

INVESTIGATION OF  
A GENERALIZED VAPOR-LIQUID  
K CORRELATION FOR HYDROCARBONS

By

JURIS VAIROGS

Bachelor of Science  
University of Nebraska  
Lincoln, Nebraska  
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Thesis Approved

*K C Chao*

Thesis Adviser

*John H. Eubank*

Dean of the Graduate School

## PREFACE

A correlation method is proposed whereby the vapor liquid equilibrium ratio,  $K$ , defined as the ratio of mole fraction of a component in the vapor to that in the liquid, is calculated from three quantities: an ideal equilibrium value,  $K^*$ , a liquid activity coefficient,  $\gamma^L$ , and a vapor activity coefficient,  $\gamma^V$ . If both vapor and liquid phases are ideal solutions so that their activity coefficients are equal to unity, then the equilibrium  $K$  value is equal to  $K^*$ . This quantity is determined from pure component properties and thus is a function of temperature, pressure and component identity only. In most cases the two phases of a component of an equilibrium mixture do not follow the Lewis-Randall fugacity rule (11). The activity coefficients differ from unity depending on the effect of the other components of a mixture upon the component in question. Thus the activity coefficients adjust for the composition effect. Multiple linear regression was used in the correlation work.

I wish to thank Professor Wayne C. Edmister for his continuous advice and guidance during the course of this project. I sincerely appreciate the help received from Professor John H. Erbar and Dr. A. Nelson Stuckey, Jr. of the School of Chemical Engineering as well as the Computing Center at Oklahoma State University. Appreciation is expressed to the Natural Gas Processors Association for the research

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## TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION.....	1
Literature Survey.....	2
II. VAPOR-LIQUID EQUILIBRIUM RELATIONS.....	5
Ideal K Concept.....	5
Imperfection Pressure Correction.....	5
III. PRESSURE SERIES CORRELATION.....	8
Correlation of $K^*$ .....	8
Correlation of $\ln \theta$ .....	11
IV. EQUATION OF STATE CORRELATION.....	22
Redlich-Kwong Equation.....	22
Modified Redlich-Kwong Equation.....	25
Benedict-Webb-Rubin Equation.....	27
V. DISCUSSION OF RESULTS.....	28
Pressure Series Correlation.....	28
Equation of State Correlation.....	29
Vapor Activity Coefficients.....	33
VI. CONCLUSIONS AND RECOMMENDATIONS.....	41
Conclusions.....	41
Recommendations.....	42
BIBLIOGRAPHY.....	43
APPENDIX A - NOMENCLATURE.....	45
APPENDIX B - IDEAL K TABLES.....	48
APPENDIX C - IMPERFECTION PRESSURE CORRECTION AND F(P <sub>r</sub> ) TABLES.....	54
APPENDIX D - EQUATIONS USED IN CALCULATIONS.....	69

LIST OF TABLES

Table	Page
I. Smoothed Degree and Prime Coefficients for K*.....	12
II. Degree Intercepts $\ln \theta_0^\circ$ .....	17
III. Degree Coefficients for $F^\circ(P_r)$ .....	18
IV. Prime Intercepts $\ln \theta_C$ .....	20
V. Prime Coefficients for $F'(P_r)$ .....	21
VI. Imperfection Pressure Correction Comparison for Ethane-n-Pentane System.....	26
VII. Compressibility Factors.....	24
VIII. Original and Back-calculated $F(P_r)$ Values.....	30
IX. Comparison of Imperfection Pressure Correction $\ln \theta$ .....	36
X. Vapor and Liquid Activity Coefficients for Ethane in n-Pentane.....	37
XI. Vapor and Liquid Activity Coefficients for n-Pentane in Ethane.....	31
B. Smoothed Ideal K Values Calculated by Equations D-11 and II-2.....	49
C-I. Imperfection Pressure Corrections.....	55
C-II. Values of $F^\circ(P_r) = \frac{\ln \theta^\circ - \ln \theta_0^\circ - \beta^\circ P_r}{P_r}$ At Various $T_r$ and $P_r$ Values for Simple Fluid.....	62
C-III. Values of $F'(P_r) = \frac{\ln \theta_B - \ln \theta_C - b' P_r}{P_r}$ .....	65

## LIST OF FIGURES

Figure		Page
1.	Smoothing of Ideal K Ratios Calculated for Reduced Convergence Pressure of 15.0.....	10
2.	Demonstration of Reduced Asymptotic Convergence Pressure Concept.....	14
3.	Smoothing Asymptotic $\ln \theta$ Curves.....	15
4.	Imperfection Pressure Correction vs. $P_r$ for Ethane.....	34
5.	Imperfection Pressure Correction vs. Reduced Pressure for n-Pentane.....	35
6.	Vapor Activity Coefficients of Ethane in n-Pentane.....	39
7.	Liquid Activity Coefficients of Ethane in n-Pentane.....	39
8.	Vapor Activity Coefficients of n-Pentane in Ethane.....	40
9.	Liquid Activity Coefficients of n-Pentane in Ethane.....	40

## CHAPTER I

### INTRODUCTION

Many industrial calculations require knowledge of component distributions in coexisting equilibrium liquid and vapor phases. The ratio of mole fraction of a component in the vapor to that in the liquid is unique for a mixture of given composition at a specified temperature and pressure. Consequently, this ratio,  $K$ , is used to calculate bubble and dew points.

During the early years of the chemical and petroleum industries the  $K$  was calculated by a combination of Raoult's and Dalton's laws (11). As more and more non-ideal systems were encountered it became necessary to develop a new equation or procedure to calculate this ratio. Indeed, many methods have been published. Although they vary in accuracy and simplicity, they all have a common drawback in that they are limited in pressure and temperature range as well as the systems to which they are applicable.

The purpose of this work was to develop a method to calculate  $K$  ratios which is easy to use and is applicable to many hydrocarbons over wider ranges of temperature and pressure. To this end the acentric factor, reduced temperature, reduced pressure and solubility parameter were used to describe the system. The acentric factor,  $\omega$ , is a function of



reduced vapor pressure at  $T_r = .7$  and therefore a characteristic parameter for each fluid as is the solubility parameter,  $\delta$ , (11). The concept of ideal equilibrium ratio  $K^*$  was also utilized. A fluid that obeys the Lewis-Randall fugacity rule (11) is an ideal fluid and its activity coefficients are equal to unity. As a result, the  $K$  value for such a fluid is equal to its ideal equilibrium ratio  $K^*$ . Departures of the phases from ideality are accounted for by the activity coefficients.

### Literature Survey

Since the days when Raoult's Law was the only way of calculating  $K$  ratios, many correlation methods have been proposed and developed. These methods can be divided into two groups, namely those using the convergence pressure principle and those applying some other approach. Among the latter one finds the MIT  $K$  charts (14) which were developed from the fugacity coefficient correlation of Lewis and Kay (1). Other notable works in this group are the Michigan (2) and Kellogg (3)  $K$  charts and correlations by Edmister and Ruby (5), Watson et al. (4), Prausnitz, Edmister and Chao (6), and Chao and Seader (7). Which is the best? A thorough discussion of these works was presented by Stuckey (8).

The convergence pressure concept was based upon the observation that, when experimental  $K$  data of both components in a binary mixture were plotted against pressure, the two curves approached  $K = 1.0$  at some high pressure. This pressure was called the convergence pressure. The curve for the heavy component crossed the  $K = 1.0$  line at its vapor pressure also. Since the

convergence pressure was different for each system, it was obvious that it could be used as a parameter in a generalized correlation. For systems containing more than two components the convergence pressure varied with composition.

No theory has been developed for the calculation of a convergence pressure. In fact, the definition of convergence pressure for a multicomponent system has not been firmly agreed upon yet. However, many empirical methods have been published. An excellent summary of them was presented by Hipkin (9).

The two most outstanding and comprehensive works in this area are the NGPA (10) and Braun (9) K charts. The NGPA method is a complex one because for a given component and convergence pressure a separate chart is needed. Convergence pressure is determined by comparing the critical locus curve for the system in question against curves developed in the correlation. An improvement by Hinshaw (15) reduces the number of charts needed.

The Braun correlation is somewhat simpler to use. The convergence pressure is taken from a correlation of generalized critical loci. The K value at a pressure of 10 psia has been correlated as a function of temperature and component identity. The K value at the system pressure is presented as function of convergence pressure and K at 10 psia.

Stuckey (8) attempted several different procedures in trying to obtain a generalized K correlation. The best was the  $K^*$  correlation based on a reduced convergence pressure of 6.29. The  $K^*$  values were calculated from two parameters: acentric factor and reduced temperature. Although the calculation method

was thus greatly simplified, the procedure was lacking in accuracy and greatly limited by the temperature range.

## CHAPTER II

### VAPOR LIQUID EQUILIBRIUM RELATIONS

#### Ideal K Concept

The relationship between the actual K, ideal K and the liquid and vapor activity coefficients used in this work has been previously derived by Edmister (11) and recapitulated by Stuckey (8). Thus,

$$K_i = K_i^* \frac{\gamma_i^L}{\gamma_i^V} \quad (\text{II-1})$$

where  $K_i^*$  is the ideal K of component i and  $\gamma_i^L$  and  $\gamma_i^V$  are the liquid and vapor activity coefficients, respectively.

If the phases behave as ideal fluids (12), the activity coefficients are equal to 1.0 and  $K_i = K_i^*$ . The same is true for a pure component with the additional consideration that  $K_i^* = 1.0$  at the vapor pressure. If equations for calculating the activity coefficients are available, all that is needed is an expression for  $K_i^*$ .

#### Imperfection Pressure Correction

From the derivation mentioned above one obtains

$$K_i^* = \frac{P_i^\circ}{P\theta} \quad (\text{II-2})$$

and

$$\theta = \left( \frac{f_i^V}{P} \right)_P \left( \frac{P_i^\circ}{f_i^L} \right)_P \quad (\text{II-3})$$

where  $\theta$  is the imperfection pressure correction,  $f_i^V$  and  $f_i^L$  are the fugacities of pure component  $i$  in the vapor and liquid states respectively,  $P$  is the system pressure and  $P_i^\circ$  is the vapor pressure. The subscript  $P$  indicates that both fugacities are evaluated at the system temperature and pressure. It is important to note that all quantities in Equation II-2 are for the pure component  $i$ . Upon substitution of the familiar expression for fugacity coefficients (11,12) one obtains at constant temperature

$$\ln \theta = \frac{1}{RT} \int_0^P \left( V^V - \frac{RT}{P} \right) dP - \frac{1}{RT} \int_0^{P^\circ} \left( V^V - \frac{RT}{P} \right) dP - \frac{1}{RT} \int_{P^\circ}^P V^L dP \quad (\text{II-4})$$

This equation expresses the isothermal variation of  $\ln \theta$  with pressure. The last two terms evaluate the expression  $\left( \frac{f_i^L}{f_i^\circ} \right)_P$  by calculating the vapor fugacity coefficient at the

vapor pressure and adding to it the change in  $\ln f_i^L$  from vapor pressure to system pressure.

A simplification of Equation II-4 yields

$$\ln \theta = \frac{1}{RT} \int_{P^\circ}^P \left( V^V - \frac{RT}{P} \right) dP - \frac{1}{RT} \int_{P^\circ}^P V^L dP \quad (\text{II-5})$$

Combining Equations II-5, II-2 and II-1 will give an equation for calculating  $K_i$ .

The correlation scheme followed in this work uses these three equations. Along with the Scatchard-Hildebrand equation for liquid activity coefficients (11), and the Stuckey vapor pressure and liquid volume equations given in Appendix D, they

permit obtaining an expression for  $\ln \Theta$  and a correlation for  $\gamma^V$ . Consequently, the first step was to generate ideal K values and obtain a correlation for them. The second step was to obtain a vapor activity coefficient correlation using experimental K data and the new ideal K correlation. Both correlations would then be usable in conjunction with each other only.

Equation II-5 can be readily solved by substitution of any available equation of state as it is done in Chapter IV. If the Berlin virial equation of state

$$PV = RT + B'P + C'P^2 + D'P^3 + \dots \quad (\text{II-6})$$

is substituted into Equation II-5, a series expansion is obtained. Since virial coefficients are not available, the coefficients are obtained by a curve fit discussed in Chapter III.

## CHAPTER III

### PRESSURE SERIES CORRELATION

As explained previously, the correlation of  $K^*$  can be achieved by the use of a pressure series expansion for  $\ln \theta$ . This procedure can be used to correlate either  $K^*$  or  $\ln \theta$  directly.

#### Correlation of $K^*$

In Chapter I an explanation of convergence pressure and its application to  $K$  was presented. For a generalized correlation such as this, a problem is encountered in that on a reduced basis the convergence pressures  $P_{rk}$  for the components are not equal as they are on absolute pressure basis. Stuckey (8) ignored this obstacle and correlated  $K^*$  for a single  $P_{rk} = 6.29$ . The equations developed were supposedly good for any  $P_r$  less than 6.0. However, his correlation did not give satisfactory results and he concluded that  $P_{rk} = 15.0$  would be a better choice.

Stuckey's recommendation as well as his equation for  $\ln \theta$ , equation D-11, truncated after second term on the right hand side was adopted for this work. New values of the coefficient  $c$  in equation D-11 were determined for each isotherm used in the correlation work. This can be done if it is observed that at the convergence pressure  $K^* = 1.0$  and therefore  $\ln \theta = \ln \frac{P_r^0}{P_{rk}}$ ,

leaving  $c$  as the only unknown in equation D-11.

With the  $\ln \Theta$  equation modified with new values for  $c$ ,  $K^*$  was calculated for a series of isotherms ranging from 0.6 to 2.00 and acentric factors of 0.0, 0.2 and 0.4. The  $K^*$  values were plotted vs.  $P_r$  on a log-log graph and each isotherm drawn so that it converged to  $K^* = 1.0$  at  $P_r = 15.0$ , as illustrated on Figure 1. The smoothed values are tabulated in Appendix B. All that had to be done now was to choose a model for  $\Theta$  and find the necessary coefficients by curve fit.

Substitution of the Berlin virial equation of state (12) into equation II-5, integration and simplification yields

$$\ln \Theta = \frac{B^L - V^L}{RT} (P - P^\circ) + \frac{C^L}{2RT} (P^2 - P^{\circ 2}) + \frac{D^L}{3RT} (P^3 - P^{\circ 3}) + \dots \quad (\text{III-1})$$

In generalized form this equation becomes

$$\ln \Theta = b (P_r - P_r^\circ) + c (P_r^2 - P_r^{\circ 2}) + d (P_r^3 - P_r^{\circ 3}) + e (P_r^4 - P_r^{\circ 4}) + \dots \quad (\text{III-2})$$

where

$$b = \frac{1}{T_r} \left( \frac{BP_c}{RT_c} - \frac{V_c^L}{RT_c} \right) \quad (\text{III-3})$$

The coefficients  $c$ ,  $d$ ,  $e$ , etc. can also be expressed in terms of the virial coefficients but since no generalized expression exists for them, it becomes necessary to obtain them from a curve fit.

Substitution of this equation truncated after 4th term into equation II-2 yields

$$\ln K^* - \ln P_r^\circ + \ln P_r + b (P_r - P_r^\circ) = -c (P_r^2 - P_r^{\circ 2}) - d (P_r^3 - P_r^{\circ 3}) - e (P_r^4 - P_r^{\circ 4}) \quad (\text{III-4})$$



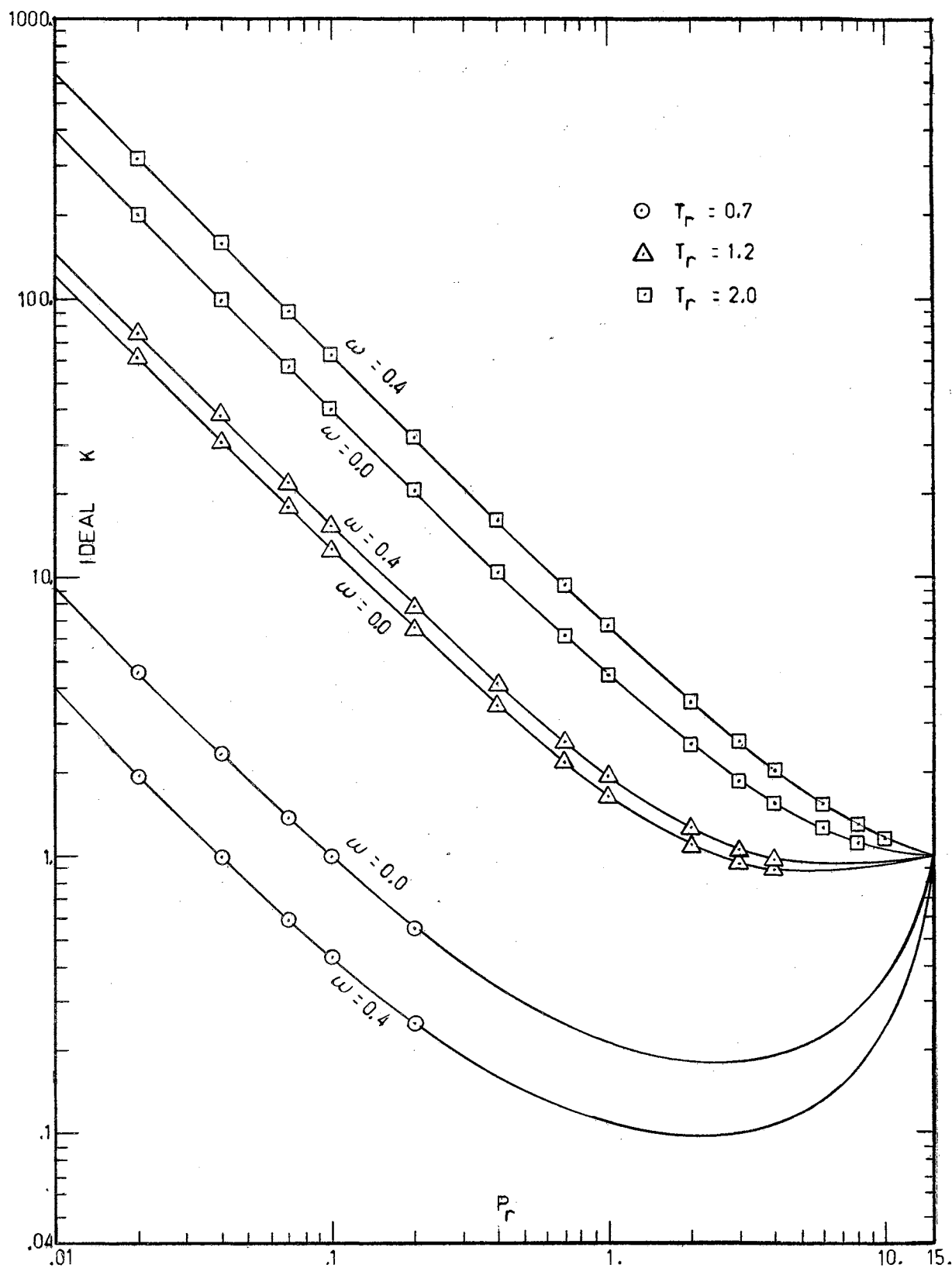


FIGURE 1  
SMOOTHING OF IDEAL K RATIOS CALCULATED FOR REDUCED  
CONVERGENCE PRESSURE OF 15.0

The left hand side of equation III-4 can be readily evaluated for a given  $T_r$  and  $\omega$  with the use of the  $K^*$  values tabulated in Appendix B. The right hand side of the equation can also be evaluated except for the coefficients  $c$ ,  $d$ , and  $e$ , the values of which can be obtained by a curve fit. Least squares method was used with equation III-4 transformed into the form

$$Y = cX_1 + dX_2 + eX_3 \quad (\text{III-5})$$

It was believed that no higher order terms were necessary since Stuckey obtained a fair relationship with only two terms.

Each of the resulting coefficients,  $c$ ,  $d$ , and  $e$ , was smoothed against temperature by plotting vs.  $T_r$  for each of the  $\omega$  values. The smoothed coefficients,  $c$ ,  $d$ , and  $e$ , were then plotted vs.  $\omega$  and straight lines drawn to obtain the expression

$$a = a^{\circ} + a' \quad (\text{III-6})$$

where,  $a$ , represents any of the coefficients  $c$ ,  $d$ , or  $e$ . The smoothed coefficients are tabulated in Table I.

#### Correlation of $\ln \theta$

If one chooses, one may work with developing equations for  $\ln \theta$  rather than  $K^*$  and then combine it with the ratio  $\frac{P_r^{\circ}}{P_r}$ . All the work would be done with equation III-2 instead of equation III-4.

The development of the "asymptotic convergence pressure" concept can best be illustrated by an example. Since the reduced convergence pressure can be chosen arbitrarily, it is possible to calculate  $\ln \theta$  and plot vs.  $P_r$  for the condition that the  $P_r$  be the convergence pressure. That means that

TABLE I

## SMOOTHED DEGREE AND PRIME COEFFICIENTS FOR K\*

## Direct Curve Fit of K\*

## Equations III-4 and III-6

$T_r$	$c^\circ$	$c'$	$d^\circ$	$d'$	$e^\circ \cdot 10^3$	$e' \cdot 10^3$
.60	-.313	-.562	.0283	.0506	-.834	-1.473
.65	-.239	-.420	.0210	.0402	-.607	-1.300
.70	-.181	-.271	.0154	.0298	-.440	-.860
.80	-.138	-.139	.0111	.0194	-.315	-.326
.85	-.107	-.086	.0082	.0109	-.221	-.223
.90	-.081	-.057	.0058	.0067	-.152	-.151
.95	-.061	-.037	.0039	.0041	-.097	-.100
1.00	-.045	-.022	.0023	.0024	-.050	-.064
1.05	-.032	-.004	.0006	.0005	.002	-.025
1.10	-.017	.001	.0001	.0002	.016	-.016
1.15	-.012	.003	-.0002	.0000	.022	-.011
1.20	-.009	.004	-.0003	.0000	.023	-.008
1.30	-.006	.004	-.0003	.0000	.017	-.005
1.40	-.005	.004	-.0002	.0000	.010	-.002
1.50	-.004	.004	-.0001	.0000	.002	-.001
1.60	-.003	.003	.0000	.0000	.000	.000
1.80	-.002	.003	.0000	.0000	.000	.000
2.00	-.002	.003	.0000	.0000	.000	.000

equation II-2 becomes

$$\ln \theta = \ln \frac{P_r^\circ}{P_r} \quad (\text{III-7})$$

This is done on Figure 2 as an example. It is obvious that the "ordinary"  $\ln \theta$  values calculated by equations II-2 and D-11 approach the "convergent"  $\ln \theta$  values calculated by equation III-7 asymptotically. The pressure at which the two values are practically equal is the reduced asymptotic convergence pressure and was assumed to be 1000.

The  $\ln \theta$  values calculated by equation II-2 from the smoothed  $K^*$  values in Appendix B were plotted vs.  $\ln P_r$  for  $\omega = 0.0$ , 0.2 and 0.4. For example see Figure 3. The curves had to meet two conditions.  $\ln \theta = 0.0$  at the vapor pressure and at high  $P_r$  the curve becomes asymptotic to a straight line with slope = -1 drawn through the point  $\ln P_r = \ln 1000$ . The latter condition can be deduced by taking the derivative  $\frac{d \ln \theta}{d \ln P_r}$  and evaluating at the asymptotic convergence pressure. The term  $\frac{d \ln K^*}{d \ln P_r}$  is 0.0 due to the asymptotic convergence of the  $K^*$  vs.  $P_r$  curves. The resulting  $\ln \theta$  values are tabulated in Appendix C.

The model chosen for curve fitting was

$$\begin{aligned} \ln \theta = & (b^\circ + \omega b') (P_r - P_r^\circ) + (c^\circ + \omega c') (P_r^2 - P_r^{\circ 2}) + \dots \\ & + (I^\circ + \omega I') (P_r^8 - P_r^{\circ 8}) \end{aligned} \quad (\text{III-8})$$

Setting  $\omega = 0.0$  and separating terms that contain  $P_r^\circ$ , one obtains

$$\begin{aligned} \ln \theta_o = & - b^\circ P_r^\circ - c^\circ P_r^{\circ 2} - d^\circ P_r^{\circ 3} - \dots - i^\circ P_r^{\circ 8} - b^\circ P_r - \\ & c^\circ P_r^2 - d^\circ P_r^3 - \dots - i^\circ P_r^8 \end{aligned} \quad (\text{III-9})$$

By plotting  $\ln \theta$  vs  $P_r$  and extrapolating to zero pressure one

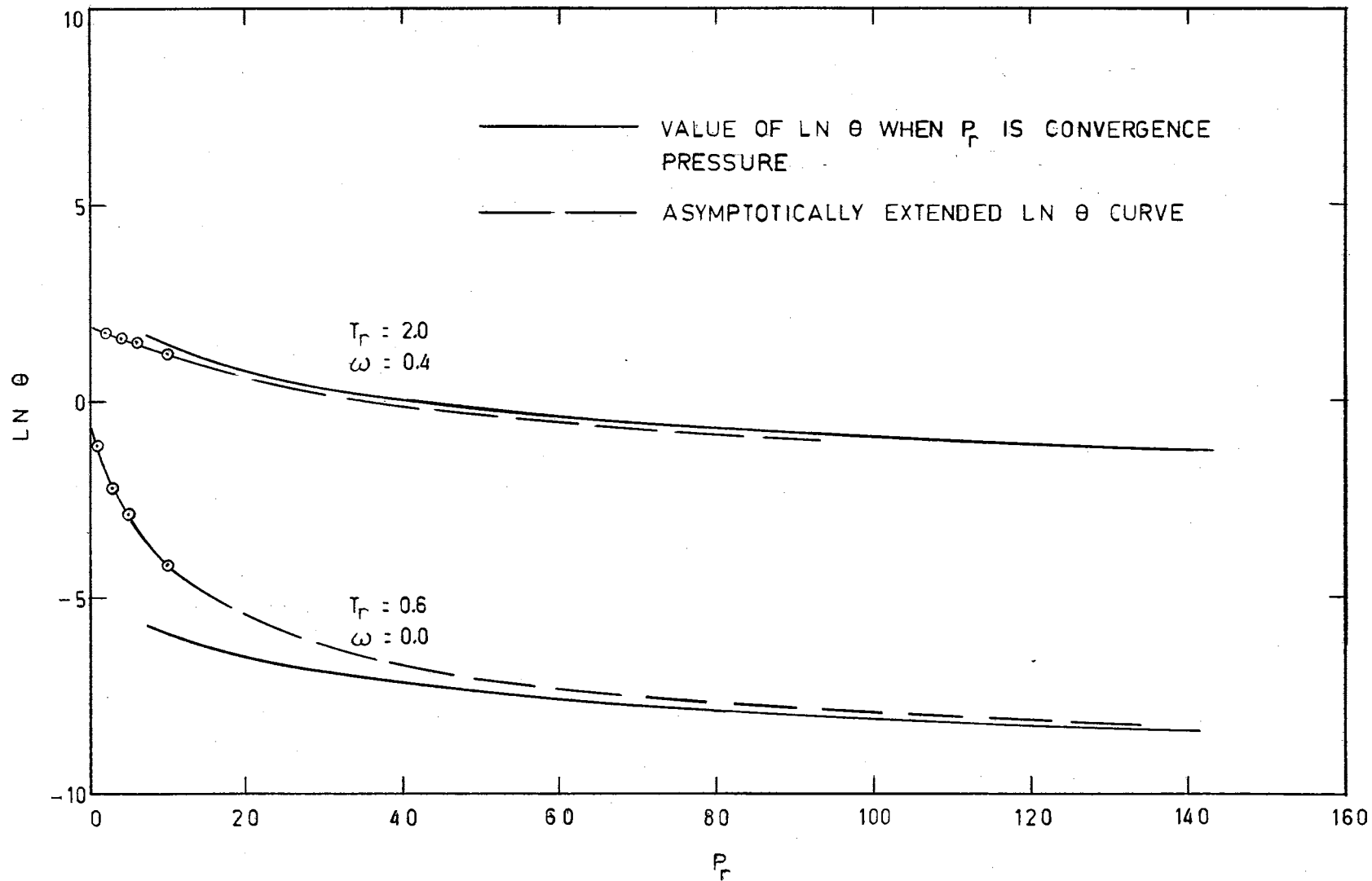


FIGURE 2  
 DEMONSTRATION OF REDUCED ASYMPTOTIC CONVERGENCE PRESSURE CONCEPT

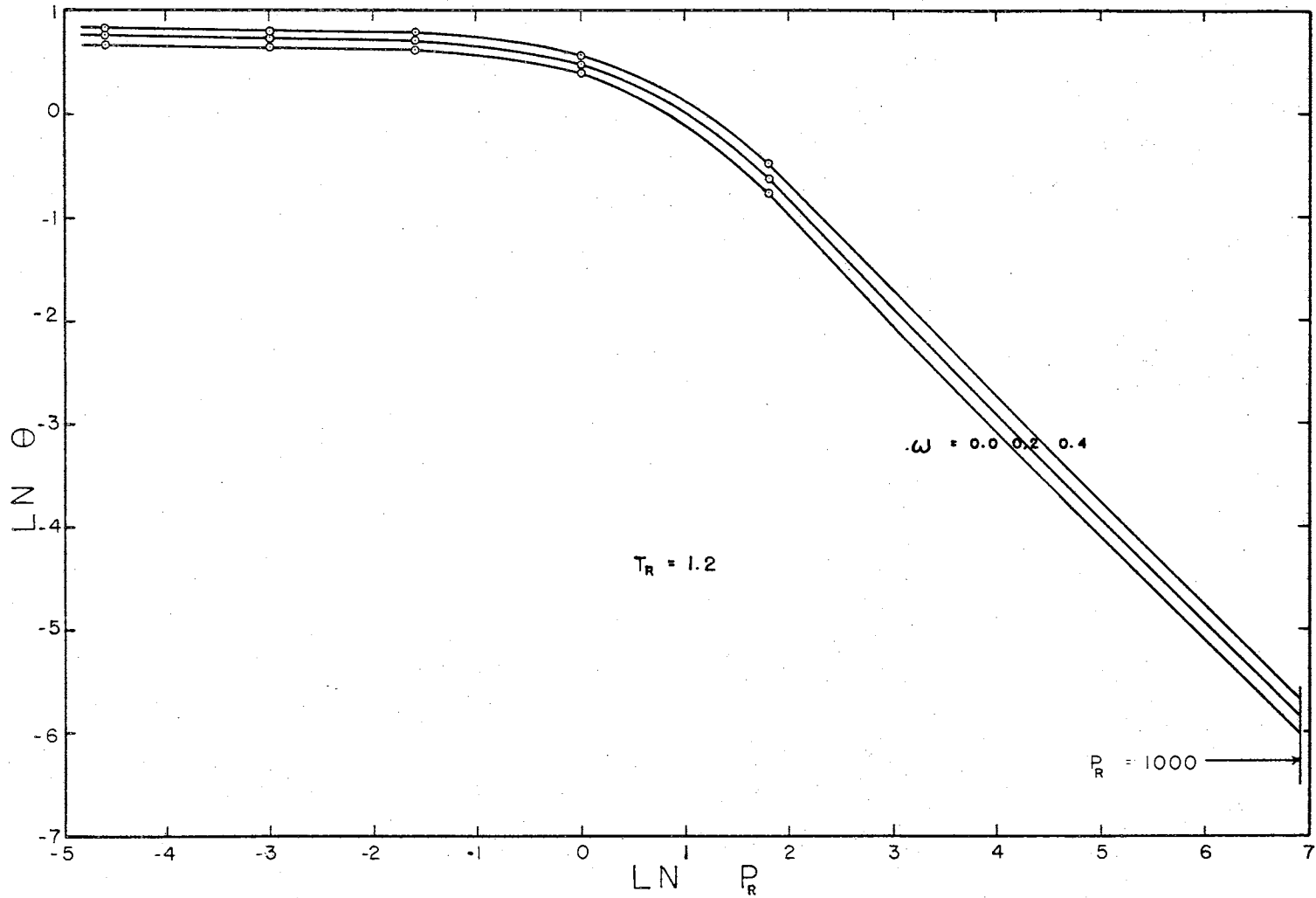


FIGURE 3

SMOOTHING ASYMPTOTIC LN  $\theta$  CURVES

obtains a value for the sum of terms containing  $P_r^\circ$  which is represented by  $\ln \theta_0^\circ$ . Since equation III-3 is retained for evaluating  $b^\circ$ , these two terms are known and can be transferred to the left to give

$$\frac{\ln \theta_0 - \ln \theta_0^\circ - b^\circ P_r}{P_r} = F^\circ(P_r) = c^\circ P_r + d^\circ P_r^2 + \dots + i^\circ P_r^7 \quad (\text{III-10})$$

This model was used to obtain coefficients for a series of isotherms. The  $\ln \theta_0^\circ$  values are given in Table II and the  $F^\circ(P_r)$  values smoothed vs.  $T_r$  and  $P_r$  in Appendix C.

To introduce temperature dependence each of the coefficients had to be curve fitted with some model of  $T_r$ . Several models were tried but the best one was

$$c^\circ = c_1^\circ T_r^{-1} + c_2^\circ T_r^{-3} + c_3^\circ T_r^{-5} + c_4^\circ T_r^{-7} + c_5^\circ T_r^{-9} \quad (\text{III-11})$$

The same form was retained for all coefficients. The final results are tabulated in Table III.

To obtain the primed coefficients the following procedure was used. Subtracting Equation III-8 written for  $\omega = 0$  from Equation III-8 written for any other value of  $\omega$  and separating terms results in

$$\begin{aligned} \ln \theta - \ln \theta_0 &= b^\circ P_{r0}^\circ + c^\circ P_{r0}^{\circ 2} + \dots + i^\circ P_{r0}^{\circ 8} - b^\circ P_{r\omega}^\circ + \\ &- c^\circ P_{r\omega}^{\circ 2} - \dots - i^\circ P_{r\omega}^{\circ 8} + \omega (b' P_r + c' P_r^2 + \dots + i' P_r^8) + \\ &\omega (-b' P_{r\omega}^\circ - c' P_{r\omega}^{\circ 2} - \dots - i' P_{r\omega}^{\circ 8}) \end{aligned} \quad (\text{III-12})$$

Let

$$\begin{aligned} \ln \theta_A &= b^\circ (P_{r0}^\circ - P_{r\omega}^\circ) + c^\circ (P_{r0}^{\circ 2} - P_{r\omega}^{\circ 2}) + \dots + \\ &(i^\circ) (P_{r0}^{\circ 8} - P_{r\omega}^{\circ 8}) \end{aligned} \quad (\text{III-13})$$

TABLE II

DEGREE INTERCEPTS LN  $\theta_0^\circ$ 

Equation III-9 for Imperfection Pressure Correction Curve Fit

$T_r$	$\ln \theta_0^\circ$
.60	.043
.65	.066
.70	.104
.75	.151
.80	.200
.85	.247
.90	.315
.95	.377
1.00	.443
1.05	.500
1.10	.561
1.15	.621
1.20	.674
1.30	.786
1.40	.878
1.50	.971
1.60	1.0371
2.00	1.272
3.00	1.600
4.00	1.800



TABLE III

DEGREE COEFFICIENTS FOR  $F^{\circ}(P_r)$ 

Curve Fitting With Equations III-10 and III-11

i	$c_i^{\circ}$	$d_i^{\circ}$
1	.044708393	-.10679523 x 10 <sup>-1</sup>
2	-.16256130	.33191974 x 10 <sup>-1</sup>
3	.17492858	-.17996541 x 10 <sup>-1</sup>
4	-.31185649 x 10 <sup>-1</sup>	-.60782460 x 10 <sup>-2</sup>
5	.14246000 x 10 <sup>-3</sup>	.22904800 x 10 <sup>-2</sup>
i	$e_i^{\circ}$	$f_i^{\circ}$
1	.78289830 x 10 <sup>-3</sup>	-.12514060 x 10 <sup>-4</sup>
2	-.16709680 x 10 <sup>-2</sup>	-.21641570 x 10 <sup>-4</sup>
3	-.79129390 x 10 <sup>-3</sup>	.14875448 x 10 <sup>-3</sup>
4	.18880003 x 10 <sup>-2</sup>	-.12823592 x 10 <sup>-3</sup>
5	-.43587800 x 10 <sup>-3</sup>	.25506840 x 10 <sup>-4</sup>
i	$g_i^{\circ}$	$h_i^{\circ}$
1	-.10124339 x 10 <sup>-5</sup>	.48390650 x 10 <sup>-7</sup>
2	.39471179 x 10 <sup>-5</sup>	-.96788930 x 10 <sup>-7</sup>
3	-.40681185 x 10 <sup>-5</sup>	-.66231080 x 10 <sup>-7</sup>
4	.12671538 x 10 <sup>-5</sup>	.12881256 x 10 <sup>-6</sup>
5	-.13787380 x 10 <sup>-6</sup>	-.29362030 x 10 <sup>-7</sup>
i	$i_i^{\circ}$	
1	-.61945910 x 10 <sup>-9</sup>	
2	.60223500 x 10 <sup>-9</sup>	
3	.26669740 x 10 <sup>-8</sup>	
4	-.29774776 x 10 <sup>-8</sup>	
5	.62894000 x 10 <sup>-9</sup>	

and

$$\ln \theta_C = -b'P_{r\omega}^{\circ} - c'P_{r\omega}^{\circ 2} - \dots - i'P_{r\omega}^{\circ 8} \quad (\text{III-14})$$

Substituting Equations III-13 and III-14 into Equation III-12

and rearranging gives

$$\frac{\ln \theta - \ln \theta_o - \ln \theta_A}{\omega} = \ln \theta_B = \ln \theta_C + b'P_r + c'P_r^2 + \dots + i'P_r^8 \quad (\text{III-15})$$

The left hand side was calculated for  $\omega = .2$  and  $.4$  and found to be essentially independent of  $\omega$  as expected. The values were plotted vs.  $P_r$  for each isotherm and extrapolated to 0 to obtain  $\ln \theta_C$  which are tabulated in Table IV. Then Equation III-15 reduces to

$$\frac{\ln \theta_B - \ln \theta_C - b'P_r}{P_r} = F'(P_r) = c'P_r + d'P_r^2 + \dots + i'P_r^7 \quad (\text{III-16})$$

$F'(P_r)$  values were calculated for  $\omega = .2$  and  $.4$  and averaged although they varied very little with  $\omega$ . The averaged  $F'(P_r)$  were smoothed by plotting vs.  $T_r$  and  $P_r$  and are tabulated in Appendix C.

Equation III-16 was curve fitted to obtain prime coefficients. Then they were cross-fitted against  $T_r$  using the model of Equation III-11. The resulting coefficients are tabulated in Table V.

Results of procedures described in this chapter are discussed in Chapter V.

TABLE IV

PRIME INTERCEPTS LN  $\theta_C$ 

From Equation III-15 For Imperfection Pressure Correction Curve Fit

.60	0.030	0.014
.65	0.051	0.030
.70	0.070	0.045
.75	0.087	0.058
.80	0.100	0.068
.85	0.108	0.076
.90	0.105	0.080
.95	0.081	0.076
1.00	0.045	0.045
1.05	- .002	- .002
1.10	- .057	- .066
1.15	- .114	- .142
1.20	- .175	- .226
1.30	- .321	- .426
1.40	- .509	- .690
1.50	- .775	- 1.795
1.60	- 1.125	- 5.585
2.00	-168.320	-554.270

TABLE V

PRIME COEFFICIENTS FOR  $F'(P_r)$ 

Curve Fitting With Equations III-16 and III-11

i	$c'_i$	$d'_i$
1	$-.97660700 \times 10^{-1}$	$.29238460 \times 10^{-1}$
2	$.21867222 \times 10^0$	$-.73731160 \times 10^{-1}$
3	$-.27762437$	$.87876900 \times 10^{-1}$
4	$.19607150 \times 10^0$	$-.52286982 \times 10^{-1}$
5	$-.33532130 \times 10^{-1}$	$.85430330 \times 10^{-2}$

i	$e'_i$	$f'_i$
1	$-.34603140 \times 10^{-2}$	$.12425564 \times 10^{-3}$
2	$.88876200 \times 10^{-2}$	$-.33397148 \times 10^{-3}$
3	$-.10187698 \times 10^{-1}$	$.37609271 \times 10^{-3}$
4	$.55780204 \times 10^{-2}$	$-.18929494 \times 10^{-3}$
5	$-.88795470 \times 10^{-3}$	$.29825920 \times 10^{-4}$

i	$g'_i$	$h'_i$
1	$.57543820 \times 10^{-5}$	$-.51385180 \times 10^{-6}$
2	$-.12173010 \times 10^{-4}$	$.11369213 \times 10^{-5}$
3	$.13115427 \times 10^{-4}$	$.12215824 \times 10^{-5}$
4	$-.77296580 \times 10^{-5}$	$.66585509 \times 10^{-6}$
5	$.11560088 \times 10^{-5}$	$-.99281026 \times 10^{-7}$

i	$i'_i$
1	$.99210520 \times 10^{-8}$
2	$-.21370423 \times 10^{-7}$
3	$.22689529 \times 10^{-7}$
4	$-.12166405 \times 10^{-7}$
5	$.17857381 \times 10^{-8}$

## CHAPTER IV

### EQUATION OF STATE CORRELATION

As mentioned earlier, Equation II-5 can be integrated with the help of an equation of state and Stuckey's liquid volume equation from Appendix D. Rearranging Equation II-5 gives

$$\ln \theta + \int_{P^\circ}^P \frac{V^L}{RT} dP = \ln \theta^* = \int_{P^\circ}^P \frac{V^V}{RT} dP - \int_{P^\circ}^P \frac{dP}{P} \quad (\text{IV-1})$$

which after substitution of  $d(PV) = PdV + VdP$  becomes

$$\ln \theta^* = \left[ \frac{PV}{RT} \right]_{P^\circ}^P - \int_{V^\circ}^V \frac{PdV}{RT} - \ln \frac{P}{P^\circ} \quad (\text{IV-2})$$

Three equations of state were substituted into Equation (IV-2) and integrated.

#### Redlich-Kwong Equation

Substitution of the well-known Redlich-Kwong equation into Equation IV-2 yields

$$\ln \theta^* = (Z - Z^\circ) - \ln \frac{P}{P^\circ} - \int_{V^\circ}^V \frac{dV}{V - b} - \frac{a}{RT^{1.5}} \int_{V^\circ}^V \frac{dV}{V(V+b)} \quad (\text{IV-3})$$

Integration and substitution of  $h = \frac{b}{V}$  gives

$$\ln \theta^* = (Z - Z^\circ) - \ln \frac{P}{P^\circ} - \ln \left( \frac{V(1-h)}{V^\circ(1-h^\circ)} \right) - \frac{A^2}{B} \ln \left( \frac{1+h}{1+h^\circ} \right) \quad (\text{IV-4})$$

where

$$\frac{A^2}{B} = \frac{a}{bRT^{1.5}} = \frac{4.933}{T_r^{1.5}}$$

$Z$  is compressibility factor at system  $T_r$  and  $P_r$  and  $Z^\circ$  is at system  $T_r$  and vapor pressure. Note that

$$\frac{V}{V^\circ} = \frac{ZP^\circ}{PZ^\circ}$$

so that substitution and simplification gives

$$\ln \theta^* = Z - Z^\circ + \ln \left( \frac{1-h^\circ}{1-h} \right) + \frac{A^2}{B} \ln \left( \frac{1+h^\circ}{1+h} \right) - \ln \frac{Z}{Z^\circ} \quad (\text{IV-5})$$

Subtracting the Poynting effect in generalized form gives

$$\ln \theta = \ln \theta^* - \frac{V_r}{T_r} (P_r - P_r^\circ) \quad (\text{IV-6})$$

Using Equation IV-6 ideal  $K$  can be evaluated on a generalized basis. The imperfection pressure corrections have been calculated for two binary systems and are compared with values calculated by other methods in Table VI. Columns 1 and 2 in Table VI are the reduced temperature and reduced pressure of the component respectively. Column three shows the corresponding values of  $\ln \theta$  obtained in this work and tabulated in Appendix C. Columns four and five present  $\ln \theta$  values calculated by the Redlich-Kwong and Benedict-Webb-Rubin equations, respectively. Column six shows the Poynting effect calculated by use of Stuckey's vapor pressure and liquid volume equations in Appendix D.

Although the Redlich-Kwong Equation is the best two constant equation available (11), it does not perform sufficiently well over the full  $T_r$  and  $P_r$  range employed in this work. Moreover, it does not utilize the acentric factor for component description. Consequently, it was decided to modify

TABLE VI

IMPERFECTION PRESSURE CORRECTION COMPARISON  
FOR ETHANE - N-PENTANE SYSTEM

$T_r$	$P_r$	ln $\theta$ From			
		Pressure Series Charts Table C-I	Redlich Kwong Eq. IV-5 and IV-6	Benedict Webb Rubin for ln $\theta^*$ and Eq. IV-6	Poynting Effect Last term of Eq. IV-6
0.908	.070	.296	.3065	.3244	-.0588
	.209	.215	.2239	.2375	-.0418
	.348	.149	.1373	.1458	-.0248
1.126	.139	.597	.6882	.6966	-.1906
	.418	.508	.5892	.5971	-.1611
	.696	.422	.4874	.4955	-.1316
	.975	.337	.3824	.3893	-.1020
	1.253	.255	.2736	.2804	-.0725
1.344	.278	.863	.8781	.8766	-.4060
	.417	.830	.8453	.8448	-.3927
	.696	.770	.7797	.7809	-.3662
	1.253	.657	.6487	.6412	-.3131
.590	.101	- .205	- .161	- .163	.015
	.304	- .625	-2.883	-2.989	.047
	.506	-1.014	-3.389	-3.506	.079
.732	.202	- .118	- .123	- .143	.016
	.607	- .502	-1.600	-1.683	.070
	1.012	- .803	-2.097	-2.199	.125
	1.416	-1.036	-2.422	-2.531	.180
	1.821	-1.270	-2.661	-2.783	.234
.873	.405	- .020	- .014	- .034	.002
	.607	- .148	- .306	- .329	.026
	1.012	- .383	- .836	- .904	.075
	1.821	- .750	-1.386	-1.482	.171

the Redlich-Kwong equation by introducing a small correction factor that will account for shortcomings in the Redlich-Kwong equation.

#### Modified Redlich-Kwong Equation

If the generalized Redlich-Kwong equation is expanded into virial form in terms of ideal reduced density,  $d_r$ , the term that corresponds to the second virial coefficient is

$$b_{\text{RK}} = .0867 - \frac{.4278}{T_r^{1.5}} \quad (\text{IV-7})$$

Subtracting this expression from the generalized second virial coefficient of Pitzer,  $b_p$ , (12) gives  $\Delta b = b_p - b_{\text{RK}}$  which is then added to the Redlich-Kwong equation to give

$$Z = \frac{h}{1-h} - \frac{A^2 h}{B(1+h)} + \frac{\Delta b h}{.0867} \quad (\text{IV-8})$$

Compressibility factors were calculated at various  $T_r$ ,  $P_r$ , and  $\omega$  values and compared against those given by Pitzer (12). Equation IV-8 compared more favorably with Pitzer's Z's than the Redlich-Kwong equation at the higher acentric factors, but not at 0.0 acentric factor. However, the improvement still is not sufficiently good. Some values are tabulated in Table VII.

An equation for  $\ln \theta^*$  can be derived from Equation IV-8 in the same manner as for the Redlich-Kwong equation. The result is the same except for the last term:

$$\ln \theta^* = Z - Z^\circ + \ln \frac{Z^\circ}{Z} + \ln \frac{1-h^\circ}{1-h} + \frac{A^2}{B} \ln \left( \frac{1+h^\circ}{1+h} \right) + \frac{\Delta b (h-h^\circ)}{.0867} \quad (\text{IV-9})$$

This equation is poor, however, because it does not always converge for mixtures as well as the Redlich-Kwong equation. It must



TABLE VII

## COMPRESSIBILITY FACTORS

$T_r$	$P_r$	RK Equation		Eq. IV-8 RK + $\Delta b$		Pitzer Tables	
		$\omega = 0.0$	$\omega = 0.4$	$\omega = 0.0$	$\omega = 0.4$	$\omega = 0.0$	$\omega = 0.4$
.8	.2	.8557	.8557	.8568	.8016	.8510	.8130
.8	1.2	.1972	.1972	.1983	.1676	.1920	.1600
.8	3.0	.4666	.4666	.4685	.4116	.4610	.3890
.8	5.0	.7467	.7467	.7489	.6749	.7460	.6420
.8	9.0	1.2742	1.2742	1.2768	1.1847	1.2800	1.1320
1.4	.2	.9755	.9755	.9763	.9829	.9770	.9834
1.4	1.2	.8574	.8574	.8634	.9108	.8590	.8990
1.4	3.0	.7375	.7375	.7532	.8695	.7200	.8000
1.4	5.0	.8003	.8003	.8156	.9410	.7810	.8250
1.4	9.0	1.0689	1.0689	1.0816	1.1941	1.0710	1.0670
2.0	.2	.9937	.9937	.9945	1.0011	.9950	1.0014
2.0	1.2	.9678	.9678	.9728	1.0129	.9710	1.0110
2.0	3.0	.9486	.9486	.9610	1.0547	.9520	1.0360
2.0	5.0	.9693	.9693	.9874	1.1224	.9720	1.0920
2.0	9.0	1.0952	1.0952	1.1171	1.2883	1.1060	1.2860
3.0	.2	1.0003	1.0003	1.0013	1.0057	1.0010	1.0050
3.0	1.2	1.0040	1.0040	1.0097	1.0352	1.0070	1.0350
3.0	3.0	1.0185	1.0185	1.0319	1.0908	1.0280	1.0960
3.0	5.0	1.0451	1.0451	1.0658	1.1546	1.0580	1.1700
3.0	9.0	1.1229	1.1229	1.536	1.2838	1.1500	1.1350

be added that it is impractical to add more terms to Equation IV-8 because the averaging rules would require taking square roots of negative numbers when it is applied to mixtures.

Benedict, Webb, and Rubin Equation

One of the better equations of state is the Benedict, Webb, and Rubin equation (11). It has one disadvantage relative to the Redlich-Kwong equation in that it has more than two constants. An equation for fugacity coefficients was derived from it by Benedict, Webb, and Rubin (13). This equation was used to calculate  $\ln \Theta$  values which are compared against others in Table VI. Like the Redlich-Kwong equation, the Benedict, Webb, and Rubin equation of state is not a function of acentric factor and therefore cannot fit Pitzer's Z tables in its present form.

The BWR equation is

$$P = RTd + \left( B_o RT - A_o - \frac{C_o}{T^2} \right) d^2 + (bRT - a) d^3 + \alpha d^6 + \frac{cd^2}{T^2} (1 + \gamma d^2) e^{-\gamma d^2} \quad (\text{IV-10})$$

where  $d$  is the density and  $A_o$ ,  $B_o$ ,  $C_o$ ,  $a$ ,  $b$ ,  $c$ ,  $\alpha$ , and  $\gamma$  are the eight constants which are to be determined for each substance.

## CHAPTER V

### DISCUSSION OF RESULTS

#### Pressure Series Correlation

The coefficients obtained by the method described in the first part of Chapter III failed to reproduce the original  $K^*$  curves well enough. It failed in two respects. First, for the low isotherms the back-calculated values on a  $\log K^*$  vs.  $\log P_r$  plot deviated enough to make the isotherms cross each other at some points. The second failure point was that relative maximums and minimums resulted in the lower isotherm region. This, of course, was completely unacceptable.

No doubt several reasons contributed to the failure, but the main one was probably the smoothing of coefficients. The coefficients presented in Table I were smoothed vs.  $T_r$  and  $\omega$  graphically. Curve fitting the smoothed values did not correct for any deviations, of course.

To decrease the curvature of the isotherms to be fitted with equations, the procedure described in the last part of Chapter III was developed. More terms were added to the curve fit model. The original  $K^*$  values for the ideal fluid were reproduced within 5 percent except for the  $T_r = 1.8$  and  $2.0$  isotherms where they were off by more than 10 percent. The  $F'(P_r)$  values were not reproduced as well, however, and therefore

the  $K^*$  calculated for higher acentric factors were completely inaccurate. Table VIII shows original and back-calculated  $F^\circ(P_r)$  and  $F'(P_r)$  values.

Once again most of the trouble was due to the excessive smoothing required in obtaining  $F^\circ(P_r)$  and  $F'(P_r)$  values. This was particularly true in the case of the prime values. Consequently, it is not surprising that  $K^*$  calculated for higher acentric factors are more unreasonable than for  $\omega = 0$ .

Even if no smoothing had been required, the results probably would have been unsatisfactory. Table VIII demonstrates the inability of the curve fitted equations to reproduce the original values. This is partly due to the truncation error introduced by the computer.

#### Equations of State Correlations

As demonstrated in Chapter IV the Redlich-Kwong and the Benedict-Webb-Rubin equations of state may be used to calculate  $\ln \Theta$  and  $\ln \Theta^*$  values. The  $\ln \Theta$  values thus calculated are compared in Table VI. The use of these equations does not always give accurate  $K$  values, however. This can be attributed to the inability of these equations to reproduce PVT data sufficiently accurately at the higher pressures and reduced temperatures below unity. Integration to obtain  $\ln \Theta$  values increases any inherent errors.

In Table IX are presented  $\ln \Theta$  values covering a wide range of temperature and pressure. Values calculated from the Redlich-Kwong and Benedict-Webb-Rubin equations of state are compared against those taken from Table C-I. Results from the two

TABLE VIII

ORIGINAL AND BACK-CALCULATED  $F(P_r)$  VALUES

$T_r$	$P_r$	$F^0$		$F'$	
		Original	Back-Calc.	Original	Back-Calc.
.6	1	0.423	0.394	0.800	0.789
	3	0.822	0.829	1.613	1.615
	5	0.984	1.003	1.883	1.889
	10	1.163	1.155	2.015	2.011
	20	1.309	1.298	2.075	2.100
1.1	1	.0150	.0265	-.007	.006
	3	.0455	.0794	-.014	.014
	5	.0765	.1271	-.015	.019
	10	.1440	.2120	-.021	.021
	20	.2150	.2940	-.025	.007
2.0	1	.00125	.0056	-.023	-.022
	3	.00375	.0097	-.040	-.038
	5	.00625	.0093	-.046	-.039
	10	.01250	.0082	-.057	-.047
	20	.0275	.0219	-.077	-.004

TABLE IX  
COMPARISON OF IMPERFECTION PRESSURE  
CORRECTION LN  $\theta$

$T_r$	$P_r$	Ethane			
		From Table C-I	From RK eq. of state	From BWR eq. of state	Poynting Effect last term of eq. IV-6
.6	2	-2.024	-4.550	-4.812	0.326
	3	-2.529	-4.941	-5.207	0.490
	5	-3.295	-5.427	-5.697	0.819
	10	-4.531	-6.079	-6.353	1.641
	20	-5.775	-6.745	*	3.285
1.0	2	-0.405	-0.609	-0.632	0.114
	3	-0.718	-0.964	-1.000	0.229
	5	-1.194	-1.406	-1.454	0.458
	10	-1.976	-2.012	-2.060	1.030
	20	-2.760	-2.674	-2.691	2.174
2.0	2	1.250	1.137	1.036	-1.325
	3	1.162	1.040	0.945	-1.248
	5	0.978	0.863	0.780	-1.094
	10	0.532	0.502	0.450	-0.710
	20	-0.082	-0.037	-0.034	0.060

\* - did not converge

TABLE IX (Continued)

N-Pentane					
$T_r$	$P_r$	From Table C-I	From RK eq. of state	From BWR eq. of state	Poynting Effect last term of eq. IV-6
.6	2	-2.358	-4.547	-5.354	0.311
	3	-2.938	-4.930	-5.751	0.468
	5	-3.794	-5.400	-6.250	0.780
	10	-5.085	-6.011	-6.922	1.562
	20	-6.345	-6.597	*	3.126
1.0	2	-0.405	-0.603	-0.639	0.109
	3	-0.718	-0.952	-1.008	0.218
	5	-1.194	-1.384	-1.466	0.435
	10	-1.976	-1.962	-2.075	0.980
	20	-2.760	-2.568	-2.696	2.068
2.0	2	1.499	1.442	1.193	-1.916
	3	1.426	1.349	1.120	-1.842
	5	1.264	1.180	0.984	-1.696
	10	0.867	0.837	0.707	-1.330
	20	0.295	0.335	0.287	-0.598

\* - did not converge

equations of state deviate rather markedly from the latter. The data of Table IX are presented in graphical form on Figure 4 for ethane and Figure 5 for n-pentane. As discussed earlier the isotherms should pass through the point  $\ln \Theta = 0.0$  at the vapor pressure or extrapolated vapor pressure. Examination of Figures 4 and 5 shows that the values taken from Table C-I do very nearly so in every case. However, values calculated by the RK equation tend to deviate from this condition, especially at the lower  $T_r$  values. Values from the BWR equation were not plotted because they are very similar to the RK values. The same trends can be observed in Table VI which shows  $\ln \Theta$  calculated for two compounds. On the basis of the above observations it can be said that  $\ln \Theta$  and therefore  $K^*$  values generated in this work appear to be more reliable and consistent than ones calculated by the best equations of state available.

#### Vapor Activity Coefficients

In Table X activity coefficients for ethane calculated by several methods are compared with each other. The same type of data are presented for n-pentane in Table IX. For both liquid and vapor, column three was calculated from  $K^*$  charts developed in this work, and column four from  $K^*$  calculated by the Redlich-Kwong equation. The Scatchard-Hildebrand equation was used to calculate  $\gamma^L$  and the Redlich-Kwong equation to calculate  $\gamma^V$  for these columns. The values were used as indicated in Table X. Column five shows  $\gamma^V$  calculated directly from the Redlich-Kwong equation and  $\gamma^L$  directly from the Scatchard-Hildebrand equation.



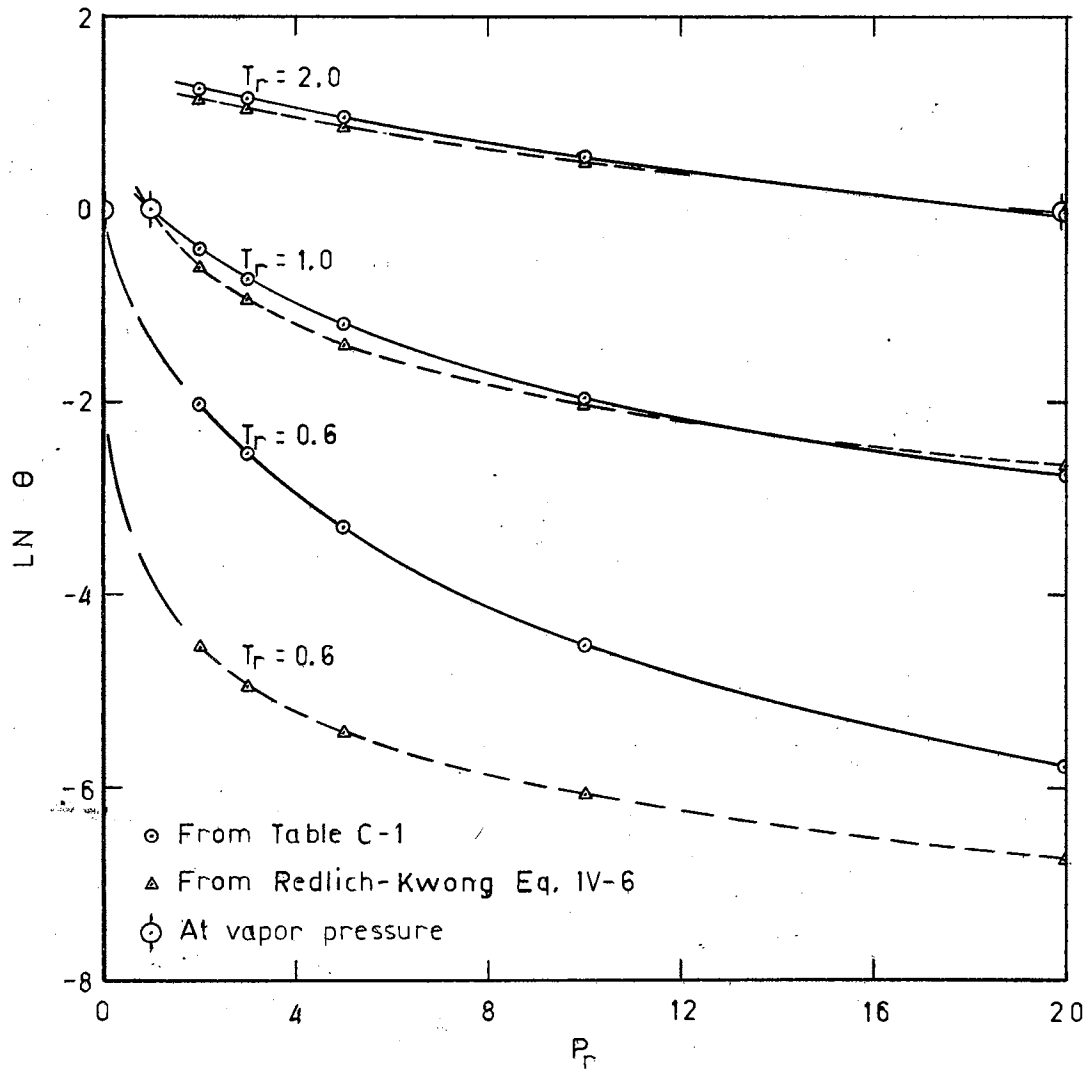


FIGURE 4  
IMPERFECTION PRESSURE CORRECTION VS  $P_r$  FOR  
ETHANE

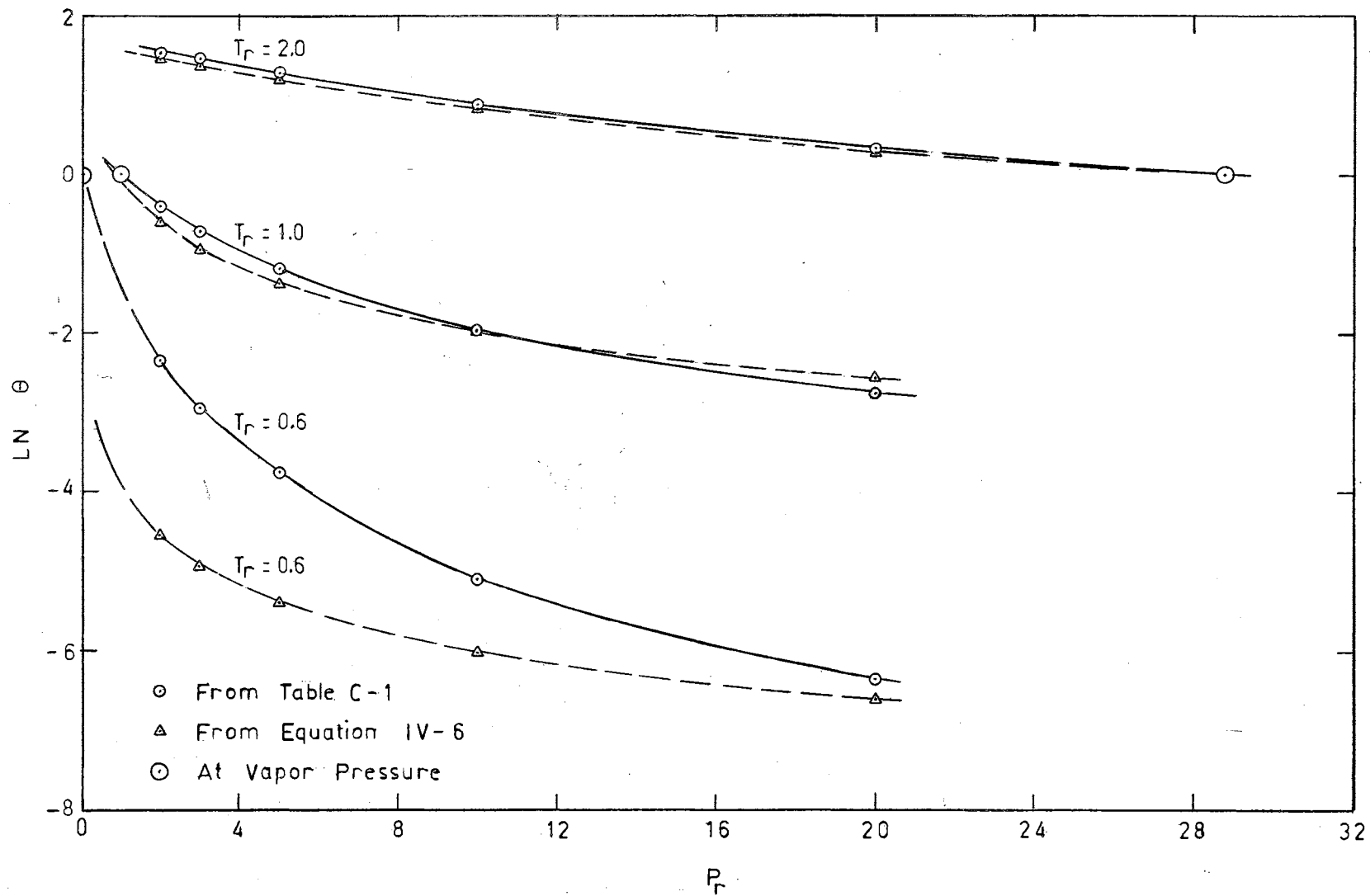


FIGURE 5  
IMPERFECTION PRESSURE CORRECTION VS REDUCED PRESSURE FOR N-PENTANE

TABLE X

VAPOR AND LIQUID ACTIVITY COEFFICIENTS FOR  
ETHANE IN N-PENTANE

$P_r$	$y$	Vapor Activity Coefficients			
		Method 1	Method 2	Method 3	Method 4
.278	.9134	1.148	.979	1.001	1.002
	.4820	1.295	1.107	1.030	1.050
	.0481	1.455	1.320	1.097	1.161
.696	.8909	1.169	.999	1.006	1.009
	.5402	1.439	1.321	1.067	1.095
	.2698	1.656	1.647	1.172	1.242
.974	.9854	1.058	.984	1.001	1.001
	.9091	1.163	1.010	1.008	1.014
	.8002	1.290	1.139	1.026	1.036
	.3359	2.090	2.038	1.329	1.398
$P_r$	$x$	Liquid Activity Coefficients			
		Method 1	Method 2	Method 3	
.278	.3201	.947	1.112	1.087	
	.0947	.882	1.032	1.109	
	.0084	.843	.927	1.115	
.696	.4940	.907	1.062	1.054	
	.2197	.805	.877	1.086	
	.1070	.778	.781	1.097	
.974	.9274	.924	1.019	1.002	
	.6579	.893	1.028	1.030	
	.4886	.835	.947	1.051	
	.2216	.685	.705	1.082	

## Vapor

Method 1 -  $K^*$  from charts,  $\gamma^L$  from Scatchard-Hildebrand equation.

Method 2 -  $K^*$  from RK eq.,  $\gamma^L$  from Scatchard-Hildebrand equation.

Method 3 - direct calculation from RK equation.

Method 4 - direct calculation from BWR equation.

## Liquid

Method 1 -  $K^*$  from charts,  $\gamma^V$  from RK equation.

Method 2 -  $K^*$  from RK eq.,  $\gamma^V$  from RK equation.

Method 3 - direct calculation from Scatchard-Hildebrand equation.

Data from (14).

TABLE XI  
 VAPOR AND LIQUID ACTIVITY COEFFICIENTS FOR  
 N-PENTANE IN ETHANE

$P_r$	y	Vapor Activity Coefficients			
		Method 1	Method 2	Method 3	Method 4
.405	.0866	1.086	3.749	5.388	6.503
	.5180	1.014	1.024	1.038	1.094
	.1519	1.021	1.006	1.000	1.041
1.012	.1091	.924	3.291	3.694	4.797
	.4508	.954	1.495	1.535	1.678
	.7302	.979	1.160	1.149	1.201
1.416	.0146	.563	3.479	4.255	4.761
	.0909	.734	2.723	3.313	4.051
	.1998	.839	2.043	2.279	2.376
	.6641	.847	1.085	1.141	1.188
$P_r$	x	Liquid Activity Coefficients			
		Method 1	Method 2	Method 3	
.405	.6799	5.036	1.148	1.010	
	.9053	1.025	1.015	1.001	
	.9916	.980	.995	1.000	
1.012	.5060	4.189	1.154	1.027	
	.7803	1.624	1.031	1.004	
	.8930	1.177	.991	1.001	
1.416	.0726	10.689	1.473	1.204	
	.3421	4.997	1.290	1.060	
	.5114	2.847	1.144	1.025	
	.7784	1.366	1.056	1.003	

See Table IX for explanation of method and for data reference.

Column six shows  $\gamma^V$  calculated directly from the Benedict-Webb-Rubin equation.

As shown above,  $K^*$  values developed in this work seem to be more consistent than those calculated by equations of state. Thus the activity coefficients from column three can be used to give an indication of whether the liquid or the vapor activity coefficients are in greater need of improvement. If the activity coefficients are plotted vs. mole fraction, they tend to  $\gamma = 1.0$  as mole fraction goes to 1.0. Then, if activity coefficients for one phase consistently approach unity closer than for the other, it must mean that the other phase is predicted more closely because it was used to calculate the phase being plotted. Table X is presented as Figures 6 and 7 and Table XI as Figures 8 and 9. Examination of these graphs indicates that the liquid activity coefficients for both compounds approach unity closer than the vapor activity coefficients. That means that at least for the system and conditions under consideration the Redlich-Kwong equation predicts vapor activity coefficients more closely than the Scatchard-Hildebrand equation predicts the liquid activity coefficients. However, both equations could be and probably are in error, but the degree varies.

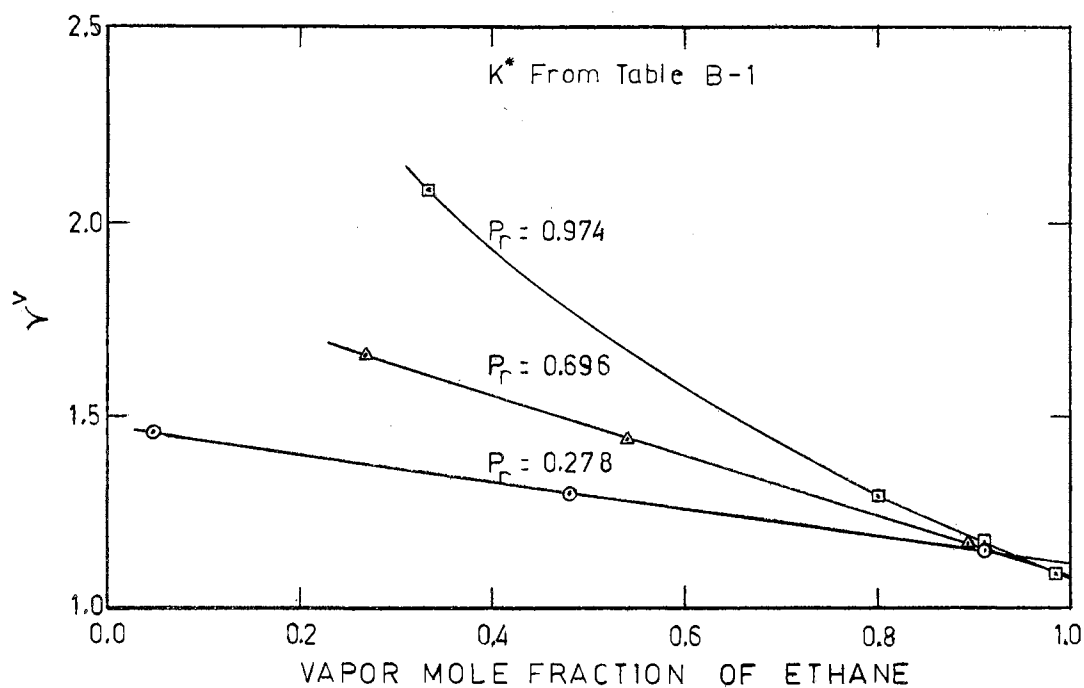


FIGURE 6  
VAPOR ACTIVITY COEFFICIENTS OF ETHANE  
IN N-PENTANE

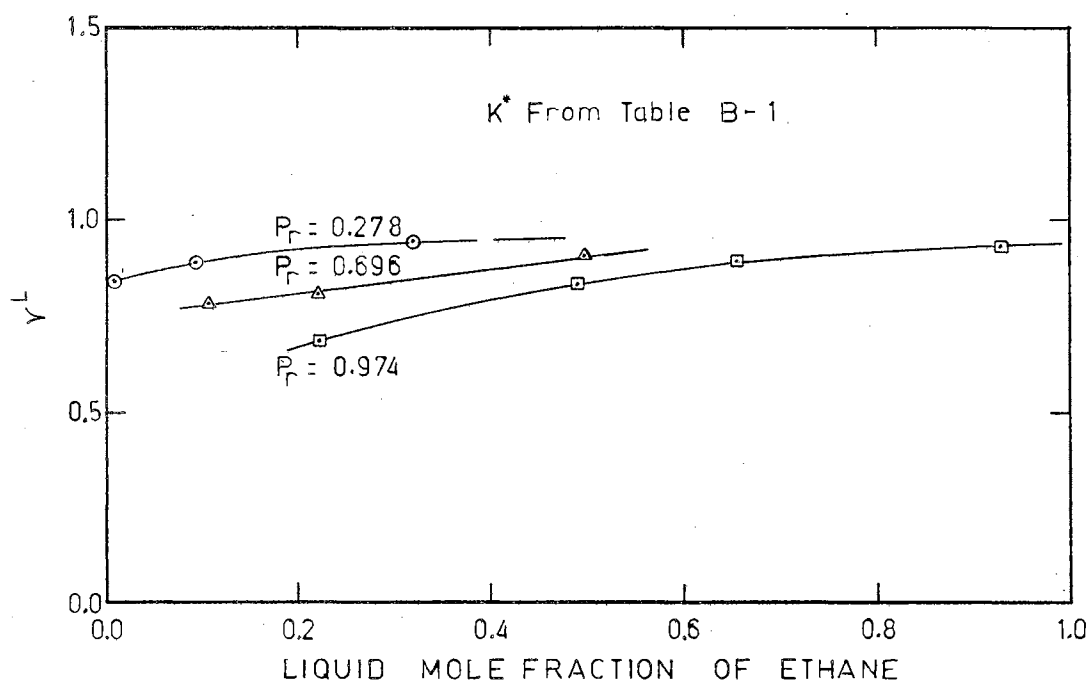


FIGURE 7  
LIQUID ACTIVITY COEFFICIENTS OF ETHANE  
IN N-PENTANE

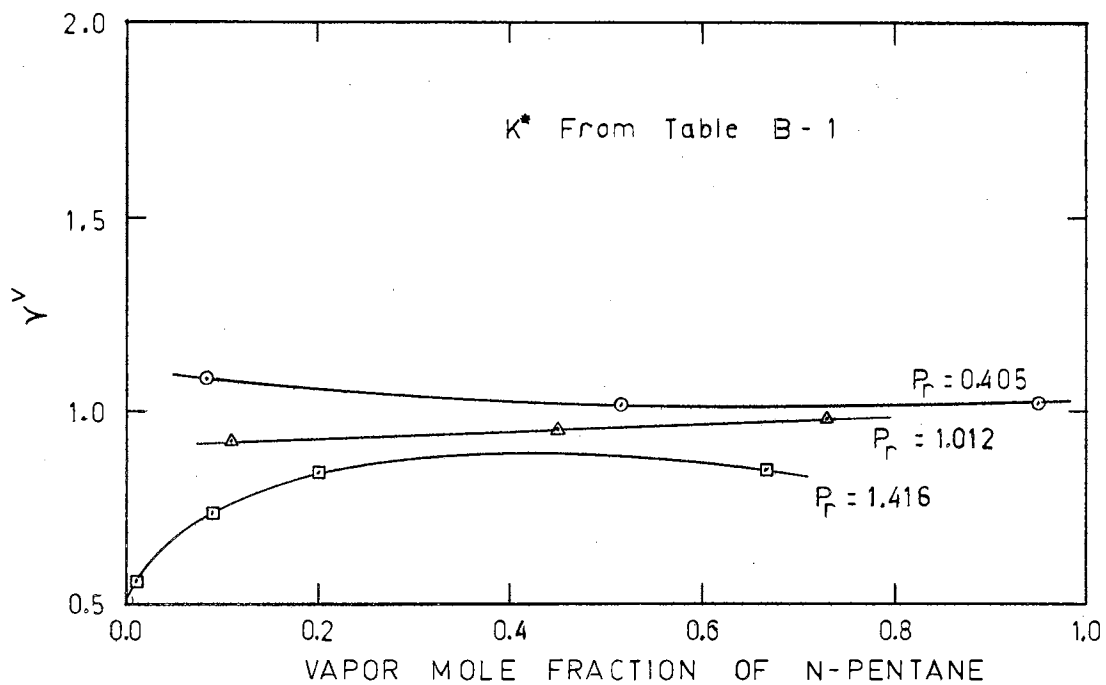


FIGURE 8  
VAPOR ACTIVITY COEFFICIENTS OF N-PENTANE  
IN ETHANE

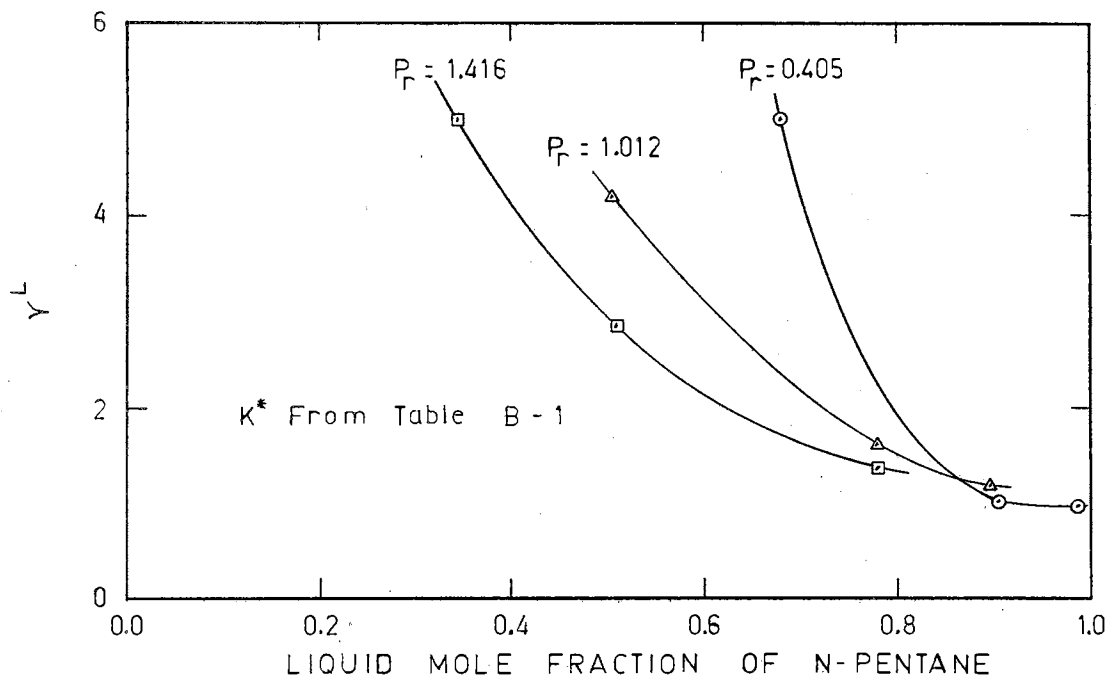


FIGURE 9  
LIQUID ACTIVITY COEFFICIENTS OF N-PENTANE  
IN ETHANE

## CHAPTER VI

### CONCLUSIONS AND RECOMMENDATIONS

#### Conclusions

The major points of this study may be summarized as follows:

1. The  $K^*$  concept for correlating  $K$  values is sound. Because of the extreme curvature of the  $K^*$  isotherms they are difficult to correlate by curve fitting, especially over a wide  $P_r$  and  $T_r$  range.
2. The imperfection pressure correction also is difficult to correlate by curve fitting. Computer truncation errors and excessive smoothing required to obtain coefficients causes difficulties. Dividing the reduced temperature and pressure range into smaller areas for curve fitting purposes helps but not sufficiently if the number of such areas is to be kept to a reasonable value.
3. The best equations of state available at the present cannot always be relied upon, especially at  $T_r$  values below unity. Inherent errors are compounded by integration necessary to calculate  $\ln \Theta$  and  $\gamma^V$  values. Equations for calculating liquid activity coefficients are also not always to be trusted.



### Recommendations

1. A model for  $\ln \Theta$  should be found. Once the  $\ln \Theta$  values generated in this work have been curve fitted with a suitable model, ideal K can be calculated.
2. The Redlich-Kwong equation should be used to calculate vapor activity coefficients. Combining it with experimental K data and ideal K from above would give liquid activity coefficients at various conditions.
3. The liquid activity coefficient data should be curve fitted with an equation in generalized form. A model similar to the Black Equation (16) would probably be the most suitable.

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## APPENDIX A

### NOMENCLATURE

- A - parameter in Redlich-Kwong equation of state
- a - parameter in Redlich-Kwong equation of state
  - parameter in the pressure series equation
- B - parameter in Redlich-Kwong equation
  - second virial coefficient, volume/mole
- b - parameter in Redlich-Kwong equation
  - parameter in Benedict-Webb-Rubin equation of state
  - parameter in the pressure series equation
  - generalized second virial coefficient
- C - third virial coefficient
- c - parameter in the pressure series equation
- D - fourth virial coefficient
- d - parameter in the pressure series equation
- e - parameter in the pressure series equation
- f - fugacity, force/area
- F - pressure series parameter
- h - parameter in Redlich-Kwong equation
- i - parameter in the pressure series equation
- K - vapor liquid equilibrium phase distribution ratio,  $y/x$
- P - system pressure, force/area
- $P^0$  - vapor pressure, force/area
- R - universal gas constant

## APPENDIX A (Continued)

- T - temperature
- V - volume
- v - parameter in liquid volume equation
- X - parameter in the pressure series equation
- x - liquid mole fraction
- y - vapor mole fraction
- z - compressibility factor,  $PV/RT$

## Greek Symbols

- $\alpha$  - parameter in Benedict-Webb-Rubin equation
- $\beta$  - reduced second virial coefficient
- $\gamma$  - activity coefficient
- parameter in BWR equation
- $\theta$  - imperfection pressure correction
- $\omega$  - acentric factor

## Subscripts

- o - quantity at zero acentric factor
- $\omega$  - quantity at other than zero acentric factor
- A - term containing all vapor pressures in Eq. III-13
- B - term in Eq. III-15
- C - intercept term of imperfection pressure correction
- c - critical property
- i - component i
- k - convergence property

## APPENDIX A (Continued)

- r - reduced property
- T - property evaluated at system temperature

## Superscripts

- \* - ideal fluid property
- ° - simple fluid property
- ' - correction to simple fluid
- L - liquid phase
- V - vapor phase

## Abbreviations

- BWR - Benedict-Web-Rubin
- RK - Redlich-Kwong
- log - logarithm to base 10
- ln - logarithm to base e
- SH - Scatchard-Hildebrand

APPENDIX B  
IDEAL K TABLES

TABLE B

SMOOTHED IDEAL K VALUES  
CALCULATED BY EQUATIONS  
D-11 AND II-2

$P_r$	$T_r = .6$			$T_r = .65$			$T_r = .7$			$T_r = .75$		
	$\omega = .0$	$\omega = .2$	$\omega = .4$	$\omega = .0$	$\omega = .2$	$\omega = .4$	$\omega = .0$	$\omega = .2$	$\omega = .4$	$\omega = .0$	$\omega = .2$	$\omega = .4$
.01	2.720	1.270	.590	5.25	2.940	1.640	9.11	5.91	3.810	14.52	10.59	7.69
.02	1.380	.650	.300	2.66	1.490	.840	4.60	2.99	1.930	7.33	5.35	3.89
.04	.710	.340	.160	1.36	.770	.430	2.35	1.53	1.000	3.73	2.73	1.99
.07	.430	.210	.098	.81	.460	.260	1.39	.91	.590	2.19	1.61	1.18
.10	.310	.150	.073	.59	.340	.190	1.00	.66	.430	1.57	1.16	.85
.20	.180	.093	.047	.33	.200	.120	.54	.36	.240	.86	.64	.48
.40	.120	.066	.037	.21	.130	.081	.330	.23	.160	.50	.39	.29
.70	.094	.058	.034	.16	.105	.066	.240	.17	.120	.35	.28	.22
1.00	.086	.056	.035	.14	.096	.061	.210	.15	.110	.29	.24	.19
2.00	.082	.060	.042	.12	.085	.056	.180	.13	.099	.25	.21	.17
3.00	.087	.070	.054	.13	.088	.059	.180	.13	.100	.25	.21	.18
4.00	.094	.082	.070	.14	.095	.065	.190	.14	.110	.26	.22	.19
5.00	.105	.095	.085	.15	.100	.071	.210	.16	.120	.27	.24	.21
6.00	.120	.110	.100	.16	.110	.078	.220	.17	.130	.29	.26	.23
7.00	.140	.130	.120	.18	.130	.088	.240	.19	.150	.32	.28	.25
8.00	.155	.150	.145	.20	.150	.100	.270	.22	.170	.34	.31	.27
10.00	.220	.215	.210	.27	.200	.150	.350	.29	.240	.41	.37	.33
12.00	.350	.340	.330	.40	.320	.240	.490	.43	.380	.54	.49	.45
15.00	1.000	1.000	1.000	1.00	1.000	1.000	1.000	1.00	1.000	1.00	1.00	1.00



TABLE B (Continued)

$P_r$	$T_r = .8$			$T_r = .85$			$T_r = .9$			$T_r = .95$		
	$\omega = .0$	$\omega = .2$	$\omega = .4$	$\omega = .0$	$\omega = .2$	$\omega = .4$	$\omega = .0$	$\omega = .2$	$\omega = .4$	$\omega = .0$	$\omega = .2$	$\omega = .4$
.01	21.58	17.28	13.80	30.28	26.11	22.49	40.50	37.03	33.89	52.09	49.89	47.81
.02	10.87	8.71	6.97	15.24	13.15	11.33	20.37	18.63	17.04	26.18	25.08	24.04
.04	5.52	4.43	3.55	7.72	6.67	5.75	10.30	9.43	8.63	13.22	12.67	12.15
.07	3.23	2.60	2.09	4.50	3.89	3.37	5.99	5.49	5.03	7.67	7.36	7.06
.10	2.31	1.87	1.50	3.21	2.78	2.41	4.27	3.91	3.59	5.45	5.23	5.02
.20	1.25	1.01	.82	1.72	1.49	1.30	2.26	2.08	1.91	2.87	2.76	2.65
.40	.73	.60	.49	.98	.87	.77	1.27	1.17	1.09	1.59	1.54	1.49
.70	.50	.42	.36	.69	.61	.55	.85	.80	.74	1.06	1.02	.98
1.00	.41	.35	.30	.57	.51	.46	.69	.65	.60	.85	.83	.80
2.00	.33	.29	.25	.44	.40	.37	.54	.51	.47	.65	.63	.61
3.00	.32	.29	.25	.41	.38	.35	.50	.47	.44	.60	.58	.56
4.00	.33	.29	.26	.41	.38	.35	.49	.46	.44	.59	.57	.55
5.00	.34	.31	.28	.42	.39	.36	.50	.47	.45	.59	.57	.56
6.00	.36	.33	.30	.44	.41	.38	.52	.49	.47	.60	.59	.57
7.00	.39	.36	.33	.47	.44	.41	.55	.52	.50	.61	.60	.59
8.00	.42	.39	.36	.50	.47	.44	.58	.55	.53	.64	.63	.62
10.00	.50	.47	.43	.58	.54	.51	.65	.62	.60	.72	.71	.70
12.00	.63	.60	.57	.70	.66	.63	.76	.74	.72	.81	.81	.81
15.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

TABLE B (Continued)

$P_r$	$T_r = 1.00$			$T_r = 1.05$			$T_r = 1.10$			$T_r = 1.15$		
	$\omega = .0$	$\omega = .2$	$\omega = .4$	$\omega = .0$	$\omega = .2$	$\omega = .4$	$\omega = .0$	$\omega = .2$	$\omega = .4$	$\omega = .0$	$\omega = .2$	$\omega = .4$
.01	64.85	64.45	64.05	78.61	80.79	82.96	93.19	98.45	103.80	108.50	117.20	126.20
.02	32.57	32.37	32.18	39.46	40.56	41.65	46.76	49.40	52.07	54.41	58.78	63.28
.04	16.43	16.34	16.24	19.89	20.44	20.99	23.55	24.88	26.21	27.38	29.58	31.83
.07	9.52	9.46	9.41	11.51	11.82	12.14	13.61	14.37	15.14	15.80	17.06	18.36
.10	6.75	6.72	6.68	8.15	8.38	8.60	9.63	10.16	10.71	11.17	12.06	12.97
.20	3.53	3.51	3.50	4.24	4.36	4.48	4.99	5.27	5.54	5.77	6.22	6.68
.40	1.93	1.92	1.92	2.30	2.36	2.42	2.68	2.82	2.97	3.08	3.31	3.55
.70	1.26	1.25	1.25	1.48	1.51	1.55	1.70	1.79	1.88	1.94	2.07	2.22
1.00	1.00	1.00	1.00	1.16	1.19	1.22	1.32	1.39	1.45	1.49	1.59	1.69
2.00	.75	.75	.75	.83	.84	.85	.92	.95	.98	1.00	1.06	1.12
3.00	.68	.68	.68	.75	.76	.78	.82	.85	.88	.88	.92	.97
4.00	.66	.66	.66	.73	.74	.75	.80	.83	.85	.85	.88	.92
5.00	.66	.67	.68	.73	.74	.75	.79	.82	.84	.84	.87	.90
6.00	.67	.68	.69	.74	.75	.76	.80	.82	.84	.84	.86	.88
7.00	.69	.70	.71	.76	.77	.78	.82	.84	.85	.85	.87	.89
8.00	.71	.73	.75	.78	.79	.80	.84	.85	.87	.86	.88	.90
10.00	.77	.79	.81	.83	.84	.85	.89	.90	.91	.90	.91	.92
12.00	.85	.87	.89	.89	.90	.91	.94	.94	.95	.94	.95	.95
15.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

TABLE B (Continued)

$P_r$	$T_r = 1.2$			$T_r = 1.3$			$T_r = 1.4$			$T_r = 1.5$		
	$\omega = .0$	$\omega = .2$	$\omega = .4$	$\omega = .0$	$\omega = .2$	$\omega = .4$	$\omega = .0$	$\omega = .2$	$\omega = .4$	$\omega = .0$	$\omega = .2$	$\omega = .4$
.01	124.30	136.90	150.00	157.40	178.50	201.40	191.90	222.70	257.70	227.50	268.90	318.30
.02	62.34	68.62	65.19	68.90	89.46	100.90	96.17	111.60	129.10	114.00	134.70	159.40
.04	31.36	34.51	37.80	39.65	44.94	50.67	48.29	56.00	64.75	57.19	67.56	79.92
.07	18.08	19.89	21.77	22.83	25.86	29.14	27.77	32.19	37.19	32.86	38.80	45.86
.10	12.77	14.04	15.36	16.10	18.23	20.53	19.57	22.66	26.16	23.13	27.29	32.24
.20	6.58	7.22	7.89	8.25	9.32	10.48	9.99	11.55	13.31	11.78	13.87	16.34
.40	3.49	3.82	4.16	4.34	4.88	5.46	5.21	6.00	6.88	6.11	7.16	8.40
.70	2.17	2.37	2.57	2.67	2.98	3.32	3.17	3.63	4.13	3.69	4.29	5.00
1.00	1.66	1.80	1.94	2.01	2.23	2.47	2.36	2.68	3.04	2.72	3.15	3.65
2.00	1.09	1.17	1.24	1.26	1.38	1.50	1.44	1.61	1.78	1.62	1.84	2.08
3.00	.94	1.00	1.04	1.05	1.13	1.21	1.16	1.27	1.39	1.28	1.42	1.58
4.00	.90	.94	.97	.96	1.02	1.08	1.04	1.12	1.20	1.12	1.22	1.34
5.00	.88	.92	.94	.93	.98	1.02	.98	1.04	1.11	1.04	1.12	1.20
6.00	.88	.91	.93	.92	.96	.98	.96	1.01	1.05	1.00	1.06	1.12
7.00	.88	.90	.93	.91	.94	.97	.95	.99	1.03	.98	1.02	1.07
8.00	.89	.91	.93	.91	.94	.96	.94	.98	1.00	.97	1.01	1.04
10.00	.92	.93	.94	.93	.95	.96	.95	.97	.99	.98	.99	1.01
12.00	.96	.97	.97	.96	.97	.98	.97	.98	.99	.98	.99	1.00
15.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

TABLE B (Continued)

$P_r$	$T_r = 1.6$			$T_r = 1.8$			$T_r = 2.0$		
	$\omega = .0$	$\omega = .2$	$\omega = .4$	$\omega = .0$	$\omega = .2$	$\omega = .4$	$\omega = .0$	$\omega = .2$	$\omega = .4$
.01	263.60	316.50	382.30	335.90	412.30	512.80	405.40	503.40	635.20
.02	132.00	158.50	191.40	168.20	206.40	256.60	202.90	251.90	317.80
.04	66.23	79.45	95.91	84.31	103.40	128.50	101.70	126.20	159.10
.07	38.03	45.59	55.00	48.36	59.27	73.63	58.28	72.28	91.09
.10	26.75	32.05	38.63	33.97	41.62	51.67	40.93	50.72	63.89
.20	13.59	16.25	19.54	17.21	21.04	26.05	20.69	25.58	32.15
.40	7.02	8.35	10.00	8.83	10.74	13.25	10.57	13.01	16.28
.70	4.21	4.97	5.91	5.24	6.34	7.76	6.23	7.63	9.48
1.00	3.09	3.63	4.28	3.81	4.58	5.57	4.50	5.48	6.77
2.00	1.80	1.07	2.39	2.16	2.54	3.02	2.50	2.98	3.60
3.00	1.39	1.57	1.78	1.62	1.87	2.18	1.84	2.15	2.55
4.00	1.20	1.33	1.48	1.37	1.55	1.77	1.52	1.75	2.04
5.00	1.10	1.20	1.31	1.22	1.36	1.53	1.34	1.51	1.73
6.00	1.04	1.12	1.20	1.13	1.24	1.37	1.23	1.36	1.53
7.00	1.01	1.07	1.13	1.08	1.16	1.27	1.15	1.26	1.39
8.00	.99	1.04	1.09	1.04	1.11	1.19	1.10	1.18	1.29
10.00	.98	1.01	1.03	1.01	1.05	1.09	1.04	1.09	1.15
12.00	.99	1.00	1.01	1.00	1.01	1.02	1.01	1.03	1.07
15.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

APPENDIX C  
IMPERFECTION PRESSURE CORRECTION AND  $F(P_r)$  TABLES

TABLE C-1

## IMPERFECTION PRESSURE CORRECTIONS

$T_r$ $\omega$	0.60			0.65			0.70		
	0	0.2	0.4	0	0.2	0.4	0	0.2	0.4
$P_r$	ln $\theta$			ln $\theta$			ln $\theta$		
0.01	0.024	0.007	-0.012	0.053	0.029	0.011	0.096	0.071	0.046
0.02	0.018	-0.019	-0.047	0.041	0.012	-0.007	0.084	0.051	0.022
0.05	-0.037	-0.077	-0.110	0.011	-0.036	-0.067	0.054	0.020	-0.019
0.10	-0.116	-0.179	-0.222	-0.059	-0.112	-0.154	0.003	-0.041	-0.089
0.20	-0.269	-0.375	-0.475	-0.186	-0.275	-0.344	-0.074	-0.140	-0.200
0.50	-0.648	-0.889	-1.108	-0.530	-0.611	-0.743	-0.367	-0.466	-0.574
1	-1.129	-1.478	-1.792	-0.988	-1.150	-1.301	-0.730	-0.862	-1.018
2	-1.776	-2.249	-2.669	-1.502	-1.686	-1.904	-1.294	-1.444	-1.611
3	-2.230	-2.799	-3.334	-1.940	-2.161	-2.367	-1.699	-1.854	-2.031
4	-2.599	-3.247	-3.872	-2.309	-2.537	-2.752	-2.042	-2.217	-2.405
5	-2.941	-3.615	-4.302	-2.605	-2.877	-3.064	-2.337	-2.510	-2.715
6	-3.235	-3.945	-4.664	-2.876	-3.105	-3.338	-2.584	-2.792	-2.992
10	-4.134	-4.890	-5.640	-3.747	-4.158	-4.650	-3.355	-3.460	-3.830
20	-5.371	-3.140	-6.930	-5.079	-5.368	-5.900	-4.450	-4.730	-5.040
30	-6.080	-6.830	-7.630	-5.942	-6.075	-6.600	-5.070	-5.390	-5.730
50	-7.100	-7.680	08.500	-6.072	-6.870	-7.448	-5.810	-6.200	-6.570
100	-7.990	-8.745	-9.560	-7.330	-7.908	-8.509	-6.760	-7.200	-7.640
1000	-10.486	-11.269	-12.054	-9.779	-10.402	-11.007	-9.209	-9.669	-10.134

TABLE C-1 (Continued)

$T_r$ $\omega$	0.75			0.80			0.85		
	0	0.2	0.4	0	0.2	0.4	0	0.2	0.4
$P_r$	ln $\theta$			ln $\theta$			ln $\theta$		
0.01	0.142	0.114	0.087	0.192	0.164	0.158	0.241	0.229	0.202
0.02	0.129	0.101	0.071	0.170	0.148	0.124	0.232	0.218	0.180
0.05	0.109	0.068	-0.027	0.156	0.123	0.101	0.224	0.191	0.159
0.10	0.063	0.202	-0.038	0.142	0.085	0.057	0.193	0.159	0.138
0.20	-0.028	-0.079	-0.137	0.045	-0.002	-0.038	0.103	0.085	0.058
0.50	-0.251	-0.362	-0.440	-0.185	-0.254	-0.314	-0.079	-0.137	-0.188
1	-0.568	-0.707	-0.819	-0.457	-0.549	-0.642	-0.385	-0.445	-0.513
2	-1.095	-1.267	-1.430	-0.927	-1.052	-1.166	-0.819	-0.895	-0.988
3	-1.505	-1.696	-1.865	-1.311	-1.439	-1.571	-1.166	-1.283	-1.338
4	-1.828	-2.029	-2.205	-1.620	-1.756	-1.892	-1.440	-1.532	-1.656
5	-2.100	-2.317	-2.514	-1.909	-2.031	-2.170	-1.728	-1.760	-1.877
6	-2.360	-2.580	-2.803	-2.123	-2.284	-2.440	-1.900	-2.018	-2.114
10	-3.090	-3.238	-3.457	-2.840	-3.000	-3.190	-2.570	-2.666	-2.784
20	-4.080	-4.328	-4.576	-3.800	-4.010	-4.220	-3.470	-3.631	-3.764
30	-4.700	-4.934	-4.206	-4.330	$\frac{3}{4}$ 4.560	-4.790	-4.000	-4.161	-4.310
50	-5.420	-5.695	-5.981	-5.000	-5.250	-5.500	-4.640	-4.833	-4.994
100	-6.310	-6.621	-6.952	-5.850	-6.125	-6.370	-5.460	-5.664	-5.829
1000	-8.699	-0.044	-0.390	-8.251	-8.501	-8.752	-7.856	-8.027	-8.198

TABLE C-1 (Continued)

$T_r$ $\omega$ $P_r$	0.90			0.95			1.00		
	0	0.2	0.4	0	0.2	0.4	0	0.2	0.4
	ln $\theta$			ln $\theta$			ln $\theta$		
0.01	0.308	0.293	0.273	0.371	0.362	0.357	0.431	0.431	0.431
0.02	0.272	0.282	0.267	0.364	0.359	0.355	0.430	0.430	0.430
0.05	0.284	0.266	0.244	0.343	0.342	0.340	0.415	0.415	0.415
0.10	0.251	0.238	0.219	0.315	0.313	0.310	0.386	0.386	0.386
0.20	0.194	0.1715	0.172	0.269	0.246	0.230	0.342	0.342	0.342
0.50	0.144	0	-0.040	0.111	0.100	0.091	0.211	0.211	0.211
1	-0.239	-0.270	-0.303	-0.126	-0.144	-0.156	0	0	0
2	-0.673	-0.719	-0.754	-0.553	-0.570	-0.578	-0.405	-0.405	-0.405
3	-1.005	-1.064	-1.098	-0.870	-0.888	-0.905	-0.718	-0.718	-0.718
4	-1.279	-1.329	-1.370	-1.139	-1.162	-1.225	-0.972	-0.972	-0.972
5	-1.511	-1.566	-1.618	-1.361	-1.396	-1.414	-1.194	-1.194	-1.194
6	-1.735	-1.786	-1.849	-1.563	-1.594	-1.618	-1.381	-1.381	-1.381
10	-2.330	-2.390	-2.450	-2.150	-2.169	-2.189	-1.976	-1.976	-1.976
20	-3.210	-3.310	-3.380	-3.000	-3.016	-3.046	-2.760	-2.760	-2.760
30	-3.730	-3.820	-3.900	-3.490	-3.511	-3.546	-3.240	-3.240	-3.240
50	-4.340	-4.470	-4.560	-4.080	-4.166	-4.205	-3.900	-3.900	-3.900
100	-5.160	-5.250	-5.360	-4.860	-4.900	-4.945	-4.580	-4.580	-4.580
1000	-7.505	-7.610	-7.715	-7.191	-7.240	-7.288	-6.909	-6.909	-6.909



TABLE C-1 (Continued)

$T_r$ $\omega$	1.05			1.10			1.15		
	0	0.2	0.4	0	0.2	0.4	0	0.2	0.4
$P_r$	ln $\theta$			ln $\theta$			ln $\theta$		
0.01	0.491	0.516	0.541	0.560	0.593	0.630	0.623	0.679	0.733
0.02	0.489	0.504	0.529	0.550	0.589	0.625	0.613	0.670	0.731
0.05	0.479	0.498	0.523	0.539	0.583	0.619	0.595	0.658	0.729
0.10	0.459	0.480	0.506	0.529	0.563	0.610	0.586	0.645	0.710
0.20	0.418	0.437	0.460	0.488	0.528	0.573	0.534	0.621	0.679
0.50	0.296	0.320	0.345	0.374	0.421	0.466	0.457	0.517	0.590
1	0.098	0.131	0.156	0.203	0.246	0.299	0.294	0.378	0.441
2	-0.233	-0.219	-0.186	-0.122	-0.069	-0.005	0.007	0.084	0.157
3	-0.555	-0.526	-0.459	-0.419	-0.399	-0.293	-0.271	-0.186	-0.096
4	-0.816	-0.787	-0.750	-0.675	-0.611	-0.563	-0.524	-0.436	-0.331
5	-1.039	-1.010	-0.973	-0.892	-0.828	-0.746	-0.735	-0.634	-0.528
6	-1.235	-1.199	-1.175	-1.081	-1.017	-0.940	-0.917	-0.811	-0.697
10	-1.800	-1.788	-1.738	-1.660	-1.580	-1.500	-1.400	-1.365	-1.240
20	-2.560	-2.540	-2.510	-2.450	-2.350	-2.260	-2.200	-2.120	-1.985
30	-3.030	-3.000	-2.960	-2.860	-2.760	-2.670	-2.620	-2.540	-2.405
50	-3.580	-3.400	-3.100	-3.380	-3.300	-3.200	-3.160	-3.070	-2.930
100	-4.340	-4.301	-4.251	-4.100	-4.000	-3.900	-3.900	-3.770	-3.634
1000	-6.654	-6.604	-6.554	-6.520	-6.327	-6.231	-6.239	-6.073	-5.937

TABLE C-1 (Continued)

$T_r$ $\omega$	1.20			1.30			1.40		
	0	0.2	0.4	0	0.2	0.4	0	0.2	0.4
$P_r$	ln $\theta$			ln $\theta$			ln $\theta$		
0.01	0.672	0.761	0.837	0.787	0.919	1.016	0.880	1.029	1.216
0.02	0.670	0.753	0.830	0.781	0.908	1.006	0.875	1.024	1.206
0.05	0.655	0.742	0.804	0.768	0.891	1.002	0.865	1.020	1.173
0.10	0.647	0.724	0.797	0.762	0.874	0.997	0.845	1.007	1.165
0.20	0.617	0.703	0.785	0.731	0.858	0.977	0.837	0.998	1.143
0.50	0.526	0.614	0.708	0.650	0.786	0.908	0.770	0.927	1.097
1	0.387	0.475	0.574	0.525	0.672	0.803	0.666	0.837	1.014
2	0.115	0.218	0.326	0.306	0.464	0.621	0.468	0.655	0.848
3	-0.143	-0.020	0.104	0.091	0.258	0.438	0.195	0.485	0.693
4	-0.387	-0.256	-0.119	-0.107	0.073	0.265	0.107	0.331	0.560
5	-0.588	-0.457	-0.310	-0.304	-0.110	0.090	-0.016	0.182	0.406
6	-0.770	-0.627	-0.479	-0.470	-0.272	-0.062	-0.202	0.029	0.278
10	-1.329	-1.150	-0.980	-1.010	-0.832	-0.609	-0.740	-0.455	-0.170
20	-2.061	-1.890	-1.710	-1.710	-1.525	-1.285	-1.450	-1.160	-0.860
30	-2.470	-2.320	-2.140	-2.120	-1.945	-1.700	-1.860	-1.570	-1.270
50	-3.000	-2.840	-2.660	-2.650	-2.450	-2.220	-2.370	-2.060	-1.780
100	-3.710	-3.538	-3.365	-3.365	-3.127	-2.887	-3.070	-2.776	-2.476
1000	-6.017	-5.831	-5.668	-5.671	-5.430	-5.190	-5.379	-5.079	-4.779

TABLE C-1 (Continued)

$T_r$ $\omega$ $P_r$	1.20			1.30			1.40		
	0	0.2	0.4	0	0.2	0.4	0	0.2	0.4
	ln $\theta$			ln $\theta$			ln $\theta$		
0.01	0.672	0.761	0.837	0.787	0.919	1.016	0.880	1.029	1.216
0.02	0.670	0.753	0.830	0.781	0.908	1.006	0.875	1.024	1.206
0.05	0.655	0.742	0.804	0.768	0.891	1.002	0.865	1.020	1.173
0.10	0.647	0.724	0.797	0.762	0.874	0.997	0.845	1.007	1.165
0.20	0.617	0.703	0.785	0.731	0.858	0.977	0.837	0.998	1.143
0.50	0.526	0.614	0.708	0.650	0.786	0.908	0.770	0.927	1.097
1	0.387	0.475	0.574	0.525	0.672	0.803	0.666	0.837	1.014
2	0.115	0.218	0.326	0.306	0.464	0.621	0.468	0.655	0.848
3	-0.143	-0.020	0.104	0.091	0.258	0.438	0.195	0.485	0.693
4	-0.387	-0.256	-0.119	-0.107	0.073	0.265	0.107	0.331	0.560
5	-0.588	-0.457	-0.310	-0.304	-0.110	0.090	-0.016	0.182	0.406
6	-0.770	-0.627	-0.479	-0.470	-0.272	-0.062	-0.202	0.029	0.278
10	-1.329	-1.150	-0.980	-1.010	-0.832	-0.609	-0.740	-0.455	-0.170
20	-2.061	-1.890	-1.710	-1.710	-1.525	-1.285	-1.450	-1.160	-0.860
30	-2.470	-2.320	-2.140	-2.120	-1.945	-1.700	-1.860	-1.570	-1.270
50	-3.000	-2.840	-2.660	-2.650	-2.450	-2.220	-2.370	-2.060	-1.780
100	-3.710	-3.538	-3.365	-3.365	-3.127	-2.887	-3.070	-2.776	-2.476
1000	-6.017	-5.831	-5.668	-5.671	-5.430	-5.190	-5.379	-5.079	-4.779

TABLE C-1 (Continued)

$T_r$ $\omega$	1.5			1.6			1.8		
	0	0.2	0.4	0	0.2	0.4	0	0.2	0.4
$P_r$	ln $\theta$			ln $\theta$			ln $\theta$		
0.01	0.973	1.146	1.336	1.041	1.249	1.471	1.158	1.432	1.750
0.02	0.964	1.142	1.332	1.034	1.246	1.458	1.157	1.429	1.740
0.05	0.956	1.139	1.320	1.028	1.239	1.452	1.153	1.427	1.730
0.10	0.951	1.131	1.314	1.019	1.233	1.437	1.147	1.424	1.720
0.20	0.930	1.128	1.301	1.011	1.215	1.432	1.134	1.398	1.710
0.50	0.872	1.064	1.254	1.000	1.179	1.380	1.096	1.328	1.690
1	0.784	0.988	1.183	0.881	1.108	1.334	1.034	1.320	1.650
2	0.607	0.990	1.048	0.731	0.967	1.224	0.912	1.220	1.600
3	0.443	0.687	0.927	0.577	0.847	1.118	0.804	1.154	1.560
4	0.280	0.551	0.796	0.443	0.724	1.015	0.680	1.044	1.460
5	0.130	0.413	0.691	0.307	0.594	0.914	0.570	0.942	1.400
6	-0.003	0.276	0.578	0.171	0.497	0.819	0.484	0.806	1.360
10	-0.480	-0.255	0.060	-0.274	-0.055	0.290	0.040	0.345	0.750
20	-1.200	-0.940	-0.603	-0.970	-0.720	-0.346	-0.640	-0.280	0.168
30	-1.600	-1.348	-1.010	-1.395	-1.126	-0.750	-1.012	-0.681	-0.230
50	-2.110	-1.840	-1.520	-1.900	-1.620	-1.260	-1.530	-1.180	-0.740
100	-2.710	-2.471	-2.123	-2.590	-2.206	-1.816	-2.220	-1.756	-1.296
1000	-5.121	-4.774	-4.426	-4.899	-4.509	-4.119	-4.564	-4.059	-3.599

TABLE C-1 (Continued)

$T_r$ $\omega$ $P_r$	2.0			3.0			4.0		
	0	0.2	0.4	0	0.2	0.4	0	0.2	0.4
	ln $\theta$			ln $\theta$			ln $\theta$		
0.01	1.272	1.573	1.867	1.599	2.008	2.399	1.799	2.250	2.682
0.02	1.263	1.566	1.861	1.598	2.006	2.382	1.799	2.249	2.684
0.05	1.254	1.559	1.855	1.597	2.005	2.380	1.798	2.248	2.688
0.10	1.245	1.552	1.849	1.594	2.004	2.378	1.795	2.247	2.698
0.20	1.236	1.544	1.843	1.588	2.000	2.375	1.791	2.246	2.695
0.50	1.226	1.536	1.836	1.570	1.985	2.369	1.776	2.235	2.694
1	1.178	1.498	1.807	1.539	1.969	2.364	1.754	2.228	2.690
2	1.073	1.411	1.749	1.481	1.934	2.360	1.708	2.208	2.686
3	0.970	1.335	1.685	1.421	1.911	2.357	1.662	2.202	2.680
4	0.871	1.240	1.615	1.366	1.861	2.340	1.616	2.162	2.680
5	0.774	1.162	1.554	1.308	1.828	2.328	1.572	2.150	2.700
6	0.669	1.089	1.493	1.255	1.818	2.330	1.525	2.140	2.740
10	0.290	0.750	1.200	1.035	1.651	2.225	1.351	2.032	2.700
20	-0.350	0.160	0.680	0.550	1.233	1.900	1.000	1.755	2.530
30	-0.760	-0.240	0.290	0.085	0.781	1.457	0.660	1.430	2.220
50	-1.250	-0.750	-0.220	-0.525	0.145	0.825	0.200	0.940	1.230
100	-1.920	-1.403	-0.883	-1.029	-0.345	0.238	-0.450	0.192	0.966
1000	-4.227	-3.706	-3.186	-3.332	-2.648	-1.965	-2.884	-2.110	-1.337

TABLE C-II

VALUES OF  $F^0(P_r) = \frac{\ln 0^0 - \ln 0^0 - \beta^0 P_r}{P_r}$  AT VARIOUS  $T_r$  AND  $P_r$  VALUES FOR SIMPLE FLUID

$P_r$	0.50	0.52	0.54	0.56	0.58	0.60	0.62	0.64	0.66	0.68	0.70	0.72	0.74	0.76	0.78	0.80
0.5	0.500	0.420	0.350	0.300	0.260	0.227	0.195	0.172	0.149	0.132	0.116	0.100	0.087	0.077	0.067	0.059
1.0	0.803	0.700	0.610	0.537	0.476	0.422	0.369	0.325	0.285	0.252	0.220	0.192	0.167	0.148	0.127	0.112
1.5	1.035	0.920	0.800	0.700	0.620	0.569	0.503	0.446	0.395	0.349	0.307	0.271	0.237	0.211	0.183	0.160
2.0	1.220	1.082	0.954	0.827	0.758	0.672	0.598	0.535	0.477	0.423	0.375	0.336	0.297	0.263	0.232	0.202
2.5	1.360	1.208	1.066	0.930	0.850	0.755	0.672	0.602	0.537	0.479	0.429	0.384	0.341	0.304	0.270	0.237
3.0	1.486	1.312	1.155	1.028	0.922	0.822	0.733	0.657	0.587	0.527	0.470	0.423	0.377	0.337	0.302	0.265
3.5	1.580	1.394	1.228	1.090	0.982	0.876	0.782	0.700	0.628	0.565	0.506	0.455	0.407	0.366	0.327	0.290
4.0	1.658	1.459	1.286	1.143	1.030	0.919	0.822	0.737	0.662	0.596	0.536	0.482	0.432	0.390	0.350	0.311
4.5	1.720	1.518	1.336	1.188	1.070	0.952	0.854	0.767	0.690	0.624	0.562	0.506	0.456	0.412	0.371	0.331
5.0	1.774	1.569	1.377	1.226	1.103	0.983	0.882	0.796	0.717	0.647	0.585	0.527	0.477	0.432	0.390	0.351
5.5	1.820	1.605	1.414	1.260	1.134	1.010	0.907	0.820	0.740	0.670	0.606	0.547	0.497	0.451	0.409	0.368
6.0	1.860	1.635	1.443	1.290	1.160	1.034	0.930	0.842	0.760	0.687	0.624	0.564	0.514	0.467	0.424	0.385
6.5	1.898	1.664	1.472	1.318	1.186	1.056	0.950	0.861	0.777	0.705	0.641	0.586	0.530	0.482	0.439	0.400
7.0	1.928	1.690	1.496	1.340	1.206	1.071	0.967	0.872	0.794	0.721	0.656	0.595	0.544	0.496	0.452	0.414
7.5	1.957	1.717	1.520	1.362	1.226	1.095	0.988	0.892	0.809	0.735	0.670	0.609	0.557	0.509	0.465	0.427
8.0	1.982	1.740	1.541	1.380	1.243	1.111	0.998	0.907	0.823	0.749	0.682	0.622	0.569	0.521	0.476	0.437
8.5	2.006	1.762	1.562	1.398	1.260	1.126	1.012	0.920	0.836	0.761	0.693	0.633	0.580	0.532	0.486	0.448
9.0	2.025	1.782	1.580	1.413	1.273	1.139	1.024	0.931	0.847	0.773	0.703	0.644	0.590	0.542	0.496	0.457
9.5	2.045	1.802	1.598	1.427	1.287	1.151	1.036	0.942	0.856	0.783	0.712	0.653	0.598	0.552	0.505	0.465
10.0	2.062	1.820	1.612	1.418	1.298	1.162	1.046	0.952	0.866	0.792	0.721	0.662	0.607	0.560	0.513	0.473
10.5	2.079	1.838	1.628	1.432	1.310	1.172	1.055	0.960	0.875	0.800	0.730	0.670	0.615	0.568	0.521	0.481
11.0	2.093	1.833	1.640	1.463	1.320	1.182	1.064	0.969	0.882	0.808	0.738	0.678	0.623	0.576	0.529	0.489
11.5	2.109	1.868	1.650	1.475	1.330	1.191	1.073	0.977	0.891	0.816	0.746	0.686	0.631	0.584	0.537	0.496
12.0	2.122	1.881	1.664	1.485	1.339	1.201	1.082	0.985	0.900	0.824	0.754	0.693	0.638	0.591	0.544	0.503
12.5	2.135	1.892	1.675	1.495	1.349	1.210	1.089	0.993	0.907	0.831	0.762	0.701	0.645	0.598	0.551	0.510
13.0	2.147	1.904	1.685	1.505	1.357	1.218	1.097	1.001	0.915	0.838	0.769	0.707	0.651	0.605	0.558	0.516
13.5	2.159	1.914	1.695	1.514	1.366	1.227	1.105	1.009	0.921	0.845	0.776	0.714	0.658	0.612	0.564	0.523
14.0	2.169	1.923	1.703	1.522	1.373	1.235	1.112	1.016	0.929	0.851	0.783	0.725	0.664	0.618	0.570	0.528
14.5	2.180	1.931	1.712	1.531	1.380	1.242	1.119	1.022	0.935	0.857	0.790	0.726	0.671	0.624	0.576	0.533
15.0	2.189	1.941	1.720	1.538	1.387	1.250	1.126	1.030	0.942	0.863	0.796	0.733	0.677	0.630	0.582	0.539
20	2.268	2.014	1.787	1.598	1.448	1.309	1.179	1.078	0.988	0.910	0.840	0.777	0.720	0.669	0.620	0.588
30	2.375	2.109	1.974	1.774	1.524	1.374	1.240	1.135	1.042	0.962	0.892	0.825	0.768	0.716	0.666	0.620
50	2.492	2.218	1.974	1.774	1.612	1.456	1.320	1.216	1.119	1.034	0.956	0.836	0.825	0.721	0.720	0.675
100	2.616	2.329	2.070	1.858	1.690	1.523	1.380	1.270	1.173	1.083	1.005	0.931	0.867	0.814	0.761	0.714

TABLE C-II (Continued)

P <sub>r</sub>	0.82	0.84	0.86	0.88	0.90	0.92	0.94	0.96	0.98	1.00	1.02	1.04	1.06	1.08	1.10	1.15
0.5	0.050	0.041	0.034	0.029	0.026	0.022	0.019	0.017	0.015	0.012	0.011	0.010	0.009	0.008	0.007	0.005
1.0	0.097	0.081	0.067	0.057	0.051	0.043	0.038	0.033	0.029	0.025	0.022	0.020	0.018	0.016	0.015	0.011
1.5	0.139	0.118	0.100	0.085	0.075	0.065	0.057	0.049	0.043	0.037	0.033	0.030	0.027	0.024	0.022	0.017
2.0	0.177	0.152	0.130	0.112	0.098	0.085	0.074	0.065	0.057	0.050	0.044	0.040	0.036	0.033	0.030	0.023
2.5	0.209	0.182	0.158	0.138	0.121	0.105	0.091	0.081	0.071	0.062	0.055	0.050	0.045	0.051	0.037	0.030
3.0	0.236	0.207	0.182	0.162	0.142	0.125	0.109	0.097	0.086	0.075	0.067	0.061	0.055	0.050	0.045	0.036
3.5	0.259	0.230	0.204	0.182	0.161	0.142	0.125	0.112	0.100	0.088	0.080	0.071	0.064	0.058	0.053	0.042
4.0	0.280	0.250	0.223	0.200	0.180	0.159	0.141	0.127	0.114	0.100	0.092	0.082	0.074	0.067	0.061	0.048
4.5	0.300	0.268	0.241	0.218	0.197	0.175	0.157	0.140	0.127	0.114	0.103	0.092	0.082	0.075	0.069	0.054
5.0	0.317	0.285	0.258	0.233	0.212	0.191	0.172	0.155	0.141	0.126	0.115	0.102	0.092	0.084	0.076	0.060
5.5	0.334	0.301	0.274	0.249	0.226	0.205	0.186	0.168	0.153	0.139	0.125	0.113	0.102	0.092	0.084	0.066
6.0	0.349	0.316	0.287	0.268	0.240	0.217	0.198	0.179	0.164	0.150	0.135	0.122	0.112	0.101	0.092	0.072
6.5	0.353	0.330	0.300	0.275	0.252	0.229	0.209	0.189	0.175	0.159	0.145	0.130	0.120	0.108	0.099	0.079
7.0	0.376	0.342	0.312	0.285	0.263	0.240	0.219	0.199	0.184	0.168	0.152	0.139	0.128	0.116	0.106	0.086
7.5	0.387	0.353	0.323	0.296	0.273	0.249	0.228	0.208	0.192	0.177	0.160	0.147	0.135	0.123	0.113	0.092
8.0	0.398	0.364	0.333	0.306	0.282	0.258	0.237	0.217	0.201	0.184	0.168	0.154	0.142	0.130	0.120	0.098
8.5	0.408	0.374	0.342	0.315	0.290	0.267	0.245	0.225	0.209	0.191	0.175	0.161	0.149	0.136	0.126	0.104
9.0	0.419	0.384	0.352	0.324	0.298	0.276	0.255	0.233	0.217	0.198	0.182	0.168	0.155	0.142	0.132	0.109
9.5	0.427	0.392	0.360	0.332	0.305	0.283	0.261	0.240	0.224	0.205	0.190	0.175	0.161	0.149	0.138	0.114
10.0	0.435	0.400	0.368	0.339	0.313	0.290	0.267	0.247	0.230	0.212	0.197	0.181	0.168	0.155	0.144	0.119
10.5	0.442	0.407	0.375	0.347	0.320	0.297	0.274	0.253	0.237	0.218	0.203	0.187	0.173	0.161	0.149	0.125
11.0	0.450	0.415	0.383	0.354	0.327	0.303	0.280	0.259	0.242	0.224	0.209	0.193	0.179	0.167	0.155	0.130
11.5	0.457	0.422	0.390	0.361	0.333	0.310	0.286	0.265	0.248	0.229	0.214	0.198	0.184	0.172	0.160	0.135
12.0	0.464	0.428	0.396	0.367	0.340	0.316	0.292	0.271	0.253	0.234	0.219	0.203	0.189	0.177	0.165	0.139
12.5	0.470	0.435	0.403	0.374	0.346	0.321	0.297	0.276	0.259	0.240	0.224	0.208	0.194	0.182	0.169	0.143
13.0	0.477	0.441	0.409	0.394	0.352	0.327	0.302	0.281	0.264	0.245	0.229	0.212	0.198	0.186	0.174	0.147
13.5	0.482	0.446	0.415	0.385	0.357	0.332	0.307	0.286	0.268	0.249	0.233	0.217	0.202	0.190	0.177	0.151
14.0	0.483	0.452	0.421	0.390	0.362	0.337	0.312	0.290	0.273	0.254	0.238	0.221	0.206	0.194	0.182	0.155
14.5	0.494	0.457	0.426	0.391	0.368	0.342	0.317	0.295	0.277	0.258	0.242	0.225	0.210	0.198	0.185	0.158
15.0	0.500	0.462	0.432	0.401	0.373	0.347	0.321	0.300	0.281	0.262	0.246	0.228	0.214	0.202	0.190	0.162
20	0.535	0.499	0.466	0.434	0.405	0.379	0.355	0.331	0.312	0.292	0.275	0.257	0.241	0.228	0.215	0.187
30	0.579	0.540	0.507	0.475	0.446	0.419	0.394	0.370	0.351	0.331	0.314	0.295	0.278	0.265	0.250	0.220
50	0.632	0.593	0.559	0.525	0.495	0.568	0.441	0.417	0.395	0.374	0.355	0.335	0.318	0.303	0.287	0.253
100	0.670	0.596	0.596	0.563	0.532	0.505	0.478	0.453	0.431	0.408	0.388	0.367	0.349	0.333	0.317	0.231

TABLE C-II (Continued)

P <sub>r</sub>	1.20	1.25	1.30	1.40	1.50	1.60	1.80	2.0	2.2	2.5	3.0	4.0
0.5	0.005	0.004	0.003	0.002	0.002	0.001	0.001	0.0006	0.0005	0.0005	0.0002	0.0001
1.0	0.010	0.008	0.007	0.005	0.004	0.003	0.002	0.0012	0.0011	0.0010	0.0004	0.0002
1.5	0.015	0.012	0.010	0.007	0.006	0.004	0.003	0.0018	0.0016	0.0014	0.0006	0.0003
2.0	0.020	0.017	0.014	0.010	0.008	0.006	0.004	0.0025	0.0022	0.0018	0.0008	0.0004
2.5	0.025	0.021	0.017	0.012	0.010	0.007	0.005	0.0033	0.0027	0.0022	0.0010	0.0005
3.0	0.030	0.025	0.021	0.015	0.012	0.009	0.006	0.0037	0.0032	0.0026	0.0012	0.0006
3.5	0.035	0.029	0.024	0.018	0.014	0.010	0.007	0.0043	0.0037	0.0030	0.0014	0.0007
4.0	0.004	0.033	0.027	0.021	0.016	0.012	0.008	0.0050	0.0041	0.0032	0.0016	0.0008
4.5	0.045	0.037	0.031	0.023	0.018	0.013	0.009	0.0056	0.0045	0.0034	0.0018	0.0009
5.0	0.050	0.042	0.035	0.026	0.020	0.015	0.010	0.0062	0.0050	0.0036	0.0020	0.0010
5.5	0.056	0.046	0.038	0.029	0.022	0.017	0.011	0.0068	0.0054	0.0038	0.0021	0.0011
6.0	0.061	0.050	0.042	0.032	0.024	0.018	0.012	0.0075	0.0058	0.0040	0.0022	0.0012
6.5	0.066	0.055	0.046	0.034	0.026	0.020	0.013	0.0081	0.0062	0.0041	0.0023	0.0013
7.0	0.072	0.060	0.049	0.037	0.028	0.021	0.014	0.0087	0.0065	0.0042	0.0024	0.0014
7.5	0.077	0.064	0.052	0.039	0.030	0.023	0.015	0.0093	0.0069	0.0043	0.0025	0.0015
8.0	0.082	0.068	0.057	0.042	0.032	0.024	0.016	0.0100	0.0072	0.0044	0.0026	0.0016
8.5	0.086	0.072	0.060	0.044	0.034	0.026	0.017	0.0106	0.0076	0.0045	0.0027	0.0017
9.0	0.091	0.076	0.064	0.047	0.036	0.028	0.018	0.0112	0.0079	0.0046	0.0028	0.0018
9.5	0.095	0.079	0.067	0.049	0.038	0.030	0.019	0.0118	0.0083	0.0048	0.0029	0.0019
10.0	0.099	0.083	0.072	0.052	0.040	0.032	0.020	0.0125	0.0090	0.0050	0.0030	0.0020
10.5	0.104	0.087	0.075	0.055	0.042	0.033	0.021	0.0131	0.0092	0.0054	0.0031	0.0021
11.0	0.109	0.091	0.078	0.057	0.044	0.035	0.022	0.0137	0.0097	0.0058	0.0032	0.0022
11.5	0.114	0.094	0.081	0.060	0.046	0.036	0.023	0.0143	0.0103	0.0062	0.0033	0.0023
12.0	0.118	0.098	0.084	0.062	0.048	0.038	0.024	0.0150	0.0100	0.0066	0.0034	0.0024
12.5	0.122	0.102	0.088	0.065	0.050	0.039	0.025	0.0156	0.0113	0.0070	0.0035	0.0025
13.0	0.126	0.106	0.091	0.067	0.052	0.041	0.026	0.0162	0.0117	0.0072	0.0036	0.0026
13.5	0.129	0.109	0.094	0.070	0.054	0.042	0.027	0.0168	0.0120	0.0074	0.0037	0.0027
14.0	0.132	0.112	0.097	0.073	0.056	0.049	0.028	0.0175	0.0125	0.0076	0.0038	0.0028
14.5	0.135	0.117	0.100	0.075	0.058	0.045	0.029	0.0181	0.0130	0.0078	0.0039	0.0029
15.0	0.138	0.120	0.103	0.078	0.060	0.047	0.030	0.0187	0.0150	0.0080	0.0040	0.0030
20	0.163	0.137	0.125	0.097	0.078	0.061	0.041	0.0275	0.0200	0.0140	0.0080	0.0040
30	0.195	0.172	0.155	0.142	0.100	0.082	0.057	0.0400	0.0310	0.0220	0.0130	0.0070
50	0.225	0.200	0.177	0.143	0.117	0.096	0.070	0.0520	0.0400	0.0290	0.0180	0.0100
100	0.251	0.224	0.201	0.163	0.135	0.112	0.082	0.0620	0.0480	0.0350	0.0230	0.0120



TABLE C-III

$$\text{VALUES OF } F'(P_r) = \frac{\ln \theta_B - \ln \theta_C - b'P_r}{P_r}$$

$P_r$	$T_r$						
	.6	.62	.64	.66	.68	.70	.72
.5	.425	.359	.308	.255	.213	.176	.144
1.0	.800	.677	.573	.480	.402	.330	.270
1.5	1.099	.932	.788	.660	.554	.455	.375
2.0	1.320	1.125	.955	.800	.671	.556	.460
2.5	1.483	1.271	1.079	.903	.759	.629	.521
3.0	1.613	1.382	1.175	.982	.826	.685	.568
3.5	1.718	1.466	1.245	1.043	.876	.728	.605
4.0	1.782	1.527	1.300	1.090	.915	.760	.631
4.5	1.839	1.571	1.336	1.122	.944	.785	.653
5.0	1.883	1.603	1.365	1.145	.965	.804	.670
5.5	1.915	1.629	1.385	1.164	.982	.819	.681
6.0	1.940	1.648	1.402	1.179	.995	.830	.690
6.5	1.959	1.665	1.415	1.190	1.005	.840	.699
7.0	1.973	1.676	1.425	1.199	1.014	.847	.705
7.5	1.984	1.685	1.433	1.207	1.020	.853	.710
8.0	1.992	1.694	1.440	1.215	1.027	.859	.714
8.5	2.000	1.702	1.448	1.220	1.032	.863	.719
9.0	2.005	1.708	1.455	1.226	1.037	.866	.721
9.5	2.010	1.714	1.460	1.230	1.040	.869	.723
10.0	2.015	1.718	1.464	1.234	1.043	.870	.724
10.5	2.018	1.721	1.467	1.235	1.044	.871	.726
11.0	2.022	1.724	1.470	1.238	1.046	.873	.725
11.5	2.025	1.727	1.472	1.240	1.048	.875	.730
12.0	2.028	1.730	1.475	1.242	1.050	.877	.731
12.5	2.032	1.732	1.477	1.245	1.052	.879	.733
13.0	2.035	1.735	1.480	1.246	1.054	.880	.735
13.5	2.037	1.737	1.482	1.248	1.055	.882	.736
14.0	2.040	1.740	1.485	1.250	1.058	.883	.737
14.5	2.043	1.742	1.487	1.253	1.060	.884	.738
15.0	2.046	1.745	1.489	1.255	1.061	.886	.740
20.0	2.075	1.765	1.507	1.270	1.075	.898	.750
30.0	2.130	1.810	1.545	1.304	1.105	.926	.775

TABLE C-III (Continued)

$P_r$	$T_r$						
	.74	.76	.78	.80	.82	.84	.86
.5	.117	.091	.074	.060	.045	.036	.028
1.0	.219	.175	.142	.115	.090	.073	.056
1.5	.305	.246	.200	.163	.133	.106	.083
2.0	.375	.305	.250	.204	.170	.135	.106
2.5	.426	.348	.286	.232	.190	.152	.122
3.0	.467	.381	.314	.253	.206	.165	.135
3.5	.497	.406	.333	.268	.219	.177	.143
4.0	.520	.426	.349	.280	.229	.185	.150
4.5	.537	.440	.358	.289	.236	.192	.155
5.0	.551	.450	.367	.296	.243	.197	.160
5.5	.561	.458	.375	.303	.250	.200	.164
6.0	.570	.465	.381	.309	.255	.204	.166
6.5	.576	.471	.387	.314	.260	.206	.168
7.0	.582	.477	.392	.219	.265	.209	.170
7.5	.587	.482	.397	.323	.269	.210	.171
8.0	.591	.486	.401	.326	.271	.212	.173
8.5	.595	.490	.404	.329	.274	.215	.175
9.0	.597	.493	.405	.331	.275	.217	.176
9.5	.598	.495	.407	.332	.276	.219	.178
10.0	.599	.497	.410	.334	.277	.220	.180
10.5	.600	.499	.412	.335	.279	.222	.181
11.0	.601	.500	.415	.337	.280	.225	.183
11.5	.603	.502	.416	.340	.282	.226	.184
12.0	.605	.503	.418	.341	.284	.228	.185
12.5	.606	.505	.420	.343	.286	.230	.187
13.0	.607	.506	.421	.345	.287	.231	.189
13.5	.609	.507	.423	.346	.289	.233	.190
14.0	.610	.509	.425	.347	.290	.234	.191
14.5	.610	.510	.426	.349	.292	.235	.192
15.0	.611	.511	.428	.350	.294	.236	.194
20.0	.620	.521	.440	.365	.305	.247	.203
30.0	.643	.541	.458	.381	.319	.260	.214

TABLE C-III (Continued)

$P_r$	$T_r$						
	.88	.90	.95	1.00	1.05	1.1	1.2
.5	.023	.018	.010	.005	.000	-.005	-.010
1.0	.045	.035	.018	.005	.000	-.007	-.014
1.5	.066	.052	.025	.011	.000	-.010	-.019
2.0	.085	.065	.032	.014	.000	-.013	-.024
2.5	.098	.078	.038	.016	.000	-.013	-.026
3.0	.108	.085	.043	.018	.000	-.014	-.027
3.5	.115	.095	.047	.019	.000	-.014	-.028
4.0	.121	.098	.051	.020	.000	-.015	-.029
4.5	.126	.102	.054	.021	.000	-.015	-.030
5.0	.130	.107	.056	.022	-.001	-.015	-.031
5.5	.135	.110	.058	.023	-.001	-.016	-.031
6.0	.137	.113	.059	.024	-.001	-.016	-.032
6.5	.139	.114	.060	.025	-.001	-.017	-.033
7.0	.140	.115	.061	.025	-.001	-.018	-.034
7.5	.141	.115	.062	.026	-.001	-.018	-.035
8.0	.142	.116	.064	.027	-.001	-.019	-.036
8.5	.144	.117	.065	.028	-.001	-.019	-.037
9.0	.145	.118	.066	.029	-.001	-.020	-.038
9.5	.145	.119	.067	.030	-.001	-.020	-.039
10.0	.146	.119	.068	.030	-.001	-.021	-.040
10.5	.147	.120	.068	.030	-.001	-.021	-.041
11.0	.149	.120	.069	.030	-.001	-.021	-.042
11.5	.150	.121	.070	.030	-.001	-.021	-.043
12.0	.152	.122	.070	.030	-.001	-.021	-.043
12.5	.153	.123	.070	.030	-.001	-.022	-.044
13.5	.154	.123	.070	.030	-.001	-.022	-.044
13.5	.155	.124	.071	.030	-.001	-.022	-.045
14.0	.156	.125	.071	.030	-.001	-.022	-.046
14.5	.157	.125	.071	.030	-.001	-.022	-.046
15.0	.158	.126	.071	.030	-.002	-.023	-.047
20.0	.165	.134	.072	.030	-.002	-.025	-.053
30.0	.174	.141	.075	.030	-.005	-.031	-.064

TABLE C-III (Continued)

P <sub>r</sub>	T <sub>r</sub>					
	1.3	1.4	1.5	1.6	1.8	2.0
.5	-.013	-.015	-.015	-.015	-.015	-.015
1.0	-.019	-.020	-.023	-.023	-.023	-.023
1.5	-.025	-.027	-.029	-.029	-.029	-.029
2.0	-.030	-.034	-.035	-.035	-.035	-.035
2.5	-.032	-.036	-.038	-.038	-.038	-.038
3.0	-.034	-.038	-.040	-.040	-.040	-.040
3.5	-.036	-.040	-.042	-.042	-.042	0.042
4.0	-.037	-.042	-.044	-.044	-.044	-.044
4.5	-.038	-.043	-.045	-.045	-.045	-.045
5.0	-.039	-.044	-.046	-.046	-.046	-.046
5.5	-.040	-.045	-.047	-.047	-.047	-.047
6.0	-.041	-.046	-.048	-.048	-.048	-.048
6.5	-.043	-.047	-.049	-.049	-.049	-.049
7.0	-.044	-.048	-.050	-.050	-.050	-.050
7.5	-.045	-.050	-.052	-.052	-.052	-.052
8.0	-.047	-.051	-.053	-.053	-.053	-.053
8.5	-.048	-.052	-.054	-.054	-.054	-.054
9.0	-.049	-.053	-.055	-.055	-.055	-.055
9.5	-.050	-.054	-.055	-.055	-.055	-.055
10.0	-.051	-.055	-.057	-.057	-.057	-.057
10.5	-.052	-.056	-.058	-.058	-.058	-.058
11.0	-.053	-.057	-.059	-.059	-.059	-.059
11.5	-.054	-.058	-.060	-.060	-.060	-.060
12.0	-.054	-.059	-.061	-.061	-.061	-.061
12.5	-.055	-.060	-.062	-.062	-.062	-.062
13.0	-.056	-.061	-.063	-.063	-.063	-.063
13.5	-.057	-.062	-.064	-.064	-.064	-.064
14.0	-.058	-.063	-.065	-.065	-.065	-.065
14.5	-.058	-.064	-.066	-.066	-.066	-.066
15.0	-.058	-.064	-.066	-.066	-.066	-.066
20.0	-.066	-.074	-.077	-.077	-.077	-.077
30.0	-.082	-.093	-.099	-.099	-.099	-.099

## APPENDIX D

### EQUATIONS USED IN CALCULATIONS

1. Vapor pressure

$$\ln P_r^\circ = (\ln P_r^\circ)^\circ + \omega \left( \frac{\partial \ln P_r^\circ}{\partial \omega} \right)_T \quad (D-1)$$

where for the simple fluid

$$(\ln P_r^\circ)^\circ = 5.366 - (5.366) T_r \quad (D-2)$$

and for  $T_r < 1.0$

$$\begin{aligned} \left( \frac{\partial \ln P_r^\circ}{\partial \omega} \right)_T = & 2.415 - .7116 T_r^{-1} - 1.179 T_r^{-2} - .7072 T_r^{-3} \\ & + .1824 T_r^{-4} \end{aligned} \quad (D-3)$$

for  $T_r = 1.0$

$$\left( \frac{\partial \ln P_r^\circ}{\partial \omega} \right)_T = 0.0 \quad (D-4)$$

and for  $T_r > 1.0$

$$\left( \frac{\partial \ln P_r^\circ}{\partial \omega} \right)_T = 5.179 - 5.133/T_r - .04566 T_r^{-2} \quad (D-5)$$

2. Liquid Volume

$$V^L = \frac{RT_c V_r}{P_c} \quad \text{where} \quad (D-6)$$

$$V_r = (.01361 - .00436\omega) (5.7 + 3.0 T_r) \quad (D-7)$$

3. Coefficient for Equation III-3

$$b = \frac{1}{T_r} \left( \frac{BP_c}{RT_c} - \frac{V^L P_c}{RT_c} \right) \quad (D-8)$$

where  $BP_c/RT_c$  is Pitzer's  $b_p$

4. Pitzer's  $b_p$

$$\begin{aligned} \frac{BP_c}{RT_c} = & (.1445 + .073\omega) - (.330 - .46\omega) T_r^{-1} \\ & - (.1385 + .50\omega) T_r^{-2} - (.0121 + .097\omega) T_r^{-3} \\ & - (.0073\omega) T_r^{-8} \end{aligned} \quad (D-9)$$

5. Redlich-Kwong  $b_{RK}$

$$b_{RK} = (.0867 - \frac{.4278}{T_r^{1.5}}) \quad (D-10)$$

6. Stuckey's  $\ln \theta$  equation

$$\ln \theta = b (P_r - P_r^o) - c (P_r^2 - P_r^{o2}) + \dots \quad (D-11)$$

where

$$c = \frac{C P_r^2}{2RT_c T_r} \text{ values of which are calculated and tabulated}$$

by Stuckey (8).

VITA

Juris Vairogs

Candidate for the Degree of  
Master of Science

Thesis: INVESTIGATION OF A GENERALIZED VAPOR-LIQUID K CORRELATION  
FOR HYDROCARBONS

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Jelgava, Latvia, May 14, 1937, the  
son of Verners and Karlina E. Vairogs.

Education: Attended grade school in Ohmstadt, Germany;  
attended high school in Stillwater, Oklahoma; graduated  
from high school in May, 1954; attended University of  
Nebraska, Lincoln, Nebraska, 1954 to 1958; received  
the degree of Bachelor of Science in Chemical Engi-  
neering, June, 1958; completed the requirements for  
the Master of Science degree in May, 1966, at Oklahoma  
State University.

Professional Experience: Served six months in the United  
States Army, 1958. Employed for four years in the  
Testing Laboratory of Nebraska Department of Roads,  
1959 to 1963. Employed for three months with Sinclair  
Research, Inc., 1965.