<td>1.072</td>
<td>1.037</td>
</tr>
<tr>
<td>103.60</td>
<td>50.0</td>
<td>56.7</td>
<td>1.052</td>
<td>1.061</td>
<td>1.004</td>
<td>0.991</td>
<td>1.056</td>
<td>1.051</td>
</tr>
<tr>
<td>103.25</td>
<td>55.0</td>
<td>61.1</td>
<td>1.041</td>
<td>1.070</td>
<td>1.004</td>
<td>0.990</td>
<td>1.045</td>
<td>1.059</td>
</tr>
<tr>
<td>102.90</td>
<td>60.0</td>
<td>65.3</td>
<td>1.030</td>
<td>1.085</td>
<td>1.003</td>
<td>0.990</td>
<td>1.033</td>
<td>1.074</td>
</tr>
<tr>
<td>102.55</td>
<td>65.0</td>
<td>69.3</td>
<td>1.019</td>
<td>1.108</td>
<td>1.002</td>
<td>0.989</td>
<td>1.021</td>
<td>1.096</td>
</tr>
<tr>
<td>102.25</td>
<td>70.0</td>
<td>73.5</td>
<td>1.011</td>
<td>1.126</td>
<td>1.002</td>
<td>0.989</td>
<td>1.013</td>
<td>1.114</td>
</tr>
<tr>
<td>101.95</td>
<td>75.0</td>
<td>77.8</td>
<td>1.008</td>
<td>1.143</td>
<td>1.002</td>
<td>0.989</td>
<td>1.010</td>
<td>1.130</td>
</tr>
<tr>
<td>101.75</td>
<td>80.0</td>
<td>82.2</td>
<td>1.004</td>
<td>1.153</td>
<td>1.001</td>
<td>0.988</td>
<td>1.005</td>
<td>1.139</td>
</tr>
<tr>
<td>101.50</td>
<td>85.0</td>
<td>86.4</td>
<td>1.001</td>
<td>1.184</td>
<td>1.001</td>
<td>0.988</td>
<td>1.002</td>
<td>1.170</td>
</tr>
<tr>
<td>101.35</td>
<td>90.0</td>
<td>90.9</td>
<td>0.998</td>
<td>1.193</td>
<td>1.001</td>
<td>0.988</td>
<td>0.999</td>
<td>1.179</td>
</tr>
<tr>
<td>101.15</td>
<td>95.0</td>
<td>95.3</td>
<td>0.998</td>
<td>1.240</td>
<td>1.000</td>
<td>0.987</td>
<td>0.998</td>
<td>1.224</td>
</tr>
</tbody>
</table>

* Z factors are from Figure 19.

From Figure 12, \( \int_0^1 \log (Y_M/Y_T) \, dx_M = 0.0270 - 0.0244 = 0.0026 \)

Using Thijssen's heat of mixing data, from Figure 12, \( \frac{1}{2.303} \int_0^1 \left( \frac{\Delta H_{mix}^L}{RT^2} \right) \, dx_M = 0.002 \)

The two sides of Equation III-25 differ by 0.0006; the data are consistent.
TABLE XI:  ACTIVITY COEFFICIENT-COMPOSITION RELATIONS FOR MCH-TOLUENE SYSTEM

AT ONE ATMOSPHERE

(Data of Quiggle and Fenske)

<table>
<thead>
<tr>
<th>T, °C</th>
<th>Mol % MCH</th>
<th>1.152</th>
<th>0.974</th>
<th>1.013</th>
<th>0.998</th>
<th>1.167</th>
<th>0.972</th>
</tr>
</thead>
<tbody>
<tr>
<td>109.55</td>
<td>5.0</td>
<td>1.160</td>
<td>1.010</td>
<td>1.011</td>
<td>0.997</td>
<td>1.173</td>
<td>1.007</td>
</tr>
<tr>
<td>108.55</td>
<td>10.0</td>
<td>1.163</td>
<td>1.012</td>
<td>1.010</td>
<td>0.996</td>
<td>1.175</td>
<td>1.008</td>
</tr>
<tr>
<td>107.65</td>
<td>15.0</td>
<td>1.145</td>
<td>1.016</td>
<td>1.009</td>
<td>0.994</td>
<td>1.155</td>
<td>1.010</td>
</tr>
<tr>
<td>106.90</td>
<td>20.0</td>
<td>1.127</td>
<td>1.021</td>
<td>1.008</td>
<td>0.994</td>
<td>1.136</td>
<td>1.015</td>
</tr>
<tr>
<td>106.20</td>
<td>25.0</td>
<td>1.107</td>
<td>1.027</td>
<td>1.007</td>
<td>0.993</td>
<td>1.115</td>
<td>1.020</td>
</tr>
<tr>
<td>105.60</td>
<td>30.0</td>
<td>1.082</td>
<td>1.043</td>
<td>1.006</td>
<td>0.992</td>
<td>1.088</td>
<td>1.035</td>
</tr>
<tr>
<td>105.00</td>
<td>35.0</td>
<td>1.064</td>
<td>1.055</td>
<td>1.005</td>
<td>0.992</td>
<td>1.069</td>
<td>1.047</td>
</tr>
<tr>
<td>104.50</td>
<td>40.0</td>
<td>1.051</td>
<td>1.069</td>
<td>1.004</td>
<td>0.991</td>
<td>1.055</td>
<td>1.059</td>
</tr>
<tr>
<td>104.00</td>
<td>45.0</td>
<td>1.041</td>
<td>1.081</td>
<td>1.004</td>
<td>0.991</td>
<td>1.045</td>
<td>1.071</td>
</tr>
<tr>
<td>103.55</td>
<td>50.0</td>
<td>1.032</td>
<td>1.094</td>
<td>1.003</td>
<td>0.990</td>
<td>1.033</td>
<td>1.083</td>
</tr>
<tr>
<td>103.15</td>
<td>55.0</td>
<td>1.030</td>
<td>1.100</td>
<td>1.003</td>
<td>0.990</td>
<td>1.033</td>
<td>1.089</td>
</tr>
<tr>
<td>102.75</td>
<td>60.0</td>
<td>1.023</td>
<td>1.109</td>
<td>1.002</td>
<td>0.989</td>
<td>1.025</td>
<td>1.097</td>
</tr>
<tr>
<td>102.45</td>
<td>65.0</td>
<td>1.018</td>
<td>1.123</td>
<td>1.002</td>
<td>0.989</td>
<td>1.020</td>
<td>1.111</td>
</tr>
<tr>
<td>102.15</td>
<td>70.0</td>
<td>1.010</td>
<td>1.146</td>
<td>1.002</td>
<td>0.989</td>
<td>1.012</td>
<td>1.133</td>
</tr>
<tr>
<td>101.90</td>
<td>75.0</td>
<td>1.002</td>
<td>1.183</td>
<td>1.001</td>
<td>0.988</td>
<td>1.003</td>
<td>1.169</td>
</tr>
<tr>
<td>101.65</td>
<td>80.0</td>
<td>0.999</td>
<td>1.222</td>
<td>1.001</td>
<td>0.988</td>
<td>1.000</td>
<td>1.207</td>
</tr>
<tr>
<td>101.40</td>
<td>85.0</td>
<td>0.999</td>
<td>1.238</td>
<td>1.000</td>
<td>0.988</td>
<td>0.999</td>
<td>1.223</td>
</tr>
<tr>
<td>101.20</td>
<td>90.0</td>
<td>1.003</td>
<td>1.193</td>
<td>1.000</td>
<td>0.987</td>
<td>1.003</td>
<td>1.177</td>
</tr>
</tbody>
</table>

* Calculated from API 44 (49) vapor pressures.

** Z factors are from Figure 19.
<table>
<thead>
<tr>
<th>T, °C</th>
<th>Mol % MCH</th>
<th>Liquid</th>
<th>Vapor</th>
<th>$\gamma_M$</th>
<th>$\gamma_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>108.6</td>
<td>10.0</td>
<td>14.6</td>
<td></td>
<td>1.199</td>
<td>1.002</td>
</tr>
<tr>
<td>106.9</td>
<td>20.0</td>
<td>27.0</td>
<td></td>
<td>1.154</td>
<td>1.009</td>
</tr>
<tr>
<td>105.6</td>
<td>30.0</td>
<td>37.9</td>
<td></td>
<td>1.117</td>
<td>1.021</td>
</tr>
<tr>
<td>104.5</td>
<td>40.0</td>
<td>47.6</td>
<td></td>
<td>1.085</td>
<td>1.037</td>
</tr>
<tr>
<td>103.6</td>
<td>50.0</td>
<td>56.6</td>
<td></td>
<td>1.058</td>
<td>1.058</td>
</tr>
<tr>
<td>102.8</td>
<td>60.0</td>
<td>65.5</td>
<td></td>
<td>1.037</td>
<td>1.085</td>
</tr>
<tr>
<td>102.2</td>
<td>70.0</td>
<td>73.6</td>
<td></td>
<td>1.021</td>
<td>1.118</td>
</tr>
<tr>
<td>101.6</td>
<td>80.0</td>
<td>82.3</td>
<td></td>
<td>1.009</td>
<td>1.157</td>
</tr>
<tr>
<td>101.2</td>
<td>90.0</td>
<td>90.8</td>
<td></td>
<td>1.002</td>
<td>1.203</td>
</tr>
</tbody>
</table>

* All these data are from reference 20.
<table>
<thead>
<tr>
<th>x&lt;sub&gt;n&lt;/sub&gt;-Hexane</th>
<th>Difference in y&lt;sub&gt;n&lt;/sub&gt;-Hexane R-M&lt;sup&gt;*&lt;/sup&gt;</th>
<th>Difference in Temperatures R-M</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.000</td>
<td>0.45°C</td>
</tr>
<tr>
<td>0.2</td>
<td>0.012</td>
<td>0.50</td>
</tr>
<tr>
<td>0.3</td>
<td>0.022</td>
<td>0.35</td>
</tr>
<tr>
<td>0.4</td>
<td>0.018</td>
<td>0.15</td>
</tr>
<tr>
<td>0.5</td>
<td>0.009</td>
<td>0.00</td>
</tr>
<tr>
<td>0.6</td>
<td>0.002</td>
<td>0.00</td>
</tr>
<tr>
<td>0.7</td>
<td>0.004</td>
<td>0.05</td>
</tr>
<tr>
<td>0.8</td>
<td>0.000</td>
<td>0.05</td>
</tr>
<tr>
<td>0.9</td>
<td>-0.002</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Accuracy of Data as Estimated by Investigators

<table>
<thead>
<tr>
<th>Investigator</th>
<th>x-y Data</th>
<th>T, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>± 0.004</td>
<td>± 0.1</td>
</tr>
<tr>
<td>M</td>
<td>± 0.004</td>
<td>No estimate</td>
</tr>
</tbody>
</table>

* R = Robinson; M = Myers
TABLE XIV: ACTIVITY COEFFICIENT-COMPOSITION RELATIONS FOR N-HEXANE-METHYLCYCLOHEXANE SYSTEM

AT ONE ATMOSPHERE
(Data of This Work)

<table>
<thead>
<tr>
<th>T, °C</th>
<th>Mol % n-Hexane</th>
<th>Liquid</th>
<th>Vapor</th>
<th>( \gamma_H^{**} )</th>
<th>( \gamma_M^{**} )</th>
<th>( Z_H^{**} )</th>
<th>( Z_M^{**} )</th>
<th>( Y_H )</th>
<th>( Y_M )</th>
</tr>
</thead>
<tbody>
<tr>
<td>98.45</td>
<td>5.0</td>
<td>12.1</td>
<td></td>
<td>1.039</td>
<td>0.991</td>
<td>1.050</td>
<td>0.997</td>
<td>1.091</td>
<td>0.988</td>
</tr>
<tr>
<td>96.10</td>
<td>10.0</td>
<td>22.7</td>
<td></td>
<td>1.034</td>
<td>0.984</td>
<td>1.046</td>
<td>0.994</td>
<td>1.082</td>
<td>0.978</td>
</tr>
<tr>
<td>93.85</td>
<td>15.0</td>
<td>32.0</td>
<td></td>
<td>1.032</td>
<td>0.981</td>
<td>1.042</td>
<td>0.990</td>
<td>1.075</td>
<td>0.971</td>
</tr>
<tr>
<td>91.75</td>
<td>20.0</td>
<td>40.2</td>
<td></td>
<td>1.028</td>
<td>0.975</td>
<td>1.038</td>
<td>0.988</td>
<td>1.067</td>
<td>0.963</td>
</tr>
<tr>
<td>89.75</td>
<td>25.0</td>
<td>47.5</td>
<td></td>
<td>1.026</td>
<td>0.971</td>
<td>1.035</td>
<td>0.985</td>
<td>1.062</td>
<td>0.956</td>
</tr>
<tr>
<td>87.80</td>
<td>30.0</td>
<td>53.7</td>
<td></td>
<td>1.021</td>
<td>0.973</td>
<td>1.031</td>
<td>0.983</td>
<td>1.053</td>
<td>0.956</td>
</tr>
<tr>
<td>85.90</td>
<td>35.0</td>
<td>59.3</td>
<td></td>
<td>1.019</td>
<td>0.977</td>
<td>1.028</td>
<td>0.980</td>
<td>1.048</td>
<td>0.957</td>
</tr>
<tr>
<td>84.05</td>
<td>40.0</td>
<td>64.3</td>
<td></td>
<td>1.017</td>
<td>0.983</td>
<td>1.025</td>
<td>0.978</td>
<td>1.042</td>
<td>0.961</td>
</tr>
<tr>
<td>82.40</td>
<td>45.0</td>
<td>68.7</td>
<td></td>
<td>1.013</td>
<td>0.990</td>
<td>1.022</td>
<td>0.976</td>
<td>1.035</td>
<td>0.966</td>
</tr>
<tr>
<td>80.85</td>
<td>50.0</td>
<td>72.7</td>
<td></td>
<td>1.009</td>
<td>0.997</td>
<td>1.019</td>
<td>0.974</td>
<td>1.028</td>
<td>0.971</td>
</tr>
<tr>
<td>79.45</td>
<td>55.0</td>
<td>76.4</td>
<td></td>
<td>1.004</td>
<td>1.003</td>
<td>1.017</td>
<td>0.972</td>
<td>1.021</td>
<td>0.975</td>
</tr>
<tr>
<td>78.05</td>
<td>60.0</td>
<td>79.8</td>
<td></td>
<td>1.001</td>
<td>1.011</td>
<td>1.015</td>
<td>0.970</td>
<td>1.016</td>
<td>0.981</td>
</tr>
<tr>
<td>76.75</td>
<td>65.0</td>
<td>82.9</td>
<td></td>
<td>0.998</td>
<td>1.021</td>
<td>1.012</td>
<td>0.969</td>
<td>1.010</td>
<td>0.989</td>
</tr>
<tr>
<td>75.50</td>
<td>70.0</td>
<td>85.7</td>
<td></td>
<td>0.995</td>
<td>1.038</td>
<td>1.010</td>
<td>0.967</td>
<td>1.005</td>
<td>1.004</td>
</tr>
<tr>
<td>74.25</td>
<td>75.0</td>
<td>88.4</td>
<td></td>
<td>0.994</td>
<td>1.054</td>
<td>1.009</td>
<td>0.966</td>
<td>1.003</td>
<td>1.018</td>
</tr>
<tr>
<td>73.05</td>
<td>80.0</td>
<td>90.9</td>
<td></td>
<td>0.994</td>
<td>1.076</td>
<td>1.007</td>
<td>0.964</td>
<td>1.001</td>
<td>1.037</td>
</tr>
<tr>
<td>71.90</td>
<td>85.0</td>
<td>93.3</td>
<td></td>
<td>0.995</td>
<td>1.097</td>
<td>1.005</td>
<td>0.962</td>
<td>1.000</td>
<td>1.055</td>
</tr>
<tr>
<td>70.75</td>
<td>90.0</td>
<td>95.6</td>
<td></td>
<td>0.999</td>
<td>1.124</td>
<td>1.003</td>
<td>0.961</td>
<td>1.002</td>
<td>1.080</td>
</tr>
<tr>
<td>69.70</td>
<td>95.0</td>
<td>97.8</td>
<td></td>
<td>0.999</td>
<td>1.165</td>
<td>1.001</td>
<td>0.960</td>
<td>1.000</td>
<td>1.118</td>
</tr>
</tbody>
</table>

* Calculated from API 44 (49) vapor pressures.

** Z factors are from Figure 19.
TABLE XV: ACTIVITY COEFFICIENT-COMPOSITION RELATIONS FOR N-HEXANE-METHYLCYCLOHEXANE SYSTEM
AT ONE ATMOSPHERE
(Data of Myers)

<table>
<thead>
<tr>
<th>T, °C</th>
<th>Mol % n-Hexane Liquid</th>
<th>Y_H*</th>
<th>Y_M</th>
<th>Z_H*</th>
<th>Z_M</th>
<th>Y_H</th>
<th>Y_M</th>
</tr>
</thead>
<tbody>
<tr>
<td>98.3</td>
<td>5.0</td>
<td>11.3</td>
<td>1.023</td>
<td>1.000</td>
<td>1.050</td>
<td>0.997</td>
<td>1.074</td>
</tr>
<tr>
<td>95.8</td>
<td>10.0</td>
<td>21.7</td>
<td>1.019</td>
<td>1.001</td>
<td>1.045</td>
<td>0.993</td>
<td>1.065</td>
</tr>
<tr>
<td>93.5</td>
<td>15.0</td>
<td>31.2</td>
<td>1.016</td>
<td>1.003</td>
<td>1.041</td>
<td>0.990</td>
<td>1.058</td>
</tr>
<tr>
<td>91.3</td>
<td>20.0</td>
<td>39.1</td>
<td>1.012</td>
<td>1.006</td>
<td>1.037</td>
<td>0.987</td>
<td>1.049</td>
</tr>
<tr>
<td>89.3</td>
<td>25.0</td>
<td>46.0</td>
<td>1.009</td>
<td>1.010</td>
<td>1.034</td>
<td>0.985</td>
<td>1.043</td>
</tr>
<tr>
<td>87.4</td>
<td>30.0</td>
<td>52.3</td>
<td>1.006</td>
<td>1.015</td>
<td>1.030</td>
<td>0.982</td>
<td>1.035</td>
</tr>
<tr>
<td>85.6</td>
<td>35.0</td>
<td>57.9</td>
<td>1.003</td>
<td>1.020</td>
<td>1.027</td>
<td>0.980</td>
<td>1.030</td>
</tr>
<tr>
<td>83.9</td>
<td>40.0</td>
<td>62.9</td>
<td>1.000</td>
<td>1.026</td>
<td>1.024</td>
<td>0.978</td>
<td>1.024</td>
</tr>
<tr>
<td>82.3</td>
<td>45.0</td>
<td>67.6</td>
<td>0.997</td>
<td>1.032</td>
<td>1.022</td>
<td>0.976</td>
<td>1.019</td>
</tr>
<tr>
<td>80.8</td>
<td>50.0</td>
<td>71.6</td>
<td>0.995</td>
<td>1.041</td>
<td>1.019</td>
<td>0.974</td>
<td>1.013</td>
</tr>
<tr>
<td>79.4</td>
<td>55.0</td>
<td>75.3</td>
<td>0.992</td>
<td>1.051</td>
<td>1.017</td>
<td>0.972</td>
<td>1.009</td>
</tr>
<tr>
<td>78.0</td>
<td>60.0</td>
<td>78.8</td>
<td>0.990</td>
<td>1.060</td>
<td>1.015</td>
<td>0.970</td>
<td>1.005</td>
</tr>
<tr>
<td>76.7</td>
<td>65.0</td>
<td>82.0</td>
<td>0.988</td>
<td>1.070</td>
<td>1.012</td>
<td>0.968</td>
<td>1.000</td>
</tr>
<tr>
<td>75.5</td>
<td>70.0</td>
<td>85.1</td>
<td>0.987</td>
<td>1.080</td>
<td>1.010</td>
<td>0.967</td>
<td>0.997</td>
</tr>
<tr>
<td>74.3</td>
<td>75.0</td>
<td>88.0</td>
<td>0.987</td>
<td>1.090</td>
<td>1.009</td>
<td>0.966</td>
<td>0.996</td>
</tr>
<tr>
<td>73.2</td>
<td>80.0</td>
<td>90.7</td>
<td>0.988</td>
<td>1.100</td>
<td>1.007</td>
<td>0.964</td>
<td>0.995</td>
</tr>
<tr>
<td>72.0</td>
<td>85.0</td>
<td>93.2</td>
<td>0.990</td>
<td>1.111</td>
<td>1.005</td>
<td>0.963</td>
<td>0.995</td>
</tr>
<tr>
<td>70.8</td>
<td>90.0</td>
<td>95.6</td>
<td>0.997</td>
<td>1.122</td>
<td>1.003</td>
<td>0.961</td>
<td>1.000</td>
</tr>
<tr>
<td>69.7</td>
<td>95.0</td>
<td>97.9</td>
<td>1.000</td>
<td>1.133</td>
<td>1.001</td>
<td>0.960</td>
<td>1.001</td>
</tr>
</tbody>
</table>

* Calculated from API 44 (49) vapor pressures.

** Z factors are from Figure 19.
### TABLE XVI
COMPARISON OF EXPERIMENTAL DATA ON N-HEXANE-TOLUENE SYSTEM

<table>
<thead>
<tr>
<th>x_{nHexane}</th>
<th>Difference in y_{nHexane} R-S*</th>
<th>Difference in Temperatures R-S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.023</td>
<td>-0.20 °C</td>
</tr>
<tr>
<td>0.2</td>
<td>0.024</td>
<td>-0.10</td>
</tr>
<tr>
<td>0.3</td>
<td>0.020</td>
<td>-0.05</td>
</tr>
<tr>
<td>0.4</td>
<td>0.015</td>
<td>-0.05</td>
</tr>
<tr>
<td>0.5</td>
<td>0.009</td>
<td>0.00</td>
</tr>
<tr>
<td>0.6</td>
<td>0.006</td>
<td>0.20</td>
</tr>
<tr>
<td>0.7</td>
<td>0.006</td>
<td>0.45</td>
</tr>
<tr>
<td>0.8</td>
<td>0.005</td>
<td>0.50</td>
</tr>
<tr>
<td>0.9</td>
<td>0.003</td>
<td>0.35</td>
</tr>
</tbody>
</table>

**Accuracy of Data as Estimated by Investigators**

<table>
<thead>
<tr>
<th>Investigator</th>
<th>x-y Data</th>
<th>T, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>± 0.002</td>
<td>± 0.1</td>
</tr>
<tr>
<td>S</td>
<td>± 0.003</td>
<td>± 0.5</td>
</tr>
</tbody>
</table>

* R = Robinson; S = Sieg
### TABLE XVII: ACTIVITY COEFFICIENT-COMPOSITION RELATIONS FOR N-HEXANE-TOLUENE SYSTEM AT ONE ATMOSPHERE
(Data of This Work)

<table>
<thead>
<tr>
<th>T, °C</th>
<th>Mol % n-Hexane</th>
<th>$Y_{H}^{*}$</th>
<th>$Y_{T}^{*}$</th>
<th>$Z_{H}^{*}$</th>
<th>$Z_{T}$</th>
<th>$Y_{H}$</th>
<th>$Y_{T}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>105.05</td>
<td>5.0</td>
<td>18.2</td>
<td>1.312</td>
<td>0.998</td>
<td>1.062</td>
<td>0.992</td>
<td>1.393</td>
</tr>
<tr>
<td>101.05</td>
<td>10.0</td>
<td>33.0</td>
<td>1.310</td>
<td>0.984</td>
<td>1.055</td>
<td>0.988</td>
<td>1.382</td>
</tr>
<tr>
<td>97.25</td>
<td>15.0</td>
<td>43.6</td>
<td>1.286</td>
<td>0.988</td>
<td>1.048</td>
<td>0.983</td>
<td>1.348</td>
</tr>
<tr>
<td>94.10</td>
<td>20.0</td>
<td>51.5</td>
<td>1.237</td>
<td>0.994</td>
<td>1.042</td>
<td>0.980</td>
<td>1.289</td>
</tr>
<tr>
<td>91.30</td>
<td>25.0</td>
<td>57.9</td>
<td>1.199</td>
<td>1.003</td>
<td>1.037</td>
<td>0.977</td>
<td>1.243</td>
</tr>
<tr>
<td>88.90</td>
<td>30.0</td>
<td>63.2</td>
<td>1.164</td>
<td>1.015</td>
<td>1.033</td>
<td>0.974</td>
<td>1.202</td>
</tr>
<tr>
<td>86.70</td>
<td>35.0</td>
<td>67.8</td>
<td>1.139</td>
<td>1.030</td>
<td>1.029</td>
<td>0.972</td>
<td>1.172</td>
</tr>
<tr>
<td>84.65</td>
<td>40.0</td>
<td>71.8</td>
<td>1.117</td>
<td>1.046</td>
<td>1.026</td>
<td>0.970</td>
<td>1.146</td>
</tr>
<tr>
<td>82.70</td>
<td>45.0</td>
<td>75.2</td>
<td>1.100</td>
<td>1.072</td>
<td>1.022</td>
<td>0.968</td>
<td>1.124</td>
</tr>
<tr>
<td>81.00</td>
<td>50.0</td>
<td>78.3</td>
<td>1.082</td>
<td>1.094</td>
<td>1.020</td>
<td>0.966</td>
<td>1.104</td>
</tr>
<tr>
<td>79.50</td>
<td>55.0</td>
<td>81.1</td>
<td>1.065</td>
<td>1.116</td>
<td>1.017</td>
<td>0.964</td>
<td>1.083</td>
</tr>
<tr>
<td>78.10</td>
<td>60.0</td>
<td>83.6</td>
<td>1.048</td>
<td>1.143</td>
<td>1.015</td>
<td>0.963</td>
<td>1.064</td>
</tr>
<tr>
<td>76.70</td>
<td>65.0</td>
<td>86.0</td>
<td>1.037</td>
<td>1.171</td>
<td>1.013</td>
<td>0.962</td>
<td>1.050</td>
</tr>
<tr>
<td>75.45</td>
<td>70.0</td>
<td>88.2</td>
<td>1.027</td>
<td>1.203</td>
<td>1.010</td>
<td>0.960</td>
<td>1.037</td>
</tr>
<tr>
<td>74.25</td>
<td>75.0</td>
<td>90.4</td>
<td>1.017</td>
<td>1.226</td>
<td>1.008</td>
<td>0.959</td>
<td>1.025</td>
</tr>
<tr>
<td>73.10</td>
<td>80.0</td>
<td>92.5</td>
<td>1.010</td>
<td>1.247</td>
<td>1.007</td>
<td>0.958</td>
<td>1.017</td>
</tr>
<tr>
<td>71.95</td>
<td>85.0</td>
<td>94.4</td>
<td>1.006</td>
<td>1.295</td>
<td>1.005</td>
<td>0.957</td>
<td>1.011</td>
</tr>
<tr>
<td>70.90</td>
<td>90.0</td>
<td>96.3</td>
<td>1.001</td>
<td>1.333</td>
<td>1.003</td>
<td>0.956</td>
<td>1.004</td>
</tr>
<tr>
<td>69.75</td>
<td>95.0</td>
<td>98.1</td>
<td>1.001</td>
<td>1.430</td>
<td>1.002</td>
<td>0.955</td>
<td>1.003</td>
</tr>
</tbody>
</table>

* Calculated from API 44(49) vapor pressures.

** Z factors are from Figure 19.
TABLE XVIII: ACTIVITY COEFFICIENT-COMPOSITION RELATIONS FOR N-HEXANE-TOLUENE SYSTEM

AT ONE ATMOSPHERE

(Data of Sieg)

<table>
<thead>
<tr>
<th>T, °C</th>
<th>Mol % n-Hexane</th>
<th>Liquid</th>
<th>Vapor</th>
<th>( \gamma_H' )</th>
<th>( \gamma_T' )</th>
<th>( Z_H^* )</th>
<th>( Z_T^* )</th>
<th>( \gamma_H )</th>
<th>( \gamma_T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>105.5</td>
<td>5.0</td>
<td>16.6</td>
<td></td>
<td>1.258</td>
<td>1.009</td>
<td>1.063</td>
<td>0.993</td>
<td>1.337</td>
<td>1.002</td>
</tr>
<tr>
<td>101.3</td>
<td>10.0</td>
<td>30.7</td>
<td></td>
<td>1.232</td>
<td>1.018</td>
<td>1.056</td>
<td>0.988</td>
<td>1.301</td>
<td>1.016</td>
</tr>
<tr>
<td>97.5</td>
<td>15.0</td>
<td>41.1</td>
<td></td>
<td>1.207</td>
<td>1.028</td>
<td>1.048</td>
<td>0.983</td>
<td>1.265</td>
<td>1.011</td>
</tr>
<tr>
<td>94.2</td>
<td>20.0</td>
<td>49.1</td>
<td></td>
<td>1.185</td>
<td>1.039</td>
<td>1.042</td>
<td>0.980</td>
<td>1.235</td>
<td>1.018</td>
</tr>
<tr>
<td>91.3</td>
<td>25.0</td>
<td>55.8</td>
<td></td>
<td>1.161</td>
<td>1.051</td>
<td>1.037</td>
<td>0.977</td>
<td>1.204</td>
<td>1.027</td>
</tr>
<tr>
<td>88.9</td>
<td>30.0</td>
<td>61.2</td>
<td></td>
<td>1.139</td>
<td>1.065</td>
<td>1.033</td>
<td>0.974</td>
<td>1.177</td>
<td>1.037</td>
</tr>
<tr>
<td>86.8</td>
<td>35.0</td>
<td>66.1</td>
<td></td>
<td>1.119</td>
<td>1.080</td>
<td>1.029</td>
<td>0.972</td>
<td>1.151</td>
<td>1.050</td>
</tr>
<tr>
<td>84.7</td>
<td>40.0</td>
<td>70.3</td>
<td></td>
<td>1.100</td>
<td>1.096</td>
<td>1.026</td>
<td>0.970</td>
<td>1.129</td>
<td>1.063</td>
</tr>
<tr>
<td>82.8</td>
<td>45.0</td>
<td>74.1</td>
<td></td>
<td>1.082</td>
<td>1.116</td>
<td>1.023</td>
<td>0.968</td>
<td>1.107</td>
<td>1.080</td>
</tr>
<tr>
<td>81.0</td>
<td>50.0</td>
<td>77.4</td>
<td></td>
<td>1.068</td>
<td>1.140</td>
<td>1.020</td>
<td>0.966</td>
<td>1.089</td>
<td>1.101</td>
</tr>
<tr>
<td>79.3</td>
<td>55.0</td>
<td>80.3</td>
<td></td>
<td>1.055</td>
<td>1.169</td>
<td>1.016</td>
<td>0.964</td>
<td>1.072</td>
<td>1.127</td>
</tr>
<tr>
<td>77.9</td>
<td>60.0</td>
<td>83.0</td>
<td></td>
<td>1.045</td>
<td>1.200</td>
<td>1.014</td>
<td>0.963</td>
<td>1.060</td>
<td>1.156</td>
</tr>
<tr>
<td>76.4</td>
<td>65.0</td>
<td>85.3</td>
<td></td>
<td>1.037</td>
<td>1.235</td>
<td>1.012</td>
<td>0.962</td>
<td>1.049</td>
<td>1.188</td>
</tr>
<tr>
<td>75.0</td>
<td>70.0</td>
<td>87.6</td>
<td></td>
<td>1.030</td>
<td>1.269</td>
<td>1.010</td>
<td>0.960</td>
<td>1.040</td>
<td>1.218</td>
</tr>
<tr>
<td>73.8</td>
<td>75.0</td>
<td>89.9</td>
<td></td>
<td>1.023</td>
<td>1.306</td>
<td>1.008</td>
<td>0.959</td>
<td>1.031</td>
<td>1.252</td>
</tr>
<tr>
<td>72.6</td>
<td>80.0</td>
<td>92.0</td>
<td></td>
<td>1.018</td>
<td>1.344</td>
<td>1.006</td>
<td>0.958</td>
<td>1.024</td>
<td>1.288</td>
</tr>
<tr>
<td>71.6</td>
<td>85.0</td>
<td>94.1</td>
<td></td>
<td>1.012</td>
<td>1.383</td>
<td>1.004</td>
<td>0.957</td>
<td>1.016</td>
<td>1.324</td>
</tr>
<tr>
<td>70.6</td>
<td>90.0</td>
<td>96.1</td>
<td></td>
<td>1.009</td>
<td>1.423</td>
<td>1.003</td>
<td>0.956</td>
<td>1.012</td>
<td>1.360</td>
</tr>
<tr>
<td>69.6</td>
<td>95.0</td>
<td>98.0</td>
<td></td>
<td>1.005</td>
<td>1.463</td>
<td>1.001</td>
<td>0.955</td>
<td>1.006</td>
<td>1.397</td>
</tr>
</tbody>
</table>

* Calculated from API 44 (49) vapor pressures.

** Z factors are from Figure 19.
### TABLE XIX

**Z FACTORS FOR N-HEXANE, METHYLCYCLOHEXANE, AND TOLUENE**

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>100</th>
<th>110</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Vapor Pressure, mm Hg (49)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Hexane</td>
<td>790</td>
<td>1,068</td>
<td>1,418</td>
<td>1,845</td>
<td>2,305</td>
</tr>
<tr>
<td>Toluene</td>
<td>204</td>
<td>291</td>
<td>408</td>
<td>478</td>
<td>747</td>
</tr>
<tr>
<td><strong>2nd Virial Coefficient, cc/gmol</strong>*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Hexane*</td>
<td>-1,193</td>
<td>-1,120</td>
<td>-1,051</td>
<td>-992</td>
<td>-935</td>
</tr>
<tr>
<td>Toluene**</td>
<td>-1,681</td>
<td>-1,561</td>
<td>-1,455</td>
<td>-1,355</td>
<td>-1,272</td>
</tr>
<tr>
<td><strong>Liquid Molal Volume, cc/gmol</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Hexane (33)</td>
<td>140.5</td>
<td>142.9</td>
<td>145.5</td>
<td>148.0</td>
<td>150.5</td>
</tr>
<tr>
<td>Toluene (4)</td>
<td>112.4</td>
<td>113.4</td>
<td>114.7</td>
<td>116.7</td>
<td>118.5</td>
</tr>
<tr>
<td><strong>Z Factor</strong>*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Hexane**</td>
<td>1.001</td>
<td>1.020</td>
<td>1.035</td>
<td>1.055</td>
<td>1.072</td>
</tr>
<tr>
<td>Toluene***</td>
<td>0.955</td>
<td>0.965</td>
<td>0.975</td>
<td>0.984</td>
<td>0.999</td>
</tr>
<tr>
<td>MCH****</td>
<td>0.960</td>
<td>0.975</td>
<td>0.984</td>
<td>0.999</td>
<td>1.013</td>
</tr>
</tbody>
</table>

---

* From the Berthelot equation.
** From the Wohl equation.
*** Calculated using Equation II-61.
**** Estimated using Scheibel's chart (53).
System: MCH-Toluene, 1 Atm.

\[
\frac{1}{2.303} \frac{\Delta H_{mix}^L}{RT^2} \frac{dT}{dx_M} = \log \left( \frac{Y_N}{Y_T} \right)
\]

Figure 12

Graphical Integration for MCH-Toluene Consistency Test
Pressure = 760 ± 0.5 mm Hg

Figure 13

$Y' \cdot x$ Relation for MCH-Toluene System
Pressure = 760 ± 0.5 mm Hg

Liquid Activity Coefficient, \( Y = \frac{\bar{y}}{y^0} \)

Mol Fraction MCH in Liquid

Figure 14

Y-x Relation for MCH-Toluene System
Pressure = 760 ± 0.5 mm Hg

Figure 15

Y'-x Relation for n-Hexane-MCH System
Figure 16

$Y-x$ Relation for n-Hexane-MCH System

Pressure = 760 ± 0.5 mm Hg

Liquid Activity Coefficient, $Y = \frac{\tilde{Y}}{x^0}$

Mol Fraction n-Hexane in Liquid

--- This Work
--- Myers
Pressure = 760 ± 0.5 mm Hg

--- This Work
--- Sieg

Figure 17

$Y' - x$ Relation for n-Hexane-Toluene System
Pressure = 760 ± 0.5 mm Hg

This Work

Sieg

Figure 18

Y-x Relation for n-Hexane-Toluene System
Figure 19

$Z = \exp \frac{1}{RT} (B_1 - Y_1) (P - P_1)$

n-Hexane
MCH
Toluene

Temperature, °C

Z Factor for Calculating Activity Coefficients
CHAPTER VI

A CHECK ON THE APPLICABILITY OF TWO EQUATIONS OF STATE TO PREDICTION OF VAPOR-PHASE FUGACITY COEFFICIENTS

There has been a recent upsurge in attempts to predict theoretically vapor-liquid equilibria data, largely in terms of K values. In several recent studies (12, 39, 40, 43), the following equation, introduced by Prausnitz, Edmister, and Chao (43), has been the basis for the data correlation:

\[ K_i = \frac{\gamma_i^L \gamma_i^L}{\phi_i^V \phi_i^V} \]  \hspace{1cm} (VI-1)

where \( \phi_i^V \) = fugacity coefficient of component "i" in the vapor-phase mixture, \( \frac{f_i^V}{P_i^V} \).

In applying Equation VI-1, each of the above studies has made use of the Redlich-Kwong (R-K) equation of state (47) to calculate \( \phi_i^V \). None of the authors of these studies has offered proof that the equation of state is applicable in the vapor region, and only Pipkin (40) confined his attention to the case where the component in question was a gas. Redlich and Kwong presented their equation of state as being applicable only in the gas phase, i.e., at temperatures above the critical temperature.

The Benedict-Webb-Rubin (BWR) equation of state (7) has also been used to predict vapor-phase properties (8). The
use of this equation has been limited because of its rather
complex form, requiring eight empirical constants for each
component. In contrast, the R-K equation is extremely simple
in form and requires only a knowledge of the critical proper-
ties of the components. More thorough discussions of the R-K
and BWR equations may be found in Appendix B.

In view of the increasing use of these equations of state
to predict properties in the vapor region, a meaningful check
of their applicability in the vapor region was needed. The
only meaningful check that can be applied is the comparison
of properties from experimental measurements with those pre-
dicted by the equations. However, experimental data on vapor-
phase properties are extremely limited. Some data were located
which permitted the equations to be tested as follows.

Sage and his co-workers have presented experimental data
on vapor-liquid equilibria in the systems methane-propane (45),
methane-n-butane (50), and propane-n-pentane (51). Sage and
Lacey (52) have presented fugacity data on pure propane, n-
butane, and n-pentane in the liquid state, the fugacities
being calculated from P-V-T data. These data were employed
to predict $\phi_i^V$ values for propane, n-butane, and n-pentane in
the following steps:

1. Equation VI-1 was rearranged to read

$$
\phi_i^V = \frac{y_i^L y_i^L}{K_i}
$$

(VI-2)

2. $K_i$ was evaluated from the experimental equilibria
data for the solvents.
3. $\gamma_i^L$ was evaluated from the liquid fugacity data for the solvents. Values of $\gamma_i^L$ for methane could not be obtained since methane is a hypothetical liquid at the system conditions.

4. The above data were selected such that the mole fraction of the solvent in the liquid phase was 0.95. From the definition of $\gamma_i^L$, $\gamma_i^L \rightarrow 1.0$ as $x_i \rightarrow 1.0$; thus, at $x_i = 0.95$, $\gamma_i^L$ was assumed to be approximately 1.0 and Equation VI-2 becomes

$$\phi_i^V = \frac{\gamma_i^L}{K_i} \quad \text{when} \quad \gamma_i^L = 1.0$$

(VI-3)

From the experimental data and Equation VI-3, values of $\phi_i^V$ were determined for the solvents in the three methane binaries.

The values of $K_i$ were calculated from $x$ and $y$ values read from smoothed plots that the author prepared from the experimental data. The $\gamma_i^L$ values were read from the plots of Sage and Lacey (52).

Values of $\phi_i^V$ were then calculated from the R-K and BWR equations. IBM 650 computer programs for both the R-K (19) and BWR (32) equations were used in making the calculations. Results of the calculations are presented in Table XX and Figures 20, 21, and 22.

Inspection of the results shows that both equations represent the fugacity coefficients for propane in methane (Figure 20)
satisfactorily for these conditions. The R-K equation gives values which differ from the experimental values by no more than 4%, while the BWR equation agrees to within 2%. For n-butane in methane, Figure 21 shows that the agreement between experimental and calculated values is poor for both equations. For n-pentane in propane, Figure 22 shows that the R-K equation gives agreement to within an average of 6%, but the BWR is again totally unsatisfactory.

In almost all regions investigated, the equations of state gave fugacity coefficients larger than those calculated from the experimental data. However, in the concentration range under study, the values of $\gamma^L$ could be 1 or 2% removed from the limiting value of unity, most probably in a positive direction, which would lead to better agreement between calculated and experimental values. Another factor of importance is that since the solvents were studied, the region of interest was the hypothetical vapor state, which places the maximum demands on the equations of state. In general, agreement of predicted and actual values for a solute would probably be better than for the solvent. Nevertheless, the solvents were in nearly the pure state ($x = 0.95$); if a study were made at low solute concentrations (requiring a knowledge of $\gamma_i^L$), the demands on the equations would be even more stringent, since the solvent would be further into the hypothetical vapor region.

The data presented here are by no means sufficient grounds for drawing definite conclusions as to the general applicability of equations of state in the vapor region. Two methane binaries
were studied, and methane cannot be considered a typical hydrocarban; nevertheless, the equations checked have been applied by others to similar data (12, 40). The failure in some cases of the equations to predict, even qualitatively, the vapor fugacity coefficients does, however, indicate that further study of the equations is needed before they are accepted as a means for evaluating the fugacity coefficients of the components of a vapor mixture. Only after such further study can the equations of state be used with confidence or proved to be unsatisfactory.
TABLE XX
COMPARISON OF CALCULATED AND EXPERIMENTAL VAPOR FUGACITY COEFFICIENTS

<table>
<thead>
<tr>
<th>T, °R</th>
<th>P, psia</th>
<th>Mol % Solvent</th>
<th>Liquid Vapour</th>
<th>T_l^L Solvent</th>
<th>Solvent Vapor Fugacity Coefficient</th>
<th>Experimental</th>
<th>R-K</th>
<th>BWR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methane-Propane System (45)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>560</td>
<td>311</td>
<td>95.0</td>
<td>65.4</td>
<td>0.500</td>
<td>0.726</td>
<td>0.744</td>
<td>0.720</td>
<td></td>
</tr>
<tr>
<td>590</td>
<td>406</td>
<td>95.0</td>
<td>75.1</td>
<td>0.530</td>
<td>0.670</td>
<td>0.702</td>
<td>0.681</td>
<td></td>
</tr>
<tr>
<td>620</td>
<td>515</td>
<td>95.0</td>
<td>83.0</td>
<td>0.565</td>
<td>0.647</td>
<td>0.664</td>
<td>0.647</td>
<td></td>
</tr>
<tr>
<td>650</td>
<td>635</td>
<td>95.0</td>
<td>89.3</td>
<td>0.582</td>
<td>0.619</td>
<td>0.632</td>
<td>0.623</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methane-n-Butane System (50)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>560</td>
<td>515</td>
<td>95.0</td>
<td>38.8</td>
<td>0.105</td>
<td>0.257</td>
<td>0.475</td>
<td>0.421</td>
<td></td>
</tr>
<tr>
<td>590</td>
<td>565</td>
<td>95.0</td>
<td>49.2</td>
<td>0.146</td>
<td>0.282</td>
<td>0.442</td>
<td>0.389</td>
<td></td>
</tr>
<tr>
<td>620</td>
<td>620</td>
<td>95.0</td>
<td>59.2</td>
<td>0.191</td>
<td>0.307</td>
<td>0.382</td>
<td>0.346</td>
<td></td>
</tr>
<tr>
<td>650</td>
<td>690</td>
<td>95.0</td>
<td>68.0</td>
<td>0.239</td>
<td>0.334</td>
<td>0.315</td>
<td>0.435</td>
<td></td>
</tr>
<tr>
<td>680</td>
<td>770</td>
<td>95.0</td>
<td>75.8</td>
<td>0.285</td>
<td>0.357</td>
<td>0.338</td>
<td>0.750</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Propane-n-Pentane System (51)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>650</td>
<td>83</td>
<td>95.0</td>
<td>75.2</td>
<td>0.675</td>
<td>0.852</td>
<td>0.887</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>680</td>
<td>118</td>
<td>95.0</td>
<td>79.8</td>
<td>0.685</td>
<td>0.816</td>
<td>0.858</td>
<td>0.962</td>
<td></td>
</tr>
<tr>
<td>710</td>
<td>162</td>
<td>95.0</td>
<td>85.0</td>
<td>0.685</td>
<td>0.784</td>
<td>0.828</td>
<td>0.977</td>
<td></td>
</tr>
<tr>
<td>740</td>
<td>219</td>
<td>95.0</td>
<td>84.7</td>
<td>0.675</td>
<td>0.757</td>
<td>0.793</td>
<td>1.005</td>
<td></td>
</tr>
<tr>
<td>770</td>
<td>288</td>
<td>95.0</td>
<td>86.8</td>
<td>0.670</td>
<td>0.733</td>
<td>0.758</td>
<td>1.058</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>369</td>
<td>95.0</td>
<td>88.6</td>
<td>0.651</td>
<td>0.698</td>
<td>0.722</td>
<td>1.160</td>
<td></td>
</tr>
<tr>
<td>830</td>
<td>474</td>
<td>95.0</td>
<td>91.5</td>
<td>0.630</td>
<td>0.654</td>
<td>0.680</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>


Comparison of Calculated and Experimental Vapor Fugacity Coefficients of Propane in Methane
System: Methane-n-Butane at $x_B = 0.95$

- Experimental Data
- R-K Equation
- BWR Equation

**Figure 21**

Comparison of Calculated and Experimental Vapor Fugacity Coefficients of n-Butane in Methane
System: Propane-n-Pentane at $x_{Pe} = 0.95$

Comparison of Calculated and Experimental Vapor Fugacity Coefficients of n-Pentane in Propane
CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

The study reported in this thesis included (a) a review of the subject of thermodynamic consistency of experimental data, (b) determination of new atmospheric vapor-liquid equilibria data on the binary systems formed among the constituents normal hexane, methylcyclohexane, and toluene, and (c) a cursory inspection of the applicability of equations of state to the vapor phase.

The major points from this study may be summarized as

1. The experimental vapor-liquid equilibria data of Garner and Hall, of Thijssen, and this work on the system MCH-toluene are in agreement and are thermodynamically consistent.

2. The data of Myers and this work on the system normal hexane-MCH do not agree. These data could not be tested for thermodynamic consistency since heat of mixing data were not available. No decision as to which set of data are better was possible.

3. The T-x data of Sieg and this work are in agreement for the system normal hexane-toluene, but their x-y data are not in agreement. No
heat of mixing data were available for this system, and no choice between the sets of data was possible.

4. The ternary data of Huang on the system normal hexane-MCH-toluene have not been rigorously demonstrated as being consistent. Thus, extension of Huang's study, based on his data, is not warranted. The conclusions reached by Huang must be regarded as tentative until all the data he employed are proven to be consistent.

5. Any meaningful test for thermodynamic consistency of vapor-liquid equilibria requires a knowledge of data other than the P-T-x-y data; for isothermal data, volumetric data are required, and for isobaric data, calorimetric data are required.

6. Vapor fugacity coefficients calculated by the Redlich-Kwong and Benedict-Webb-Rubin equations of state did not agree in all regions tested with data from experimental studies. Thus, the applicability of these equations to the vapor region was not demonstrated. Additional data must be processed to establish the value of the equations in the vapor phase.

From information gained in this study, the following recommendations concerning future work may be made.

1. In future vapor-liquid equilibria studies,
the auxiliary data required to employ thermodynamic consistency tests should be determined as an integral part of the study.

2. Further tests on equations of state should be undertaken before the equations are used with confidence to characterize the vapor phase.

3. Further investigations of the type undertaken by Huang, but using data known to be consistent, are needed to clarify the practical value of methods such as that of Wohl and of Hildebrand-Scatchard in predicting data.
A SELECTED BIBLIOGRAPHY


APPENDIX A

DEVELOPMENT OF HILDEBRAND-SCATCHARD AND WOHL FORMS
OF THE VAN LAAR EQUATION

Van Laar developed Equation III-59 through thermodynamic considerations employing the inexact van der Waals equation of state. Hildebrand and Scatchard, in the early 1930's, independently derived equivalent expressions, at the same time "freeing the van Laar treatment of the inadequacies of the van der Waals equation (26)". Scatchard's derivation will be followed in the discussion below.

The development to follow is based on the theory of "regular solutions", which may be defined by the conditions that

1. The mutual energy of two molecules is dependent only on their relative positions and orientations, and is not a function of the position of other molecules in the area or of the temperature. This is equivalent to the assumption of additivity of energy of molecular pairs and is the basis for most liquid solution theories.

2. The distributions of the positions and orientations of the molecules is random, not influenced by the nature of the other molecules or by the temperature.
This random distribution assumption is the "heart" of regular solution theory and is, at best, a good approximation.

3. The volume change on mixing at constant pressure is zero, i.e., \((\Delta V_{\text{mix}}^L) = 0\).

For a binary mixture, the above assumptions lead to the following expression for the "cohesive energy", \(-U_m\), of the mixture:

\[
-U_m = \frac{C_{11}V_1^2x_1^2 + 2C_{12}V_1V_2x_1x_2 + C_{22}V_2^2x_2^2}{V_1x_1 + V_2x_2} \quad (A-1)
\]

where \(C_{ii} = -U_i/V_i\), the "cohesive energy density".

Equation A-1 may be written in terms of volume fractions, \(\varphi\), as

\[
-U_m = (x_1V_1 + x_2V_2)(C_{11}\varphi_1^2 + 2C_{12}\varphi_1\varphi_2 + C_{22}\varphi_2^2) \quad (A-2)
\]

Scatchard then obtained the energy of mixing as

\[
\Delta U_{\text{mix}}^L = U_m - x_1U_1 - x_2U_2 = (x_1V_1 + x_2V_2)(C_{11} - 2C_{12} + C_{22})\varphi_1\varphi_2
\]

\[
= (x_1V_1 + x_2V_2)A_{12}\varphi_1\varphi_2 \quad (A-3)
\]

where \(A_{12} = C_{11} - 2C_{12} + C_{22}\)

Scatchard then assumed that \(C_{12}\) could be represented as

\[
C_{12} = (C_{11}C_{22})^{0.5} \quad (A-4)
\]

Thus,

\[
A_{12} = (C_{11}^{0.5} - C_{22}^{0.5})^2 \quad (A-5)
\]

At conditions where the vapor is nearly ideal, \(-U\) may be identified as the energy of vaporization, \(\Delta U^V\), and Equation A-3 becomes
\[
\Delta U_{\text{mix}}^L = (x_1 V_1 + x_2 V_2) \left[ \left( \frac{\Delta U}{V} \right) \right] ^{0.5} - \left( \frac{\Delta U}{V_2} \right) ^{0.5} \phi_1 \phi_2 \]  
(A-6)

\[
= (x_1 V_1 + x_2 V_2) (\delta_1 - \delta_2 )^2 \phi_1 \phi_2
\]

where \( \delta \) is defined by Equation A-6.

Since for a regular solution, \( \Delta V_{\text{mix}} = 0 \),

\[
\Delta H_{\text{mix}} = \Delta U_{\text{mix}}
\]  
(A-7)

Thus, differentiating Equation A-6 with respect to \( n_1 \),

\[
\Delta H_{\text{mix}} = \frac{V_1 (\delta_1 - \delta_2 )^2 \phi_1^2}{\phi_2}
\]  
(A-8)

Since \( \Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \), and in view of assumption 2,

\[
\Delta S_{\text{mix}} = -R \ln x_1
\]  
(A-9)

then

\[
\Delta G_{\text{mix}} = RT \ln x_1 + \frac{V_1 (\delta_1 - \delta_2 )^2 \phi_1^2}{\phi_2}
\]  
(A-10)

Combining Equation A-10 with Equation III-55,

\[
RT \ln Y_1 = \frac{V_1}{V_2} (\delta_1 - \delta_2 )^2 \phi_1^2
\]  
(A-11)

or

\[
\ln Y_1 = \frac{\frac{V_1}{V_2} (\delta_1 - \delta_2 )^2 (x_2 V_2)^2}{RT (x_1 V_1 + x_2 V_2)^2}
\]  
(A-12)

By rearrangement,

\[
\ln Y_1 = \frac{A}{\left[ \frac{x_1 V_1}{x_2 V_2} + 1 \right]^2}
\]  
(A-13)
where

\[ A = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \quad (A-14) \]

Defining a similar quantity for the second component,

\[ B = \frac{V_2}{RT} (\delta_1 - \delta_2)^2 \quad (A-15) \]

note that

\[ \frac{A}{B} = \frac{V_1}{V_2} \quad (A-16) \]

and Equation A-13 becomes

\[ \ln \gamma_1 = \frac{A}{\left[ \frac{A}{B} \frac{x_1}{x_2 + 1} + 1 \right]^2} \quad (A-17) \]

Equation A-17 is identical to the van Laar equation, except that A and B are defined by Equations A-14 and A-15.

A completely analogous derivation for a ternary mixture would yield

\[ \Delta H_1 = \frac{V_1}{A} (\delta_1 - \delta_o)^2 \psi_o^2 \quad (A-18) \]

where

\[ \delta_o = \left( \frac{\psi_2 \delta_2 + \psi_3 \delta_3}{\psi_2 + \psi_3} \right) / (\psi_2 + \psi_3) \]

\[ \psi_o = \psi_2 + \psi_3 \]

By rearrangements similar to those for a binary system,

\[ \ln \gamma_1 = \frac{A_1}{\left[ \frac{A_1}{A_23} \frac{x_1}{1-x_1} + 1 \right]^2} \quad (A-19) \]
where $A_1 = \frac{V_1}{RT} (\delta_1 - \delta_0)^2$

$A_{23} = \frac{V_{23}}{RT} (\delta_1 - \delta_0)^2$

$V_{23} = x_2 V_2 + x_3 V_3$

This equation is analogous to Equation A-17 for a binary mixture. Using Equations A-17 and A-19, binary and ternary activity coefficients may be predicted from pure-component data.

**Wohl's Expression of the van Laar Equation**

Wohl (60) noted that the van Laar equation could be obtained from certain empirical expressions for the free energy of mixing. For a ternary system, assume that the excess free energy of mixing may be represented by the expansion

$$G^E_{2,3RT} = \frac{x_1 x_2 q_1 q_2 2a_{12} + x_1 x_3 q_1 q_3 2a_{13} + x_2 x_3 q_2 q_3 2a_{23}}{x_1 q_1 + x_2 q_2 + x_3 q_3}$$

(A-20)

where $a, q =$ empirical constants.

Introduce

$$z_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2 + x_3 q_3}$$

(A-21)

with similar expressions for components 2 and 3. Equation A-20 becomes

$$G^E_{2,3RT} = (x_1 + \frac{q_1 x_2}{q_2} + \frac{q_3 x_3}{q_1}) q_1 (2a_{12} z_1 z_2 + 2a_{13} z_1 z_3 + 2a_{23} z_2 z_3)$$

(A-22)
If the following abbreviations are used

\[ A_{12} = 2a_{12}q_1 \quad ; \quad A_{21} = 2a_{12}q_2 \]

\[ A_{13} = 2a_{13}q_1 \quad ; \quad A_{31} = 2a_{13}q_3 \]

\[ A_{23} = 2a_{23}q_2 \quad ; \quad A_{32} = 2a_{23}q_3 \] (A-23)

Equation A-22 may be rearranged to read

\[
\frac{G^E}{2.3RT} = \frac{x_1x_2A_{21} + x_1x_3A_{31} + x_2x_3A_{32}}{A_{13} x_1 + x_2 \frac{A_{21}}{A_{12}} + x_3 \frac{A_{31}}{A_{13}}} \] (A-24)

From Equation III-55,

\[
\ln \gamma_i = \begin{bmatrix} \frac{\partial \left( \sum_{n_1} g^E \right)}{\partial n_1} \\ \delta n_i \\ \delta \gamma_i \\ \delta T, \delta P \end{bmatrix} \] (A-25)

The result of performing such an operation on Equation A-24 is

\[
\log \gamma_1 = \frac{x_2^2 A_{12} \left( \frac{A_{21}}{A_{12}} \right)^2 + x_3^2 A_{13} \left( \frac{A_{31}}{A_{13}} \right)^2 + x_2 x_3 A_{32} \frac{A_{21}}{A_{12}} \frac{A_{31}}{A_{13}} (A_{12} + A_{13} - A_{32} A_{31})}{\left( x_1 + x_2 \frac{A_{21}}{A_{12}} + x_3 \frac{A_{31}}{A_{13}} \right)^2} \] (A-26)

Similar expressions for \( \log \gamma_2 \) and \( \log \gamma_3 \) may be obtained from equation A-26 by advancing all subscripts in the order 1→2→3→1. For a binary system \( x_3 = 0 \), Equation A-26 becomes

\[
\log \gamma_1 = \frac{A_{12}}{\left[ \frac{A_{12} x_1}{A_{21} x_2 + 1} \right]^{\frac{2}{2}}} \] (A-27)
which is exactly the van Laar equation, Equation III-59, with $A_{12} = A$, $A_{21} = B$. Thus, from binary van Laar constants, ternary $Y$ values may be predicted from Equation A-26.
APPENDIX B

DISCUSSION OF THE REDLICH-KWONG AND BENEDICT-WEBB-RUBIN EQUATIONS OF STATE FOR CALCULATING VAPOR FUGACITY COEFFICIENTS

Redlich-Kwong Equation of State

The Redlich-Kwong equation is an empirical, two-constant equation of state. Introduced in 1949, the equation was recommended by its authors for applications to both pure and multicomponent gas mixtures at all conditions above the critical temperature (47). The equation was specifically designed to fit high-pressure data. Since the R-K equation is empirical, it is justified solely by its applicability.

The R-K equation is explicit in pressure, being defined as

$$P = \frac{RT}{(V-b)} - \frac{a}{T^{\frac{3}{2}}V(V-b)}$$  \hspace{1cm} (B-1)

where $a$ and $b$ are the two constants in the equation. For practical applications, Equation B-1 may be expressed in terms of the compressibility factor, $z$, through the following rearrangements;

$$z = \frac{1}{1 - \frac{A^2}{B}} \frac{h}{(1 + h)}$$  \hspace{1cm} (B-2)

$$z = \frac{PV}{RT}$$  \hspace{1cm} (B-3)

$$A^2 = \frac{a}{R T^{2.5}} = 0.4278 \frac{T^{2.5}}{P_c T^{2.5}} \text{ atm}^{-1}$$  \hspace{1cm} (B-4)
\[ B = \frac{b}{RT} = 0.0867 \frac{T_c}{P_c} \text{ atm}^{-1} \quad (B-5) \]

\[ h = \frac{BP}{z} = \frac{b}{V} \quad (B-6) \]

where \( T_c, P_c \) = critical temperature and pressure, respectively.

Thus, Equation B-2 is determined for a pure component from a knowledge of the critical properties of the component.

Redlich and Kwong state that they expect the equation to be equally applicable to both pure components and gaseous mixtures. For mixtures, they present the following mixture rules:

\[ b = \sum y_i b_i \quad ; \quad B = \sum y_i B_i \quad (B-7) \]

\[ a = a_1 y_1 + a_2 y_2 + \cdots + 2a_{12} y_1 y_2 + \cdots \quad (B-8) \]

\[ a_{12} = (a_1 a_2)^{1/2} \]

\[ A = \sum y_i^2 A_i \quad (B-9) \]

For gaseous mixtures, the fugacity coefficient may be given by Equation III-33,

\[ \ln \phi_i = \left( \frac{P}{RT} - 1 \right) \int_0^P \left( \frac{PV_i}{RT} - 1 \right) d\ln P \quad (III-33a) \]

The integration of Equation III-33a, in terms of the R-K equation, has been performed by Redlich and Kwong and will not be repeated here. The result is

\[ \log \phi_i = 0.4343(z - 1) \frac{B_i}{B} - \log(z - BP) - \frac{A}{B} \left[ \frac{2A_i}{A} - \frac{B_i}{B} \right] \log(1 + \frac{BP}{z}) \quad (B-10) \]

Thompson and Erbar (19) programmed this equation for the
IBM 650 computer, and the values presented in this thesis are from the computer program.

**Benedict-Webb-Rubin Equation of State**

The Benedict-Webb-Rubin equation of state is an empirical, eight-constant equation. The authors of the equation present it as being applicable to both gas and liquid phases (7). The equation is explicit in pressure,

\[
P = RTd + \left( B_o \frac{RT}{T^2} - A_o - C_o \right) d^2 + (bRT - a)d^3 + aad^6 + \frac{cd^3}{T^2} \left( 1 + \gamma d^2 \right) e^{-\gamma d^2}
\]

(B-11)

where
d = molal density, moles/volume.
A_o, B_o, C_o, a, b, c, a, \gamma = empirical constants.

The authors of the equation present the following mixture rules:

\[
B_o = \sum x_i B_{oi}
\]

\[
A_o = \left( \sum x_i A_{oi}^{0.5} \right)^2
\]

\[
C_o = \left( \sum x_i C_{oi}^{0.5} \right)^2
\]

\[
b = \left( \sum x_i b_{i}^{0.33} \right)^3
\]

\[
a = \left( \sum x_i a_{i}^{0.33} \right)^3
\]

\[
c = \left( \sum x_i c_{i}^{0.33} \right)^3
\]

\[
a = \left( \sum x_i a_{i}^{0.33} \right)^3
\]

\[
\gamma = \left( \sum x_i \gamma_{i}^{0.5} \right)^2
\]
A complete discussion of the Benedict-Webb-Rubin equation of state is presented by its authors (7,8). All eight constants in the equation are empirical and must be evaluated for each component from experimental data. No method is known for prediction of the constants; constants for a limited number of components have been determined.

The authors of the equation integrated it to calculate fugacities; the results of the integration are

\[
RT \ln \frac{T_i^Y}{y_i} = RT \ln dRT \qquad + \frac{3}{2} \left[ \frac{\text{RT}(b_i^2 b_i)^{0.33} - (a_{a_i}^2 a_i)^{0.33} \right] d^2 \\
+ \frac{3}{5} \left[ a(a_{a_i}^2 a_i)^{0.33} + a(a_{a_i}^2 a_i)^{0.33} \right] d^5 \\
+ \frac{3d}{T^2} \left[ \frac{1 - \exp(-\gamma d^2)}{\gamma d^2} - \exp(-\gamma d^2) \right] \\
- \frac{2d^2 c}{T^2} \left[ \frac{1 - \exp(-\gamma d^2)}{\gamma d^2} - \exp(-\gamma d^2) \right] \\
- \frac{\gamma d^2 \exp(-\gamma d^2)}{2} \right]
\] (B-13)

Equation B-13 was programmed by Joyner (32) for the IBM 650 computer and was used in the calculations of Chapter VI. \( \phi_i^Y \) values were obtained in the program by dividing Equation B-13 by \( P \). (In Equation B-13, the number 0.33 has been used to represent the number one-third, which was used in the actual calculations.)
NOMENCLATURE

\[ A = \text{parameter in the van Laar equation for activity coefficients.} \]
\[ = \text{parameter in the Redlich-Kwong equation of state.} \]
\[ A_0 = \text{parameter in the Benedict-Webb-Rubin equation of state.} \]
\[ a = \text{activity, } \frac{f}{f^0}. \]
\[ = \text{parameter in Redlich-Kwong equation of state.} \]
\[ = \text{parameter in Benedict-Webb-Rubin equation of state.} \]
\[ = \text{parameter in Wohl's excess free energy expansion.} \]
\[ B = \text{second virial coefficient, volume/mole.} \]
\[ = \text{parameter in the van Laar equation for activity coefficients.} \]
\[ = \text{parameter in Redlich-Kwong equation of state.} \]
\[ B_0 = \text{parameter in the Benedict-Webb-Rubin equation of state.} \]
\[ b = \text{parameter in Margules equation for activity coefficients.} \]
\[ = \text{parameter in the Redlich-Kwong equation of state.} \]
\[ = \text{parameter in the Benedict-Webb-Rubin equation of state.} \]
\[ C = \text{centigrade temperature.} \]
\[ = \text{number of components is a system (phase rule).} \]
\[ C_{ii} = \text{Scatchard's cohesive energy density, } -\frac{U_i}{V_i}, \text{ energy/mole.} \]
\[ C_0 = \text{parameter in the Benedict-Webb-Rubin equation of state.} \]
\[ c = \text{parameter in Margules equation for activity coefficients.} \]
\[ = \text{parameter in the Benedict-Webb-Rubin equation of state.} \]
\[ D = \text{parameter in Herington's test for thermodynamic consistency.} \]
\( d = \) molal density, moles/volume.

\( F = \) number of variables that must be specified to fix the state of a system (phase rule).

\( f = \) fugacity, force/area.

\( G = \) \( H - TS \), Gibbs free energy, energy.

\( H = \) \( U + PV \), enthalpy, energy.

\( h = \) parameter in Redlich-Kwong equation of state.

\( I = \) parameter in Herington's test for thermodynamic consistency.

\( J = \) parameter in Herington's test for thermodynamic consistency.

\( K = \) vapor-liquid equilibria phase-distribution ratio, \( y/x \).

\( n = \) number of moles.

\( P = \) pressure, force/area.

\( = \) number of phases in a system (phase rule).

\( p = \) vapor pressure, force/area.

\( Q = \) heat added to a system, energy.

\( q = \) parameter in Wohl's excess free energy expansion.

\( R = \) universal gas constant.

\( = \) Rankine temperature.

\( S = \) entropy, energy/degree.

\( T = \) temperature.

\( U = \) internal energy, energy.

\( V = \) volume.

\( W = \) work performed on the system, energy.

\( x = \) mole fraction in the liquid phase.

\( y = \) mole fraction in the vapor phase.

\( Z = \) activity coefficient correction factor.

\( z = \) compressibility factor, \( PV/RT \).
\( z \) = generalized "q"-fraction in Wohl's development.

\( z_i \) = compressibility factor in terms of partial volume, \( \bar{P} \bar{V}/RT \).

**Greek Symbols**

\( \bar{x} = (RT/P) - \bar{V} \), residual partial volume.

\( \alpha \) = parameter in the Benedict-Webb-Rubin equation of state.

\( \gamma \) = \( f/f_0 \), activity coefficient.

\( \Delta \) = parameter in the Benedict-Webb-Rubin equation of state.

\( \delta \) = change in a property.

\( \delta = (\Delta U/V)^{0.5} \), solubility parameter, (energy/mole-volume)^{0.5}.

\( \Theta \) = binary boiling range, \( T_{\text{max}} - T_{\text{min}} \).

\( \mu_i = (\delta G/\delta n_i)_{T,P,n_j} \), chemical potential of component "i".

\( \gamma = f/P \), pure-component fugacity coefficient.

\( \xi \) = fractional change in the mass of a system.

\( \Sigma \) = summation over all \( N \) components in a system.

\( \Sigma' \) = parameter in Herington's test for thermodynamic consistency.

\( \phi = f/f_y \), fugacity coefficient.

\( \varphi \) = volume fraction.

**Subscripts**

1 = component 1 (lighter component).

2 = component 2 (heavier component).

\( i,j,k \) = component \( i \), \( j \), or \( k \), respectively.

I = ideal gas state.

\( N \) = total number of components.

\( T_i,P,n \) = variables held constant.

\( \text{subbar} \) = molar quantity.

mix = mixture property.
vap = vaporization to ideal-gas state.

Ω = condition where $|G^E|^M$ occurs.

Superscripts

E = excess property.

M = maximum value.

o = reference state.

V,L = vapor and liquid phase, respectively.

superbar = partial molar quantity.

' = approximate relation.

* = ideal gas state.

Abbreviations

BWR = Benedict-Webb-Rubin.

exp = exponential, i.e., e to the power.

log = logarithm to the base 10.

ln = logarithm to the base e.

MCH = methylcyclohexane.

R-K = Redlich-Kwong.

Miscellaneous

\{ = integral sign.
VITA

Robert Louis Robinson, Jr.
Candidate for the Degree of
Master of Science

Thesis: A THEORETICAL AND EXPERIMENTAL INVESTIGATION OF VAPOR-LIQUID EQUILIBRIA IN THE BINARY SYSTEMS FORMED AMONG THE CONSTITUENTS NORMAL HEXANE, METHYLCYCLOHEXANE AND TOLUENE

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Muskogee, Oklahoma, June 14, 1937, the son of Robert L. and Bess W. Robinson. Married to G. Gayle Nixon, Muskogee, Oklahoma, in May, 1958.

Education: Attended elementary school in Muskogee, Oklahoma; graduated from Muskogee Central High School in 1955; received the Bachelor of Science degree in Chemical Engineering from Oklahoma State University in 1959; completed requirements for the Master of Science degree in May 1962.

Professional Experience: Employed as an engineering trainee with Brockway Glass Company in the summer of 1957. Employed as an engineering trainee with Humble Oil and Refining Company in the summer of 1958. Employed in the summer of 1960 as an engineer (temporary) with Jersey Production Research Company.