VAPOR-LIQUID EQUILIBRIA FROM GENERALIZED P-V-T RELATIONS

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FROM
GENERALIZED P-V-T RELATIONS

By

JOHN NELSON HESTER

A THESIS

Submitted to the College of Engineering
Michigan State University of Agriculture and
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ABSTRACT

This investigation is a study of the satisfactoriness of current methods for calculating the pressure-volume-temperature relations of mixtures, with particular emphasis on the use of these methods to predict binary vapor-liquid equilibria.

Pitzer's generalized correlation, which expresses thermodynamic properties in terms of reduced temperature, reduced pressure and an "acentric factor", accurately predicts the vapor pressure of pure compounds. It does not predict the azeotropic temperature, pressure and composition for any of the systems studied, viz., ethyl alcohol - water, ethyl alcohol - benzene and ethyl acetate - normal hexane. Various combinations of the critical properties and acentric factors were attempted for the pure compounds but the results obtained were not an improvement on those acquired with a simple molar average of the properties of the pure compounds. However, Pitzer's correlation, with this simple molar average combination of the critical properties, predicted volumetric properties of methyl alcohol - normal butane mixtures with greater accuracy than Amagat's law or critical compressibility charts developed by Maxwell and by Hougen and Watson.

The past success of the Benedict-Webb-Rubin equation of state in predicting hydrocarbon vapor-liquid equilibria prompted a study of the relation between the critical properties of pure compounds and the pseudocritical properties obtained with these equations. For the ethane - normal heptane system, the critical compressibility

of the 0.8 mole fraction ethane mixture is 0.211 while it is 0.228 for the 0.5 mixture. In direct contrast, the critical compressibility of pure ethane and pure normal heptane are 0.285 and 0.260 respectively. In addition, the effective pseudocritical pressure for the 0.5 mole fraction ethane mixture calculated by this method is 25.2 atmospheres while the critical pressure of ethane is 48.2 atmospheres and that for normal heptane is 27.0 atmospheres.

These anomalous findings cast doubt on the adequacy of the usual assumption that a single phase mixture behaves like a single compound with properties which are intermediate between the properties of the pure components of the mixture.

This study indicates that reliable calculation of vapor-liquid equilibria from the P-V-T relations of mixtures will not be successful until an exact equation of state relationship is established between pure compounds and mixtures.

APPROVED: Carl Cooper
Major Professor

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INTRODUCTION

INTRODUCTION

A prime requisite for the successful design of mass transfer processes such as distillation, absorption and extraction, is accurate phase equilibrium data.

The experimental determination of reliable vapor-liquid equilibria requires a complex laboratory technique. Several experimental methods have been proposed but there is considerable doubt about the accuracy of the data that has been obtained with each.

Difficulties encountered in the experimental determination of such data make calculation techniques for vapor-liquid equilibria important. In addition, such calculations illustrate the general behavior of vapor-liquid mixtures.

Predictions of vapor-liquid equilibria are based upon rigorous thermodynamic relationships. There are two basic methods for calculating vapor-liquid equilibria. One of these methods, Method I, uses experimental vapor pressures, fugacity charts and activity coefficients; while the second method employs an equation of state that is applicable to the mixture and to its pure components.

Method I is in use today by most persons interested in vapor-liquid equilibria. However, it has several disadvantages of which the principal one is its dependence on experimental activity coefficients for the mixture; these are seldom available.

In direct contrast, Method II does not require any experimental data on properties of the mixture. However, it does demand an accurate equation of state and a precise method for combining the arbitrary constants of the equation of state when applied to mixtures.

The elusive element in Method II has been a determination of the exact relationship between properties of a mixture and properties of its pure components. The establishment of this element has been the dominant motivation for this study.

THEORY

A. Pure Compounds

Equations that involve only pressure, volume, temperature and arbitrary constants are called "equations of state". These equations attempt to predict the behavior of pure compounds over a practical range of conditions. Dodge (8) has pointed out that over 100 equations of state have been proposed, although only a few have come into common use.

The equations of state that are directly related to this work are listed below:

Ideal Gas Law (1)

$$P = RT/V$$

van der Waals' Equation (2a)

$$P = RT/(V - b) - a/V^2$$

Reduced Form of van der Waals' Equation (2b)

$$P_r = 8T_r/(3V_r - 1) - 3/V_r{}^2$$

Beattie-Bridgeman Equation (3)

$$P = RTd + (B_oRT - A_o - Rc/T^2)d^2 + (-B_obRT + A_oa - RB_oc/T^2)d^3 + RB_obcd^4/T^2$$

Benedict, Webb and Rubin Equation (4)

$$P = RTd + (B_oRT - A_o - C_o/T^2)d^2 + (bRT - a)d^2 + \alpha ad^6 + cd^3/T^2 \left[(1 + \gamma d^2)e^{-\gamma d^2}\right]$$

Compressibility Charts (5)

$$Z = f(P_r, T_r)$$

Pitzer Correlation (6)

$$Z = f(P_r, T_r, \omega)$$

Riedel Correlation (7)

$$Z = f(P_r, T_r, \alpha_c)$$

Lydersen, Greenkorn and Hougen Correlation (8)

$$Z = f(P_r, T_r, Z_c)$$

These relationships vary in complexity, ranging from no arbitrary constants in the ideal gas law to eight arbitrary constants in the Benedict, Webb and Rubin equation.

A comparison of the complexity and the accuracy that may be achieved in predicting some properties of pure compounds is given in Table 1. This table illustrates the application of the listed equations of state to a large number of compounds though the comparison may not be accurate for any single compound.

In the low pressure region each of the relationships represent the properties of pure compounds accurately but there are major inaccuracies in Equations (1) and (2) for the high pressure region. Only Equations (4), (6), (7) and (8) give reasonable results when applied to the prediction of liquid densities.

In the critical region each of the equations except the ideal gas law gives a family of isothermal curves in the pressure-volume plane which have a horizontal inflection point at the critical temperature and pressure. The critical pressure, temperature and volume may be determined by utilizing the fact that the isotherm passing through the critical point has zero slope at that point which is also a point of inflection. This

TABLE 1

ACCURACY AND COMPLEXITY OF EQUATIONS OF STATE

Equation	Low Pressure Gases	High Pressure Gases	Critical Region	Liquid Densities	Vapor Pressures	Number of Constants	Type of Relation
(1)	Good	Poor	No	No	No	0	Analytical
(2)	Excellent	Fair	Fair	Poor	Poor	2	Analytical
(3)	Excellent	Good	Fair	Poor	Poor	5	Analytical
(4)	Excellent	Excellent	Good	Fair	Good	8	Analytical
(5)	Excellent	Fair	Fair	No	No	2	Graphical
(6)	Excellent	Good	Good	Fair	Fair	3	Graphical*
(7)	Excellent	Good	Good	Fair	Fair	3	Graphical*
(8)	Excellent	Good	Good	Fair	Fair	3	Graphical*

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* Also Tabular

satisfies the following mathematical requirements:

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \tag{9}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \tag{10}$$

The prediction of vapor pressures with these relationships is based upon the thermodynamic requirements that at equilibrium:

$$P_L = P_V \tag{11}$$

$$T_L = T_V \tag{12}$$

$$\int_{V_l}^{V_V} V dP = 0 \tag{13}$$

The actual calculation of vapor pressure with an equation of state involves finding the vapor volume and liquid volume at which the fugacity of the vapor and the liquid phases are equal. The pressure of both phases must be equal and is the calculated vapor pressure.

The ideal gas law was the first equation of state. It may be derived from a kinetic viewpoint with the following assumptions: (a) the volume of the molecules of the gas is negligible when compared to the total volume of the gas and (b) there are no attractive forces between the molecules of the gas. Actual gases do not conform to the behavior predicted by the ideal gas law but merely approach these conditions at low pressures.

In 1873 van der Waals (33) proposed the first practical equation of state to improve upon the ideal gas law. He considered that (a) a portion of the space occupied by a gas is taken up by the molecules themselves so that the "free space" through which the molecules can move is not equal to the total volume and (b) there is a force of attraction between the molecules of the gas.

Despite these refinements, van der Waals' equation is only an approximation and exhibits large deviations from actual behavior as the pressure increases.

Equation (2a) is another form of van der Waals' equation of state expressed in terms of reduced properties. This was probably the first expression of the theory of corresponding states and may be considered as a forerunner of Equations (5) through (8).

The Beattie-Bridgeman equation of state (2) is one of the most notable improvements on van der Waals' equation. It is an example of a more complex equation of state, with five arbitrary constants. It has proved to be very accurate in the range of conditions for which the constants were determined, but it gives extremely poor results at pressures of the order of 250 atmospheres (10).

The Benedict, Webb and Rubin equation (4) is probably the most accurate equation of state in use today. This equation was developed as a modification of the Beattie-Bridgeman equation of state to improve the prediction of the properties of fluids at high densities. It has successfully predicted P-V-T (pressure-volume-temperature) properties within 0.34% of the actual values for hydrocarbons and other compounds up to densities twice the critical density.

Equations (5) through (8) are graphical representations of the compressibility factor, Z, in terms of reduced properties. This compressibility factor modifies the ideal gas law to account for the deviation of the properties of a real gas from those of an ideal gas. This factor is not a constant but is a function of (a) the gas itself, (b) the pressure and (c) the temperature.

The behavior of any actual gas can be represented by means of a graph of compressibility factor vs. pressure, with temperature as a parameter. It has been found that the graphs for each gas showed the same general trends though they were different in magnitude. These similarities led to the application of this relationship to the theory of corresponding states as proposed by van der Waals (33).

The theory of corresponding states asserts that the P-V-T relations of all gases are the same when each variable is expressed in terms of reduced properties. Reduced pressure, reduced temperature, reduced volume and reduced density may be defined as follows:

$$P_r = P/P_c$$

$$T_r = T/T_c$$

$$V_r = V/V_c$$

$$d_r = d/d_c$$

where the subscript, c, refers to the critical state.

This theory led to the relationship expressed in Equation (5) which several investigators (11, 20, 21) have used to develop generalized compressibility charts. These charts give a good degree of accuracy with errors primarily due to the approximate nature of the theory of corresponding states.

In recent years, several methods have been presented for improving the accuracy of the generalized compressibility charts by the introduction of a third parameter. Equations (6), (7) and (8) are some of the more prominent methods.

Pitzer (25) introduced as his third parameter the acentric factor, ω, which is a measure of the deviation of the "intermolecular potential" from that of a "simple fluid". The acentric factor was defined as

$$\omega = -\log P_r - 1.000 \qquad (14)$$

where P_r is the reduced vapor pressure measured at a reduced temperature of 0.7. The compressibility factor was then expressed as a power series in the acentric factor

$$Z = Z^o + \omega Z' + \omega^2 Z'' + \ldots\ldots \qquad (15)$$

where Z^o, Z' and Z'' are different graphical functions of reduced pressure and reduced temperature. It was determined that the first two terms in Equation (15) were sufficient in almost every region. Pitzer and his coworkers (26) attempted to evaluate the quadratic term Z'' for the small region in which it appeared to be significant. However, the resulting values were not used because they showed irregular behavior. This correlation without the Z'' term, has also been applied with fair success to the prediction of the properties of both saturated liquids and saturated gases.

Riedel (28) introduced a temperature derivative of the vapor pressure at the critical point, α_c, as a third parameter for the estimation of generalized vapor pressure and liquid density data, where

$$\alpha_c = \frac{T_c}{P_c}\left(\frac{\partial P}{\partial T}\right)_c \qquad (16)$$

Pitzer (26) points out that α_c is related to his acentric factor by the following equation:

$$\alpha_c = 5.808 + 4.93\,\omega \qquad (17)$$

Lydersen, Greenkorn and Hougen (18) have selected as their choice for a third parameter, the critical compressibility factor, defined as

$$Z_c = P_cV_c/RT_c \qquad (18)$$

The results of this work were presented in four groups of compounds by their values of Z_c. This correlation includes the liquid region and it can also be related to Pitzer's correlation. Pitzer (26) gives the following equation as the relation between Z_c and his acentric factor:

$$Z_c = 0.288 - 0.863\,\omega \qquad (19)$$

B. Mixtures

The solution to the perplexing problem of predicting the properties of mixtures has been elusive to scientists and engineers who have pursued this course. The ideal way to express the P-V-T behavior of a mixture, when its composition is known, is in terms of the known behavior of the pure components. Thus if there is an equation of state for each component in the mixture, the simplest way to describe the behavior of the mixture would be by means of some combination of the arbitrary constants of the equation for the pure components.

The success achieved with the application of reduced properties to pure compounds suggested their use for mixtures. However, it was determined that the true critical point was of little value in correlating the physical properties of mixtures. When it is used for calculating reduced properties, the compressibility curves deviate considerably from those for pure compounds, especially in the critical region. Further investigation showed that a fictitious value of critical temperature and pressure could be employed so that the compressibility curves for the mixture correspond with those for pure compounds. The point for these fictitious values was called the pseudocritical point and the values were termed pseudocritical properties by Kay (13).

This pseudocritical point for a mixture is analogous to the critical point of a pure compound whose P-V-T relations in the superheated region are identical with those for the mixture. It has however no real existence and therefore cannot be measured experimentally. Only for mixtures of narrow boiling range is it approximately equal to the true critical point.

There have been a number of methods proposed for combining the constants of an equation of state and for predicting the pseudocritical properties of a mixture. Some of the more prominent methods are listed below:

Amagat's Law (20)

$$V_m = Y_a V_a + Y_b V_b + ----$$

van der Waals' Combination (21)

(a) $b_m = Y_a b_a + Y_b b_b + ----$

(b) $(a_m)^{1/2} = Y_a (a_a)^{1/2} + Y_b (a_b)^{1/2} + ----$

(c) $\left(\frac{T_c}{P_c}\right)_m = Y_a \left(\frac{T_c}{P_c}\right)_a + Y_b \left(\frac{T_c}{P_c}\right)_b$

(d) $\left(\frac{T_c}{\sqrt{P_c}}\right)_m = Y_a \left(\frac{T_c}{\sqrt{P_c}}\right)_a + Y_b \left(\frac{T_c}{\sqrt{P_c}}\right)_b$

Lorentz Combination (22)

$$K_m = \left[Y_a (K_a)^{1/3} + Y_b (K_b)^{1/3}\right]^3 / 8$$

Kay's Rule (23)

(a) $T_{c_m} = Y_a T_{c_a} + Y_b T_{c_b} + ----$

(b) $P_{c_m} = Y_a P_{c_a} + Y_b P_{c_b} + ----$

Beattie-Bridgeman Combinations (24)

$K_m = Y_a K_a + Y_b K_b + ----$

where $K = a, b, A_o^{1/2}, B_o^{1/3}$, or $c^{1/2}$

Benedict, Webb and Rubin Combinations (25)

$K_m = Y_a K_a + Y_b K_b + ----$

where $K = A_o^{1/2}, B_o, C_o^{1/2}, a^{1/3}, b^{1/3}$,
$c^{1/3}, \alpha^{1/3}$, or $\gamma^{1/2}$

Prausnitz and Gunn Combinations (26)

(a) $P_{c_m} = \frac{RT_{c_m}}{V_{c_m}} \sum_i Y_i Z_{c_i}$

(b) $T_{c_m} = \frac{\beta + (\beta^2 + rV_{c_m}\gamma)^{1/2}}{2sV_{c_m}}$

(c) $\beta = \sum_{ij} Y_i Y_j (V_c T_c)_{ij}$

$$\text{(d)} \quad \gamma = \sum_{ij} Y_i Y_j (V_c T_c^2)_{ij}$$

$$\text{(e)} \quad T_{c_{ij}} = (T_{c_i} T_{c_j})^{1/2} - \Delta T_{c_{ij}}$$

$$\text{(f)} \quad V_{c_{ij}} = 0.5(V_{c_i} + V_{c_j}) - \Delta V_{c_{ij}}$$

Amagat's (1) law of additive volumes, which states the volume occupied by a mixture of gases is equal to the sum of the volumes occupied separately by each component at the same conditions of temperature and pressure, has been applied to both ideal and real mixtures of gases. It is accurate for ideal gas mixtures and also gives good results for many mixtures of real gases and liquids.

Van der Waals' combination (33) for the constant a is based upon the fact the attractive forces between the molecules is equal to the geometric mean of the forces that each molecule possesses when attracted by a like molecule. The combination for the constant b assumes that the volume occupied by the molecules is equivalent to their arithmetic mean. Equations (21c) and (21d) are extensions of van der Waals' combinations to the prediction of pseudocritical temperatures and pressures.

Kay's rule (13) is an application of the theory of corresponding states to mixtures of gases by the use of pseudocritical constants to evaluate the reduced properties.

The Lorentz combination (17) takes into account the packing effect between large and small molecules where the small molecules may occupy the space between the large molecules.

Beattie-Bridgeman (2) and Benedict-Webb-Rubin (5) extended the hypothesis of van der Waals to the calculation of constants for mixtures for their equations.

The combinations of Prausnitz and Gunn (27) represent the first attempt to account for the probability of differences between the behavior of mixtures and of the pure compounds composing the mixtures. This method incorporates Pitzer's correlation and introduces two graphical corrections to the characteristic critical temperature and characteristic critical volume, ΔT_{c12} and ΔV_{c12}.

C. Prediction of Vapor-Liquid Equilibria

There are two methods that may be employed for the calculation of vapor-liquid equilibria.

Method I - The first method involves the use of experimental vapor pressures with the basic thermodynamic relations. A general relationship for the prediction of vapor-liquid equilibria by this method may be written as follows:

$$Y = \frac{P_o \nu P_o \gamma X}{P \nu P \gamma'} \; e \; \frac{V_1(P_o - P)}{RT} \qquad (27)$$

This relationship is actually Raoult's law

$$Y = P_o X/P \qquad (28)$$

with additional factors to correct the various deviations from ideality. This method has several disadvantages, the principal one being the dependence on experimental activity coefficients for the mixture which are generally unavailable.

Method II - The second method embodies only the use of an equation of state for the pure compounds and the mixture. This method is based upon the thermodynamic requirements that at equilibrium

$$P_L = P_V \tag{11}$$

$$T_L = T_V \tag{12}$$

$$\text{(a)}\ \tilde{F}_{L_1} = \tilde{F}_{V_1} \tag{29}$$

$$\text{(b)}\ \tilde{F}_{L_2} = \tilde{F}_{V_2}$$

The actual calculation of vapor-liquid equilibria by this method requires the use of the equation of state to predict the P-V-T properties of the mixture and then evaluating the following thermodynamic equations:

$$\tilde{A} = \int_0^V \left[(P - RT/V)dV\right]_{x,T} - RT \ln RT/V +$$

$$XRT \ln X + (1 - X)RT \ln (1 - X) \tag{30}$$

$$\tilde{F}_{L_1} = (1-X)(\partial\tilde{A}_L / \partial X)_{T,V} + \tilde{A}_L \tag{31}$$

$$\tilde{F}_{V_1} = (1-Y)(\partial\tilde{A}_V / \partial Y)_{T,V} + \tilde{A}_V \tag{32}$$

The criteria for equilibrium requires that the partial molal free energies obtained in Equations (31) and (32) must be equal. The fugacity may be then calculated from the work content, A, by the thermodynamic relation

$$RT \ln f = (\partial A/\partial N)_{V,T,N} \tag{33}$$

and vapor-liquid equilibria may be predicted from the fugacity.

The principal disadvantage of this method is that it requires a complex equation of state which must be accurate in both the liquid and vapor regions and which must also predict correct vapor pressures.

A distinct advantage that the use of an equation of state enjoys over the more commonly used first method is that no experimental data on the properties of the mixture are necessary.

HISTORY

HISTORY

The existence of a relationship between equations of state and vapor-liquid equilibria has been recognized for some time. Van der Waals demonstrated the relation between his equation of state and the vapor pressure of a pure compound. Berthelot (6) and Galitzine (9) extended van der Waals' equation to mixtures and van Laar (34) obtained his equation for liquid activity coefficients by a semi-theoretical derivation from these van der Waals' mixture equations.

Studies of vapor-liquid equilibria in high pressure mixtures were motivated by the petroleum industry's interest in the distillation and absorption of light hydrocarbons. In 1932, generalized correlations of pure component compressibility factors were published by Lewis of Massachusetts Institute of Technology and Brown et al of the University of Michigan. These correlations were used to determine the values of the fugacity coefficients from which the values of y/x for the individual hydrocarbons were then calculated. This calculation was performed in the manner described under Method I in the theory section assuming that γ and γ' were equal to unity.

A more rigorous approach was made by Benedict, Webb and Rubin in 1940 using Method II under theory. Their work (4) involved the development of a new equation of state for pure compounds and a set of rules for applying this equation to mixtures. Employing Method II, they calculated K charts for pressures up to 3600 psia and correction factor charts for each of the twelve light hydrocarbons investigated. The correction factor charts were necessary since γ and γ' in Method I were not actually equal to unity.

Smith and Watson (30) employed a similar approach based upon the fugacity charts and Kay's rule. The work of Benedict and his coworkers has led to a number of other investigations based upon their equation of state. Sage and coworkers (16, 22) have shown its utility over higher ranges of pressure than 3600 psia. Schiller and Canjar (29) and Stotler and Benedict (32) have applied the Benedict, Webb and Rubin equation and Method II to the nitrogen-carbon monoxide and nitrogen-methane systems respectively with success. However, Cullen and Kobe (7) attempted to apply this equation to the non-ideal system carbon dioxide and propane but found the correlation to be unsatisfactory.

OBJECTIVES

OBJECTIVES

The ultimate object of this work was to satisfactorily predict the vapor-liquid equilibria of mixtures from equations of state. Benedict, Webb and Rubin and Smith and Watson have had some success with this approach but their best applications have been with mixtures of hydrocarbons which form nearly ideal solutions.

The only limitation in predicting the vapor-liquid equilibria for both ideal and non-ideal systems is the lack of an accurate equation of state for pure compounds and their mixtures.

It was hoped that a combination of the correlations recently developed by Pitzer and others for pure compounds and simple rules for obtaining the three constants for mixtures might be useful in working toward this ultimate objective.

An attempt was first made to apply these equations and rules to azeotropic mixtures. When this proved unsuccessful, the same equations and rules were applied to volumetric data on non-ideal mixtures. Only moderate success was achieved.

It seemed that the principal difficulty encountered was the inaccuracy of the rules for combining constants when determining the pseudocritical temperatures and pressures and the acentric factors. Therefore it was decided to determine what relation exists between the critical constants for pure compounds and the pseudocritical constants for mixtures when the reputedly successful Benedict, Webb and Rubin method is applied. From these results, an effort was made to develop rules for combining pseudocritical constants. Moreover, an evaluation and a comparison were made of the prominent methods that have been proposed for estimating pseudocritical constants.

LIST OF CALCULATIONS

LIST OF CALCULATIONS

A. Pitzer Correlations vs. Vapor Pressures

1. Benzene
2. Water
3. Ethyl Alcohol
4. Normal Hexane
5. Ethyl Acetate
6. Methyl Alcohol

B. Azeotropes and Their Relationship to the Reduced Vapor Pressure Line

1. Benzene - Ethyl Alcohol
2. Water - Ethyl Alcohol
3. Normal Hexane - Ethyl Acetate

C. Azeotropes and Their Relationship to $(\partial P/\partial X)_T$ Along Saturation Line

1. Benzene - Ethyl Alcohol
2. Water - Ethyl Alcohol
3. Normal Hexane - Ethyl Acetate

D. Liquid Volume Predictions For Methanol-Normal Butane Mixtures

1. Amagat's Law
2. Pseudocritical Method
3. Maxwell Method
4. Pitzer Correlation

E. Pitzer Correlations for Liquid Volume Predictions

1. Normal Butane
2. Benzene
3. Normal Pentane

F. Pseudocritical Properties of Ethane-Normal Heptane System

1. Benedict-Webb-Rubin Equation of State
2. Prausnitz-Gunn Correlation
3. Kay's Rule
4. Van der Waals' Combinations

G. Miscellaneous Calculations

1. Empirical Combination for Pseudocritical Properties
2. Martin-Hou Equation of State

PROCEDURE

PROCEDURE

A. Pitzer Correlations vs. Vapor Pressures

These series of calculations were performed to ascertain the accuracy that could be achieved with the Pitzer correlations. The following procedure was used:

1. Calculate the reduced temperature and pressure from the experimental vapor pressure and temperature.
2. Determine the common logarithm of the reduced pressure.
3. Determine the negative of the common logarithm of the reduced pressure.
4. Determine the values of $-\log P_r^0$ and $-(\partial \log P_r/\partial \omega)_T$ corresponding to the reduced temperature by interpolation of Table VI of Pitzer's work. The term $-\log P_r^0$ refers to when the acentric factor is equal to zero.
5. a. Calculate the change in the logarithm of the reduced pressure

$$-\Delta \log P_r = -\omega (\partial \log P_r/\partial \omega)_T$$

   b. The acentric factors for several compounds are presented in Table I of Pitzer's work. They may also be calculated by this relationship

$$-\log P_r = -\log P_r^0 + \omega(-\partial \log P_r/\partial \omega)_T$$

(Experimental)

6. Calculate the theoretical value of the common logarithm of the reduced pressure.

$$- \log P_r = - \log P_r - \log P_r{}^{o}$$

(Theoretical)

B. <u>Azeotropes and Their Relationship to the Reduced Vapor Pressure Line</u>

These calculations were performed to determine if the azeotropes lay on the reduced pressure line.

1. These calculations followed the six steps outline in calculation (A) with the exception of the use of five different methods for combining the acentric factors, critical temperatures and critical pressures for the azeotropic mixtures.

2. <u>Assumption I</u> - Kay's rule was applied to the pseudocritical temperatures and pressures while the acentric factors were combined linearly.

   a. $P_{c_m} = X_i P_{c_i} + X_j P_{c_j}$

   b. $T_{c_m} = X_i P_{c_i} + X_j P_{c_j}$

   c. $\omega_m = X_i \omega_i + X_j \omega_j$

3. <u>Assumption II</u> - Van der Waals' combinations were applied to the pseudocritical temperatures and pressures while the acentric factors were again combined linearly.

   a. $\left(\frac{T_c}{P_c}\right)_m = X_i \left(\frac{T_c}{P_c}\right)_i + X_j \left(\frac{T_c}{P_c}\right)_j$

   b. $\left(\frac{T_c}{\sqrt{P_c}}\right)_m = X_i \left(\frac{T_c}{\sqrt{P_c}}\right)_i + X_j \left(\frac{T_c}{\sqrt{P_c}}\right)_j$

c. $\omega_m = X_i\,\omega_i + X_j\,\omega_j$

4. <u>Assumption III</u> - Kay's rule was used for the pseudocritical temperatures and pressures. The acentric factors were determined by an empirical relationship.

   a. $P_{c_m} = X_i P_{c_i} + X_j P_{c_j}$

   b. $T_{c_m} = X_i T_{c_i} + X_j T_{c_j}$

   c. $$\left(0.1 - 0.1^{\omega + 1}\right)^{1/2}_m = X_i\left(0.1 - 0.1^{\omega + 1}\right)^{1/2}_m + X_j\left(0.1 - 0.1^{\omega + 1}\right)^{1/2}_m$$

5. <u>Assumption IV</u> - An empirical relationship was used to calculate the pseudocritical temperatures and pressures. This relationship was derived with results obtained in a later calculation with the Benedict-Webb-Rubin equation of state. The acentric factors were determined in the same manner as used in Assumption III.

   a. $$\left(\frac{T^{1.8}}{\sqrt{P}}\right)_m = X_i\left(\frac{T^{1.8}}{\sqrt{P}}\right)_i + X_j\left(\frac{T^{1.8}}{\sqrt{P}}\right)_j$$

   b. $$\left(\frac{T}{P^{0.1}}\right)_m = X_i\left(\frac{T}{P^{0.1}}\right)_i + X_j\left(\frac{T}{P^{0.1}}\right)_j$$

   c. $$\left(0.1 - 0.1^{\omega + 1}\right)^{1/2}_m = X_i\left(0.1 - 0.1^{\omega + 1}\right)^{1/2}_m + X_j\left(0.1 - 0.1^{\omega + 1}\right)^{1/2}_m$$

6. <u>Assumption V</u> - Van der Waals' combinations were used for the pseudocritical temperatures and pressures. The acentric factors were combined with an empirical relationship.

a. $\left(\frac{T_c}{P_c}\right)_m = X_i\left(\frac{T_c}{P_c}\right)_i + X_j\left(\frac{T_c}{P_c}\right)_j$

b. $\left(\frac{T_c}{\sqrt{P_c}}\right)_m = X_i\left(\frac{T_c}{\sqrt{P_c}}\right)_i + X_j\left(\frac{T_c}{\sqrt{P_c}}\right)_j$

c. $\frac{1}{\omega_m^3} = \frac{X_i}{\omega_i^3} + \frac{X_j}{\omega_j^3}$

C. Azeotropes and Their Relationship to $(\partial P/\partial X)_T$ Along Saturation Line

These calculations were performed to determine if the $(\partial P/\partial X)_T$ along the saturation line was zero at the azeotropic composition. Three methods of combining the acentric factors, critical temperatures and critical pressures were employed.

1. Assumption I was used to combine the parameters.

   a. $A = BC + D + E$

   b. $A = (\partial \log P_r/\partial X)_T$

   c. $B = (\partial \log P_r/\partial T_r)_X$

   d. $C = (\partial T_r/\partial X)_T = -(T_r/T_c)(dT_c/dX)$

   $= -T_r/T_c(T_{ci} - T_{cj})$

   e. $D = (\partial \log P_r/\partial X)_{T_r} = (\partial \log P_r/\partial\omega)_{T_r}(d\omega/dX)$

   $= (\partial \log P_r/\partial\omega)_{T_r}(\omega_i - \omega_j)$

   f. $E = (d \log P_c/dX) = (d \ln P_c/dX)/2.303$

   $= (P_{ci} - P_{cj})/2.303\ P_c$

   The values for 'B' were determined by taking the difference in two values for Pitzer's value of $-\log P_r$ and dividing it by the difference between the corresponding reduced temperatures. The remaining values were obtained from simple substitutions.

2. **Assumption III was used here to combine the parameters and the same procedure of part (A) was followed with this variation for the acentric factor.**

   a. $$\left(0.1 - 0.1^{\omega} + 1\right)_m^{1/2} = X_i \left(0.1 - 0.1^{\omega} + 1\right)_i^{1/2} + X_j \left(0.1 - 0.1^{\omega} + 1\right)_j^{1/2}$$

   b. $$\frac{d\left(0.1 - 0.1^{\omega} + 1\right)_m^{1/2}}{dX} = \left(0.1 - 0.1^{\omega} + 1\right)_i^{1/2} + \left(0.1 - 0.1^{\omega} + 1\right)_j^{1/2}$$

   c. $$\frac{d\omega}{dX} = \frac{2\left(0.1 - 0.1^{\omega_i} + 1\right)^{1/2} - \left(0.1 - 0.1^{\omega_j} + 1\right)^{1/2}}{2.303\left(0.1 - 0.1^{\omega_m} + 1\right)^{-1/2} 0.1^{\omega_m} + 1}$$

3. **Assumption V was used to combine the parameters with the following modifications.**

   a. $$\frac{d(1/\omega^3)}{dX} = \frac{1}{\omega_i^3} - \frac{1}{\omega_j^3}$$

   b. $$\frac{d\omega}{dX} = -\frac{1}{3}\omega^4\left(\frac{1}{\omega_i^3} - \frac{1}{\omega_j^3}\right)$$

   c. $$\frac{d(T_c/P_c)}{dX} = \frac{1}{P_c}\left(\frac{dT_c}{dX}\right) - \frac{T_c}{P_c^2}\left(\frac{dP_c}{dX}\right) = \left(\frac{T_c}{P_c}\right)_i - \left(\frac{T_c}{P_c}\right)_j$$

   d. $$\frac{d(T_c/P_c)}{dX} = \frac{1}{\sqrt{P_c}}\left(\frac{dT_c}{dX}\right) - \frac{T_c}{2P_c\sqrt{P_c}}\left(\frac{dP_c}{dX}\right) = \left(\frac{T_c}{\sqrt{P_c}}\right)_i - \left(\frac{T_c}{\sqrt{P_c}}\right)_j$$

   e. $$\frac{dP_c}{dX} = \frac{2P_{c_m}^2}{T_{c_m}}\left\{\frac{1}{\sqrt{P_{c_m}}}\left[\left(\frac{T_c}{P_c}\right)_i - \left(\frac{T_c}{P_c}\right)_j\right] - \left(\frac{T_c}{\sqrt{P_c}}\right)_i + \left(\frac{T_c}{\sqrt{P_c}}\right)_j\right\}$$

   f. $$\frac{dT_c}{dX} = P_{c_m}\left\{\frac{2}{P_{c_m}}\left[\left(\frac{T_c}{P_c}\right)_i - \left(\frac{T_c}{P_c}\right)_j\right] - \left(\frac{T_c}{\sqrt{P_c}}\right)_i + \left(\frac{T_c}{\sqrt{P_c}}\right)_j\right\}$$

D. Liquid Volume Predictions for Methanol-Normal Butane Mixtures

This calculation was initiated with a comparison of experimental data with volumetric predictions obtained with the Pitzer correlation. The large deviations from the experimental results prompted a study of the volumetric properties of several pure compounds which are discussed under Calculation (E).

The volumetric calculations for the methanol-normal butane mixtures were continued to include predictions by (a) Amagat's Law, (b) a pseudocritical method with the "Chemical Process Principles Charts" of Hougen and Watson and (c) Maxwell's method using a correction factor with compressibility charts. A comparison of the values obtained with each method was made in relation to the experimental volumes.

Calculations were made on mixtures containing 0.25, 0.50 and 0.75 mole fractions methanol at 40 psia and temperatures of 200°F, 240°F, and 280°F. The same calculations were repeated with these mixtures at 125 psia and 280°F.

1. Pitzer Correlation

a. Determine the reduced temperature and the reduced pressures from the experimental temperatures and pressures.

b. Determine the values of Z^0 and Z' for each reduced temperature and reduced pressure by interpolation with Tables II and IV of Pitzer's work.

c. Calculate the value of Z with Equation (1-15).

$$Z = Z^0 + \omega Z'$$

d. Calculate the volume by the following equation:

$$V = ZRT/P$$

2. **Amagat's Law**

The volumes were calculated by applying Equation (1-20).

$$V_m = Y_i V_i + Y_j V_j$$

3. **Pseudocritical Method**

a. Determine the pseudocritical temperatures and pressures with Kay's rule.

$$P_{c_m} = X_i P_{c_i} + X_j P_{c_j}$$

$$T_{c_m} = X_i T_{c_i} + X_j T_{c_j}$$

b. Determine the reduced temperature and reduced pressure.

c. Calculate the compressibility factor, Z, from page 103 of "Chemical Process Principles Charts" by Hougen and Watson.

d. Calculate the volume in the same manner described in step (d) of the Pitzer correlation.

4. **Maxwell Method**

a. Determine the reduced temperature.

b. Calculate the reduced pressure for each component by the following correction.

$$P_{r_i} = P/P_c(Y_i)^{1/2}$$

c. Determine the compressibility factors from pages 152-3 of Maxwell's "Data Book on Hydrocarbons" for each component.

d. Calculate the volume by the following equation.

$$V = RT/P(Y_i Z_i + Y_j Z_j)$$

E. Pitzer Correlations for Liquid Volume Predictions

These calculations were performed to determine the accuracy of Pitzer's correlation when it is applied to the calculation of liquid volumes for pure compounds. Benzene, normal butane and normal pentane were the selected pure compounds. Several vapor pressures were chosen and the calculations followed the procedure outlined under "Pitzer's Correlation" in Calculation (D).

F. Pseudocritical Properties of Ethane-Normal Heptane System

1. The Benedict-Webb-Rubin equation of state was used to determine the relationship between the critical constants for pure compounds and the pseudocritical constants for mixtures. The eight arbitrary constants of the equation were combined in the manner suggested by Benedict and his coworkers and reported as Equation (24) in the theory section.

$$K_m = X_i K_i + X_j K_j + ----$$

where $K = A_o^{1/2}, B_o, C_o^{1/2}, a^{1/3}, b^{1/3}, c^{1/3}, \alpha^{1/3}$ or $\gamma^{1/2}$

Five significant figures were used with each constant as recommended by Benedict et al. They pointed out that six figures should be used in calculating the properties of liquids and four or five figures should be used for gases. They detected that a change of one in the sixth place of one constant by itself would alter the calculated pressure of a liquid by approximately 0.01 atmospheres. However, they stated that it is possible to change all the constants simultaneously by about five percent without seriously affecting the calculated results.

Critical densities were assumed for the mixture and the critical temperature was obtained by a trial and error calculation employing the mathematical requirement presented in Equations (9) and (10) of the section on theory.

$$\left(\frac{\partial P}{\partial d}\right)_T = 0$$

$$\left(\frac{\partial^2 P}{\partial d^2}\right)_T = 0$$

In this case the volume is replaced by the density since the Benedict-Webb-Rubin equation expresses the pressure as a function of temperature and density.

The Benedict-Webb-Rubin equation of state was differentiated and equated to zero to obtain the following relations:

$$0 = ce^{-\gamma d^2}(3d^2 + 3\gamma d^4 - 2\gamma^2 d^6) - 2dC_o +$$
$$(-2A_o d - 3ad^2 + 6a\alpha d^5)T^2 + (R + 3bRd^2 + 2B_o Rd)T^3$$

$$0 = ce^{-\gamma d^2}(6d + 6\gamma d^3 - 18\gamma^2 d^5 + 4\gamma^3 d^7) - 2C_o +$$
$$(-2A_o - 6ad + 30a\alpha d^4)T^2 + (6bRd + 2B_o R)T^3$$

These cubic equations in the absolute temperature were solved with a trigonometric solution using common logarithms to obtain the required accuracy. These equations have the form:

$$Ax^3 + Bx^2 + D = 0$$

and were solved as follows

$$\text{Let} \quad \sin\theta = (3D/2B)(3/B)^{1/2}$$

$$\text{or} \quad \log\sin\theta = \log 1.5 + 0.5\log 3 + \log D - 1.5\log B$$

$$\text{then the required root} = 2(B/3)^{1/2}\sin\theta/3$$

$$= \log 2 + \log\sin\theta/3 - 0.5\log 3 - 0.5\log B$$

The antilog of the required root is equal to the pseudocritical temperature. The correct pseudocritical density is obtained when the pseudocritical temperatures calculated by Equations (1-9) and (1-10) are equal. The pressure was then calculated at this point by employing the original form of the equation of state.

These calculations were carried out for mixtures containing 0.5 and 0.8 mole fraction ethane. In addition, a comparison was made of these results with values obtained using Kay's rule and van der Waals' combinations. Also the values were used to calculate the compressibility factors for the pure compounds and the two mixtures.

2. The recent work of Prausnitz and Gunn was employed to calculate pseudocritical temperatures and pressures for the ethane-normal heptane system. Difficulties were encountered in evaluating the corrections for the characteristic critical temperature because this system was not included in the graph presented for determining these corrections.

a. Calculate the characteristic critical temperature and volume by the following equations.

$$T_{cij} = (T_{ci}T_{cj})^{1/2} - \Delta T_{cij}$$

$$V_{cij} = 0.5\ (V_{ci} + V_{cj})$$

The correction, ΔT_{cij}, may be obtained from a graph of this correction vs. the critical volume ratio V_{ci}/V_{cj} included in the authors' work.

b. Calculate the pseudocritical volume.

$$V_{cm} = Y_i^2 V_{ci} + 2Y_iY_jV_{cij} + Y_j^2 V_{cj}$$

c. Calculate the acentric factor.

$$\omega_m = Y_i \omega_i + Y_j \omega_j$$

d. Calculate β .

$$\beta = Y_i^2(V_{c_i}T_{c_i}) + 2Y_iY_j(V_{cij}T_{cij}) + Y_j^2(V_{cj}T_{cj})$$

e. Calculate γ .

$$\gamma = Y_i^2(V_{ci}T_{ci}^2) + 2Y_iY_j(V_{cij}T_{cij}^2) + Y_j^2(V_{cj}T_{cj}^2)$$

f. Calculate the pseudocritical temperature.

$$T_{c_m} = \frac{\beta(\beta^2 + rV_{cm}\gamma)^{1/2}}{2sV_{cm}}$$

The constants, r and s, may be determined from Table 2 of Prausnitz's work.

g. Calculate the pseudocritical pressure.

$$P_{c_m} = RT_{cm}/V_{cm}\ (Y_iZ_{ci} + Y_jZ_{cj})$$

where the critical compressibility factor, Z_c, may be calculated by one of the following relations

$$Z_c = P_cV_c/RT_c$$

$$Z_c = Z_c^o + \omega Z_c^{\prime}$$

G. Miscellaneous Calculations

1. At the conclusion of the calculations with the Benedict-Webb-Rubin equation, an attempt was made to establish an empirical relationship for determining the pseudocritical temperatures and pressures for a mixture. The values obtained in Calculation (F) were used and the resulting relationship was employed as Assumption IV in determining the relationship of azeotropes to the reduced vapor pressure line.

2. An effort was made to use the Martin-Hou equation of state,

$$P = \frac{RT}{V - S} + \frac{A_2 + B_2T + C_2e^{-5.475T_r}}{(V - S)^2} + \frac{A_3 + B_3T + C_3e^{-5.475T_r}}{(V - S)^3}$$

$$+ \frac{A_4}{(V - S)^4} + \frac{B_5T}{(V - S)^5}$$

to calculate the critical compressibility of an ethane-normal heptane mixture containing 0.5 mole fraction ethane. The arbitrary constants for each component were calculated by the method outlined by Martin and Hou and they were combined for the mixture by the rules employed with the Benedict-Webb-Rubin equation.

RESULTS OF CALCULATIONS

TABLE 2

Pitzer Correlation vs. Vapor Pressure

1. Benzene

T_c = 562.7 °K; P_c = 48.7 Atm; ω = 0.215 (26)

Vapor Pressures (12)

T, °K	P, Atm	T_r	P_r	Log P_r	- Log P_r (Experimental)	- Log P_r^o	$-(\partial \text{ Log } P_r/\partial\omega)_T$	$-\Delta$Log P_r	- Log P_r (Theoretical)
546.4	40	0.9711	0.8220	0.9149-1	0.0851	0.0731	0.0616	0.0132	0.0863
522.6	30	0.9288	0.6165	0.7899-1	0.2101	0.1874	0.1593	0.0342	0.2216
494.6	20	0.8790	0.4110	0.6138-1	0.3862	0.3330	0.2880	0.0619	0.3949
451.9	10	0.8031	0.2055	0.3128-1	0.6872	0.5812	0.5342	0.1148	0.6960
415.6	5	0.7386	0.1027	0.0116-1	0.9884	0.8390	0.8066	0.1734	1.0124
376.5	2	0.6691	0.0411	0.6138-2	1.3862	1.1516	1.1908	0.2560	1.4076
353.2	1	0.6277	0.0206	0.3128-2	1.6872	1.3810	1.4820	0.3190	1.7000

TABLE 2 (continued)

2. **Water**

T_c = 647.7 °K; P_c = 219.5 Atm; ω = 0.348 (26)

Vapor Pressures (15)

T,°K	P,Atm	T_r	P_r	Log P_r	- Log P_r (Experimental)	- Log P_r^0	$-(\partial \text{Log } P_r/\partial\omega)_T$	$-\Delta$Log P_r	- Log P_r (Theoretical)
583.1	97.39	0.9003	0.4436	0.6470-1	0.3530	0.2691	0.2225	0.0774	0.3465
552.5	62.82	0.8531	0.2862	0.4567-1	0.5433	0.4131	0.3657-	0.1273	0.5404
519.2	36.74	0.8017	0.1674	0.2238-1	0.7762	0.5860	0.5390	0.1876	0.7736
453.1	9.90	0.6996	0.0451	0.6542-2	1.3458	1.0020	1.0020	0.3490	1.3510
388.7	1.70	0.6001	0.0077	0.8865-3	2.1135	1.5460	1.6940	0.5895	2.1350
363.1	0.69	0.5606	0.0032	0.5052-3	2.4948	1.8300	2.0740	0.7218	2.5510

TABLE 2 (continued)

3. **Ethyl Alcohol**

$T_c = 516.2$ °K; $P_c = 63.1$ Atm; Vapor Pressures (12)

$\omega = 0.6351$ (35)

T, °K	P, Atm	T_r	P_r	Log P_r	- Log P_r (Experimental)	- Log P_r^o	$-(\partial \text{Log } P_r/\partial\omega)_T$	$-\Delta$Log P_r	- Log P_r (Theoretical)
463.1	23.94	0.8971	0.3801	0.5799-1	0.4201	0.2787	0.2380	0.1512	0.4299
433.1	12.39	0.8390	0.1967	0.2938-1	0.7162	0.4584	0.4085	0.2594	0.7178
413.1	7.49	0.8002	0.1189	0.0752-1	0.9248	0.5913	0.5443	0.3457	0.9370
363.1	1.56	0.7034	0.0248	0.3944-2	1.6056	0.9850	0.9830	0.6243	1.6093
358.1	1.30	0.6937	0.0206	0.3139-2	1.6861	1.0300	1.0380	0.6592	1.6892
313.1	0.18	0.6065	0.0028	0.4472-3	2.5528	1.5110	1.6480	1.0467	2.5577
293.1	0.06	0.5687	0.0009	0.9542-4	3.0458	1.7770	2.0020	1.2715	3.0485

TABLE 2 (continued)

4. **Normal Hexane**

$T_c = 507.9\ ^\circ K$; $P_c = 29.6$ Atm; Vapor Pressures (12)

$\omega = 0.2899$ (35)

$T, ^\circ K$	P,Atm	T_r	P_r	$\log P_r$	$-\log P_r$ (Experimental)	$-\log P_r^o$	$-(\partial \log P_r/\partial \omega)_T$	$-\Delta \log P_r$	$-\log P_r$ (Theoretical)
482.5	20	0.9500	0.6757	0.8298-1	0.1702	0.12900	0.10900	0.0316	0.1606
439.7	10	0.8657	0.3378	0.5286-1	0.4714	0.37400	0.32800	0.0951	0.4691
404.8	5	0.7970	0.1689	0.2276-1	0.7724	0.60300	0.55500	0.1609	0.7639
366.1	2	0.7208	0.0676	0.8299-2	1.1701	0.90600	0.89100	0.2583	1.1643
341.4	1	0.6722	0.0338	0.5289-2	1.4711	1.13600	1.17100	0.3395	1.4755

TABLE 2 (continued)

5. **Ethyl Acetate**

T_c = 523.2 °K; P_c = 37.9 Atm; Vapor Pressures (12)

ω = 0.3691

T, °K	P, Atm	T_r	P_r	Log P_r	- Log P_r (Experimental)	- Log P_r^o	$-(\partial \text{Log } P_r/\partial\omega)_T$	$-\Delta$Log P_r	- Log P_r (Theoretical)
473.1	17.35	0.9042	0.4578	0.6607-1	0.3393	0.2580	0.2200	0.0810	0.3390
453.1	12.26	0.8660	0.3235	0.5099-1	0.4901	0.3730	0.3270	0.1210	0.4940
413.1	5.48	0.7896	0.1446	0.1602-1	0.8398	0.6300	0.5840	0.2160	0.8460
373.1	1.99	0.7131	0.0525	0.7202-2	1.2798	0.9400	0.9310	0.3440	1.2840
350.2	1.00	0.6693	0.0264	0.4216-2	1.5784	1.1510	1.1900	0.4390	1.5900
313.1	0.25	0.5984	0.0065	0.8129-3	2.1871	1.5620	1.7130	0.6320	2.1940
303.1	0.16	0.5793	0.0041	0.6128-3	2.3872	1.6930	1.8870	0.6960	2.3890

TABLE 2 (continued)

6. **Methyl Alcohol**

T_c = 513.1 °K; P_c = 78.7 Atm; Vapor Pressures (12)

ω = 0.5666

T, °K	P, Atm	T_r	P_r	Log P_r	- Log P_r (Experimental)	- Log P_r^0	$-(\partial \text{Log } P_r/\partial \omega)_T$	$-\Delta$Log P_r	- Log P_r (Theoretical)
463.1	32.23	0.9026	0.4097	0.6125-1	0.3875	0.2620	0.2240	0.1270	0.3890
433.1	17.11	0.8441	0.2175	0.3374-1	0.6626	0.4420	0.3930	0.2230	0.6650
413.1	10.63	0.8051	0.1351	0.1306-1	0.8694	0.5740	0.5270	0.2990	0.8730
363.1	2.49	0.7076	0.0317	0.5010-2	1.4990	0.9660	0.9600	0.5440	1.5100
353.1	1.67	0.6882	0.0213	0.3284-2	1.6716	1.0570	1.0740	0.6080	1.6650
343.1	1.22	0.6687	0.0155	0.1903-2	1.8097	1.1540	1.1940	0.6760	1.8300
337.8	1.00	0.6584	0.0127	0.1038-2	1.8962	1.2070	1.2610	0.7140	1.9210

TABLE 3

Azeotropes and Their Relationship to the Reduced Vapor Pressure Line

1. **Benzene - Ethyl Alcohol** (24)

Azeotropic temperature = 341.3 °K; Pressure = 1 Atm; Composition = 0.448 Mole Fraction Ethanol

Assumption	T_r	P_r	Log P_r	- Log P_r (Experimental)	- Log P_r^o	$-(\partial \text{Log } P_r/\partial \omega)_T$	$-\Delta$Log P_r	- Log P_r (Theoretical)
I	0.6299	0.0181	0.2577-2	1.7423	1.3680	1.4660	0.5923	1.9590
II	0.6328	0.1860	0.2695-2	1.7305	1.3500	1.4440	0.5834	1.9320
III	0.6300	0.0181	0.2577-2	1.7423	1.3670	1.4650	0.4980	1.8650
IV	0.6352	0.0194	0.2878-2	1.7122	1.3360	1.4260	0.4850	1.8210
V	0.6328	0.0186	0.2695-2	1.7305	1.3500	1.4440	0.3746	1.7240

TABLE 3 (continued)

2. Water - Ethyl Alcohol (24)

Azeotropic temperature = 351.3 °K; Pressure = 1 Atm; Composition = 0.1057 Mole Fraction Water

Assumption	T_r	P_r	Log P_r	- Log P_r (Experimental)	- Log P_r^o	$-(\partial \text{ Log } P_r/\partial \omega)_T$	$-\Delta$Log P_r	- Log P_r (Theoretical)
I	0.6626	0.0126	0.1004-2	1.8996	1.1850	1.2330	0.7457	1.9290
II	0.6801	0.0159	0.2014-2	1.7986	1.0960	1.1200	0.6774	1.7734
III	0.6626	0.0126	0.1004-2	1.8996	1.1850	1.2330	0.7276	1.9126
IV	0.6677	0.0139	0.1430-2	1.8570	1.1590	1.2000	0.7081	1.8671
V	0.6801	0.0159	0.2014-2	1.7986	1.0960	1.1200	0.6162	1.7122

TABLE 3 (continued

3. **Normal Hexane - Ethyl Acetate**

Azeotropic Temperature = 339.1 °K; Pressure = 1 Atm; Composition = 0.586 Mole Fraction Hexane

Assumption	T_r	P_r	Log P_r	- Log P_r (Experimental)	- Log P_r^o	$-(\partial \text{Log } P_r/\partial\omega)_T$	$-\Delta$Log P_r	- Log P_r (Theoretical)
I	0.6595	0.0303	0.4814-2	1.5186	1.2010	1.2540	0.4047	1.6057
II	0.6637	0.0309	0.4900-2	1.5100	1.1790	1.2260	0.3956	1.5746
III	0.6595	0.0303	0.4814-2	1.5186	1.2010	1.2540	0.4032	1.6042
IV	0.6566	0.0300	0.4771-2	1.5229	1.2170	1.2740	0.4096	1.6266
V	0.6637	0.0309	0.4900-2	1.5100	1.1790	1.2260	0.3938	1.5728

TABLE 4

Azeotropes and Their Relationship to $(\partial P/\partial X)_T$ Along Saturation Line

$A = BC + D + E$

	B	C	BC	D	E	A
1. Benzene - Ethyl Alcohol						
a. Assumption I	8.95	0.054	0.483	- 0.614	0.113	- 0.018
b. Assumption III	8.45	0.054	0.456	- 0.507	0.113	+ 0.062
c. Assumption V	7.85	0.056	0.440	- 0.214	0.107	- 0.333
2. Water - Ethyl Alcohol						
a. Assumption I	9.05	0.164	1.488	- 0.353	- 0.853	+ 0.282
b. Assumption III	8.95	0.164	1.471	- 0.333	- 0.853	+ 0.286
c. Assumption V	8.70	0.060	0.520	- 0.622	- 0.174	- 0.275
3. Normal Hexane - Ethyl Acetate						
a. Assumption I	7.80	0.020	0.156	+ 0.099	- 0.109	+ 0.146
b. Assumption III	7.75	0.020	0.155	+ 0.091	- 0.109	+ 0.138
c. Assumption V	7.20	0.016	0.118	- 0.764	- 0.053	- 0.699

TABLE 5

MEASURED BOILING POINTS VS. PREDICTED BOILING POINTS

	(Benzene - Ethanol)	(Water - Ethanol)	(Hexane - Ethyl Acetate)
Boiling Points (°C)			
Component A	**Ethanol** - 78.37	**Ethanol** - 78.37	**Hexane** - 68.32
Component B	**Benzene** - 80.10	**Water** - 100.00	**Ethyl Acetate** - 77.10
Azeotrope			
Measured	68.24	78.15	66.00
Predicted			
Assumption I	81.86	79.84	72.65
Assumption II	81.10	76.80	70.69
Assumption III	75.58	78.69	72.96
Assumption IV	76.33	78.86	71.58
Assumption V	67.80	72.93	70.54

TABLE 6

MEASURED PRESSURES VS. PREDICTED PRESSURES

	(Benzene - Ethanol)	(Water - Ethanol)	(Hexane - Ethyl Acetate)
Pressures (Atm)			
Measured	1.000	1.000	1.000
Predicted			
Assumption I	0.607	0.938	0.806
Assumption II	0.629	1.141	0.862
Assumption III	1.014	0.974	0.821
Assumption IV	0.753	0.976	0.787
Assumption V	1.013	1.314	0.866

TABLE 7

Liquid Volume Predictions for Methanol - Normal Butane Mixtures

a. Volumetric (24)

b. Butane (26)

c. Methanol (12)

d. Compressibility Factors (11) and (20)

1. 1.00 Mole Fraction Normal Butane

				Volumes, ft^3/lb mole		
Temperature, °F	Pressure, psia	Measured	Pitzer	Amagat's Law	Pseudocritical	Maxwell
200	40	169.1	169.02	-	169.07	168.19
240	40	181.2	181.13	-	182.14	180.26
280	40	192.4	192.79	-	192.14	191.95
280	125	57.4	57.43	-	59.00	57.17

TABLE 7 (continued)

2. 0.25 Mole Fraction Methanol

		Volumes, ft^3/lb mole				
Temperature, °F	Pressure, psia	Measured	Pitzer	Amagat's Law	Pseudocritical	Maxwell
200	40	170.0	168.81	166.80	171.03	169.88
240	40	181.7	181.00	180.00	181.95	181.30
280	40	193.1	192.85	191.95	193.54	193.15
280	125	58.54	57.84	56.85	58.19	56.73

3. 0.50 Mole Fraction Methanol

200	40	168.3	-	164.50	171.23	170.41
240	40	180.1	180.66	183.80	182.52	181.86
280	40	192.1	192.57	191.50	193.74	194.04
280	125	58.49	57.89	56.30	58.10	58.60

TABLE 7 (continued)

4. 0.75 Mole Fraction Methanol

				Volumes, ft^3/lb mole		
Temperature, °F	Pressure, psia	Measured	Pitzer	Amagat's Law	Pseudocritical	Maxwell
200	40	166.1	-	162.20	171.53	171.26
240	40	178.9	-	177.60	182.89	182.33
280	40	192.4	192.07	191.05	193.94	193.50
280	125	57.71	57.13	55.76	58.76	58.84

5. 1.00 Mole Fraction Methanol

200	40	159.9	-	-	171.73	169.96
240	40	176.4	-	-	182.89	181.20
280	40	190.6	191.54	-	192.84	192.55
280	125	55.21	56.58	-	58.00	57.80

TABLE 8

Pitzer Correlations for Liquid Volume Predictions

Critical temperatures, critical pressures and acentric factors. (26)

Specific gravities and vapor pressures. (20)

Benzene	Volumes, ft^3/lb mole	
Temperature, °F	Actual	Pitzer
110	1.463	2.327
125	1.476	2.289
150	1.503	1.946
175	1.530	2.230
Normal Butane		
0	1.507	1.901
10	1.519	1.920
20	1.531	1.862
30	1.544	1.891
Normal Pentane		
60	1.826	2.269
70	1.840	2.061
80	1.863	2.234
90	1.874	2.215

TABLE 9

Pseudocritical Properties of Ethane-Normal Heptane System

Data

Ethane (3)

Normal Heptane (31)

		T_c, °K	P_c, Atm	d_c, lb mole/ft^3	Z_c
1.	**Pure Compounds**				
	Ethane	305.37	48.20	0.41800	0.2850
	Normal Heptane	540.11	27.00	0.13111	0.2600
2.	**0.5 Mole Fraction Ethane**				
	Experimental	481.00	68.00	0.26300	-
	Benedict-Webb-Rubin	414.81	25.21	0.21897	0.2280
	Prausnitz-Gunn	419.43	33.30	0.22100	0.2730
	Kay's Rule	422.74	37.60	0.28595	0.2268
	Van der Waal's Combinations	415.43	31.54	0.26564	0.2379

TABLE 9 (continued)

	T_c, °K	P_c, Atm	d_c, lb mole/ft^3	Z_c
3. <u>0.8 Mole Fraction Ethane</u>				
Experimental	405.35	84.38	0.40300	-
Benedict-Webb-Rubin	345.07	31.44	0.30400	0.2280
Prausnitz-Gunn	356.84	38.17	0.31000	0.2500
Kay's Rule	352.32	43.96	0.36762	0.2876
Van der Waals' Combinations	345.37	38.07	0.35036	0.2880

DISCUSSION OF RESULTS

DISCUSSION OF RESULTS

The ultimate objective of predicting vapor-liquid equilibria from an equation of state was not achieved. The principal difficulties seem to arise from a failure to determine the exact relationship between the properties of a mixture and the properties of the pure compounds in the mixture. This relationship requires an accurate equation of state and a precise method for combining the arbitrary constants of the equation of state when it is applied to mixtures.

The fact that these calculations proved unsuccessful does not minimize the importance of predicting vapor-liquid equilibria by Method II with an equation of state, nor does it repudiate the generally accepted belief that an equation of state that applies accurately to pure compounds can be applied to mixtures of these compounds provided they do not react chemically.

Method II is potentially the most advantageous way of accurately predicting vapor-liquid equilibria because it does not require experimental activity coefficients for the mixture. These are difficult to determine and are seldom available in the literature.

Table 9 depicts the many variations in pseudocritical properties for the ethane-normal heptane system obtained with the listed methods of predicting the properties of mixtures. A significant factor that is revealed by these calculations is that the critical compressibilities of the two mixtures are generally outside the range of those for the pure compounds. This contradicts the basic assumptions of these methods, that a single phase mixture behaves like a single compound with properties intermediate between the properties of the pure compounds in the mixture.

Values for the pseudocritical temperatures, pressures and densities are also shown graphically in Figures I, II and III to further illustrate these differences. A plot of experimental critical properties from the work of Kay (33) is included in each figure for comparison.

Figure I shows that present methods of calculating pseudocritical temperatures yield values which are of the same magnitude. The experimental actual critical temperature is higher than the pseudocritical temperature at all compositions.

Figure II illustrates that each method for calculating pseudocritical pressures give values that show marked differences from one another and are all considerably lower than the experimental actual critical pressures.

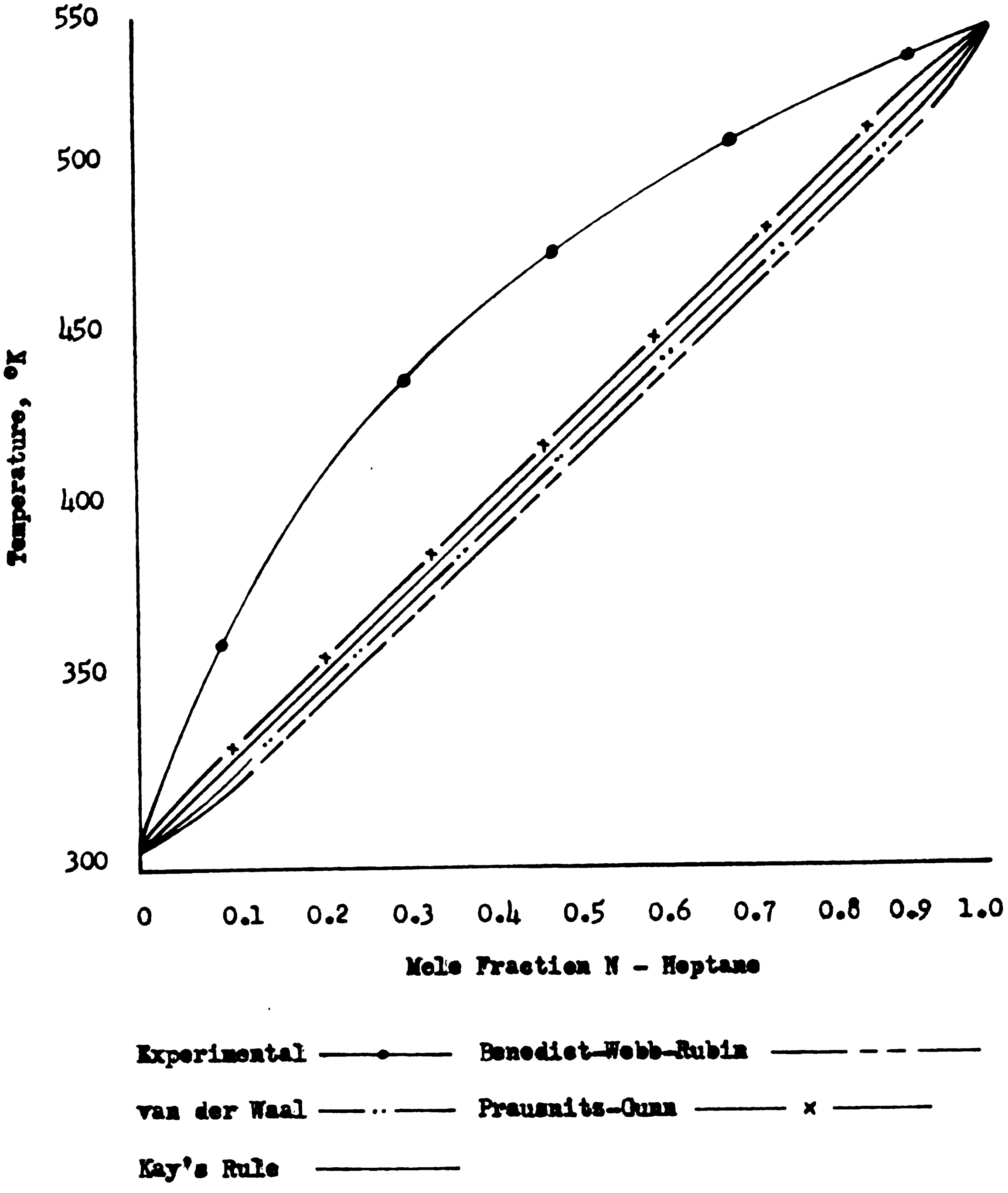
Figure III shows that the pseudocritical densities follow the same general pattern as the experimental actual critical densities.

The vapor pressures of pure compounds calculated with the Pitzer correlation were generally in good agreement with accepted experimental values. The maximum deviation was 5.47% while the average deviation was less than 1.0%.

The prediction of liquid volumes of pure compounds by the Pitzer correlation is presented in Table 8. In each case the predicted volumes were higher than the actual volumes. The volumes

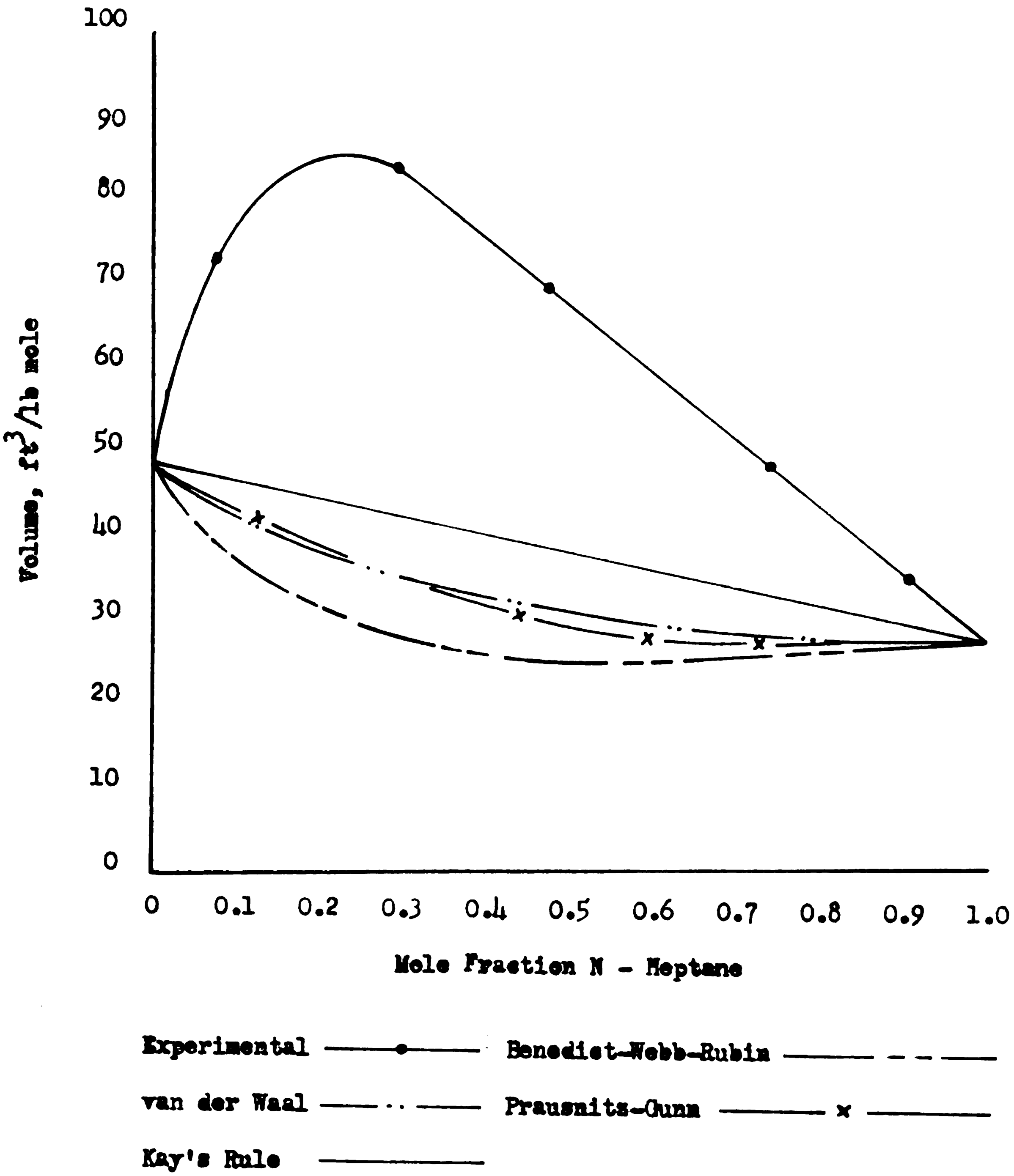
ETHANE - NORMAL HEPTANE

Figure I



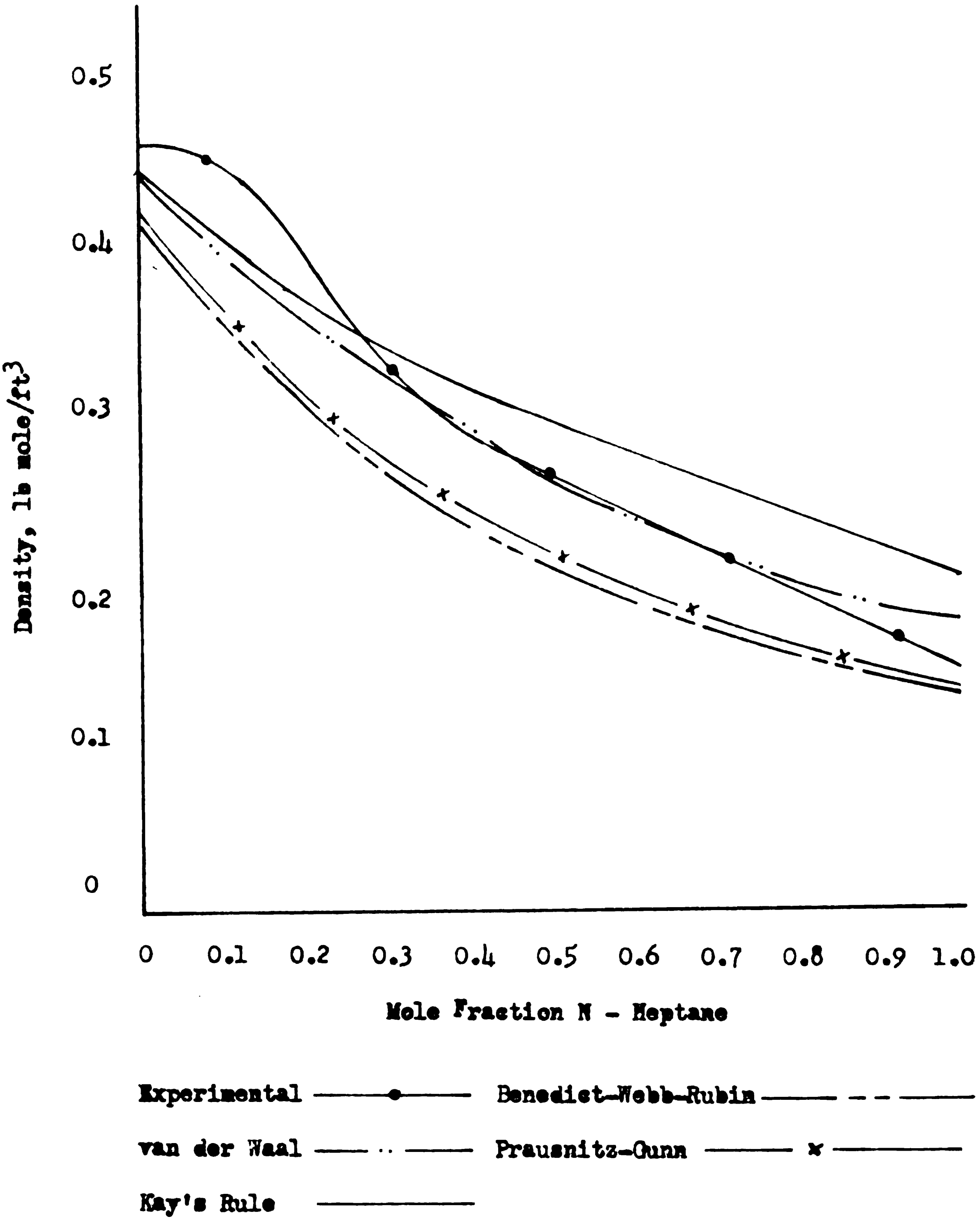
ETHANE - NORMAL HEPTANE

Figure II



ETHANE - NORMAL HEPTANE

Figure III



of benzene were from 29.0 to 59.0% larger, for normal butane from 6.0 to 22.5% larger and for normal pentane from 12.0 to 24.3% larger.

The application of the Pitzer correlation to azeotropes produced some significant deviations from the experimental pressure at the azeotropic point. The best result was obtained when using Assumption V, consisting of van der Waals' combinations for the pseudocritical properties, and combining the acentric factor as the reciprocal of its cube. The deviations ranged from 0.35% to 12.5% with the average deviation from experimental values approximately 6.7%.

There were also large deviations encountered when calculating $(\partial P/\partial X)_T$ along the saturation line. This value should be zero at the azeotrope composition but the results obtained varied from -0.699 to -0.333.

A comparison of measured boiling points with boiling points predicted from the calculations discussed above, as shown in Table 5, revealed that the predicted values were in fair agreement for the water-ethyl alcohol system only. The predicted values for the normal hexane-ethyl acetate system were higher than the experimental boiling point for all assumptions. For the benzene-ethyl alcohol system the predicted boiling points were higher than the experimental value except in the case of Assumption V.

A similar comparison, in Table 6, of measured pressures with predicted pressures showed that the calculated pressures were always lower for the normal hexane-ethyl acetate system.

The benzene - ethyl alcohol and water - ethyl alcohol systems showed both positive and negative deviations for the five assumptions.

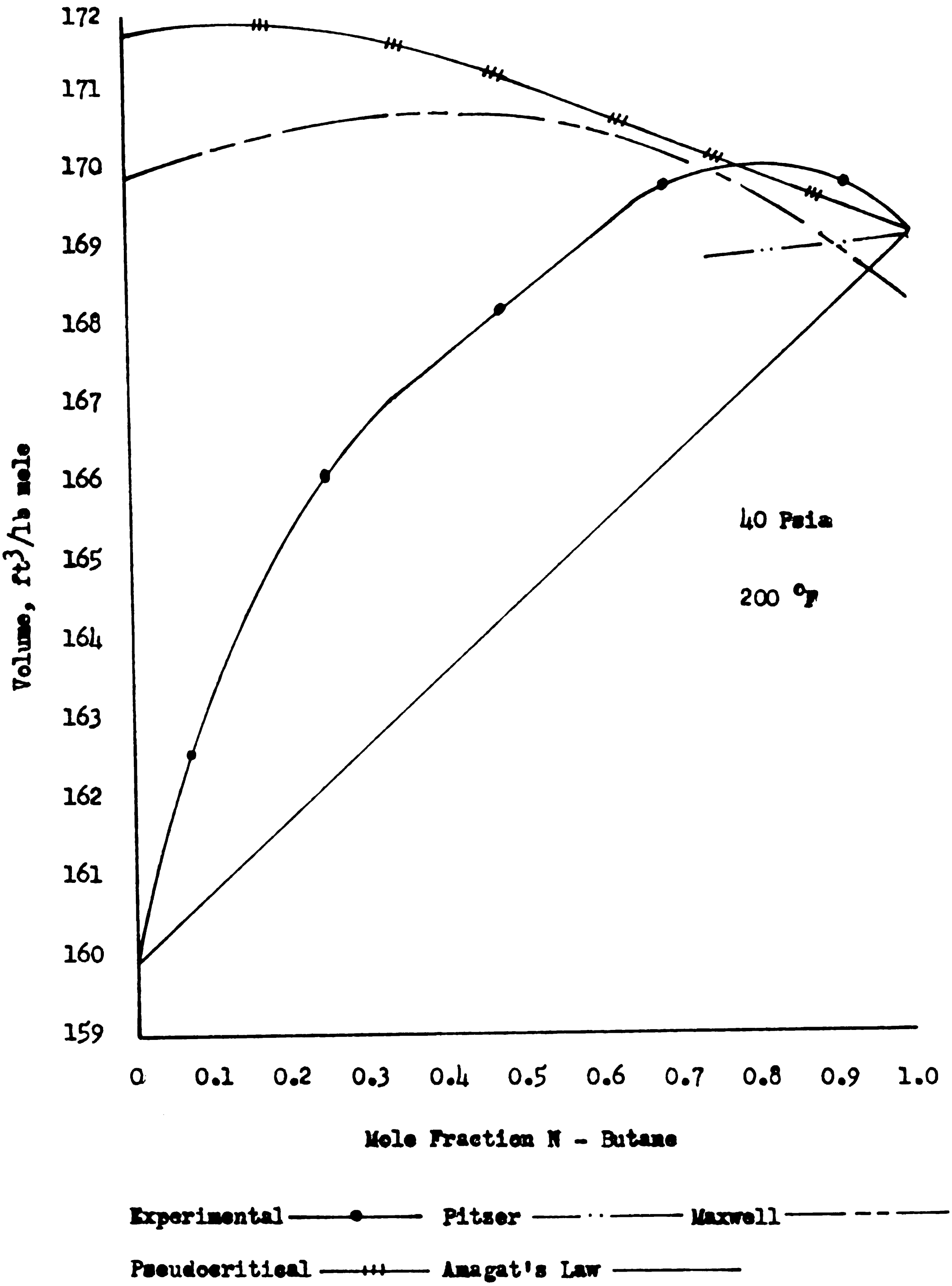
The results of the calculation of liquid volumes for the methyl alcohol - normal butane mixtures are presented in Table 7 and also in Figures IV - VII. The Pitzer correlation seems to follow the experimental volumes closer than any of the other three methods employed.

Amagat's law exhibited definite deviations at the higher pressures chosen for this calculation and it always gave lower values than the experimental volumes.

Both the pseudocritical and the Maxwell methods predicted volumes which were generally much higher than the experimental values. Considerable difficulty was encountered in accurately reading the compressibility charts associated with these two methods, hence some error was probably introduced at this point.

METHYL ALCOHOL - NORMAL BUTANE

Figure IV

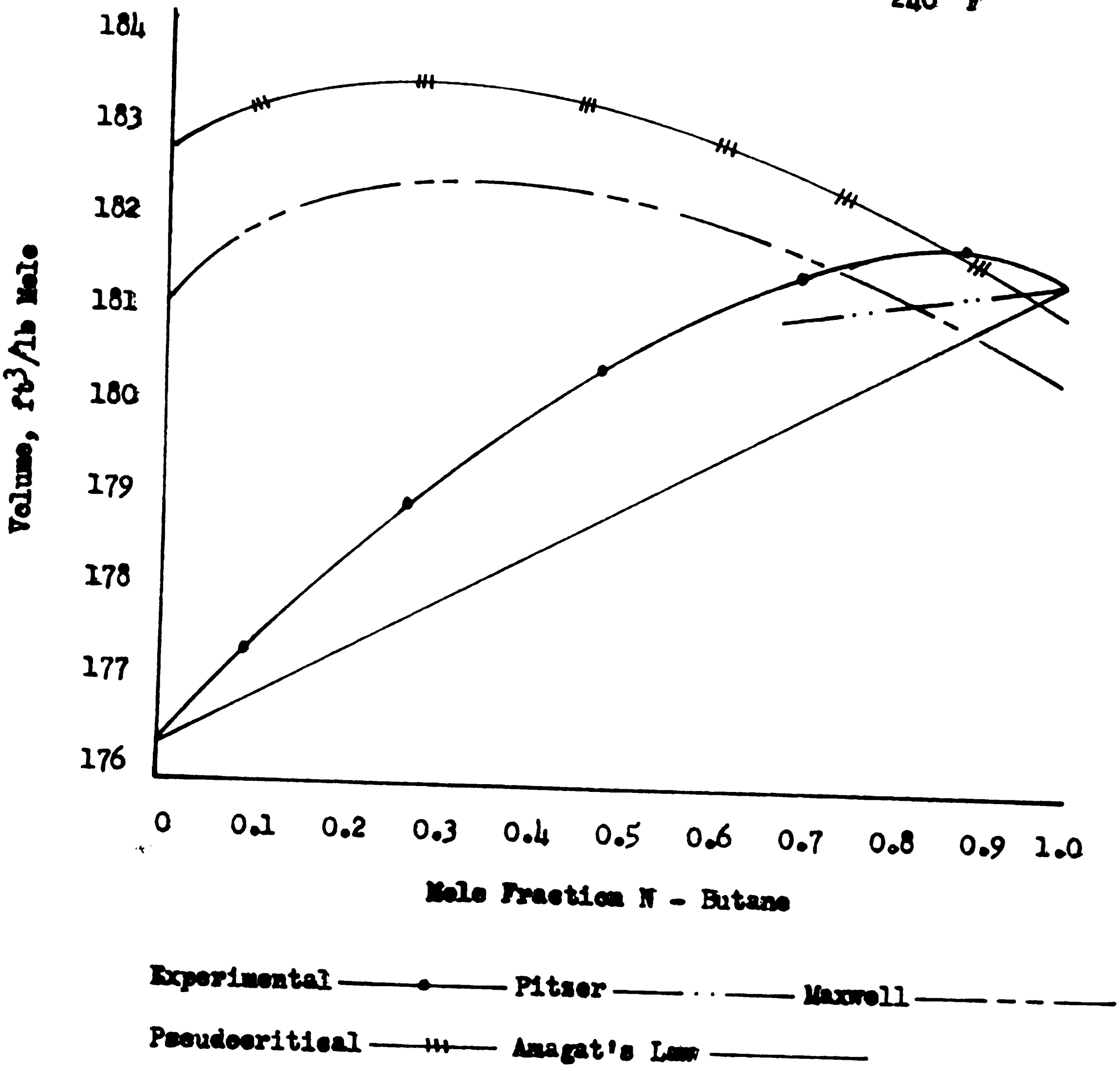


METHYL ALCOHOL - NORMAL BUTANE

Figure V

40 Psia

240 °F

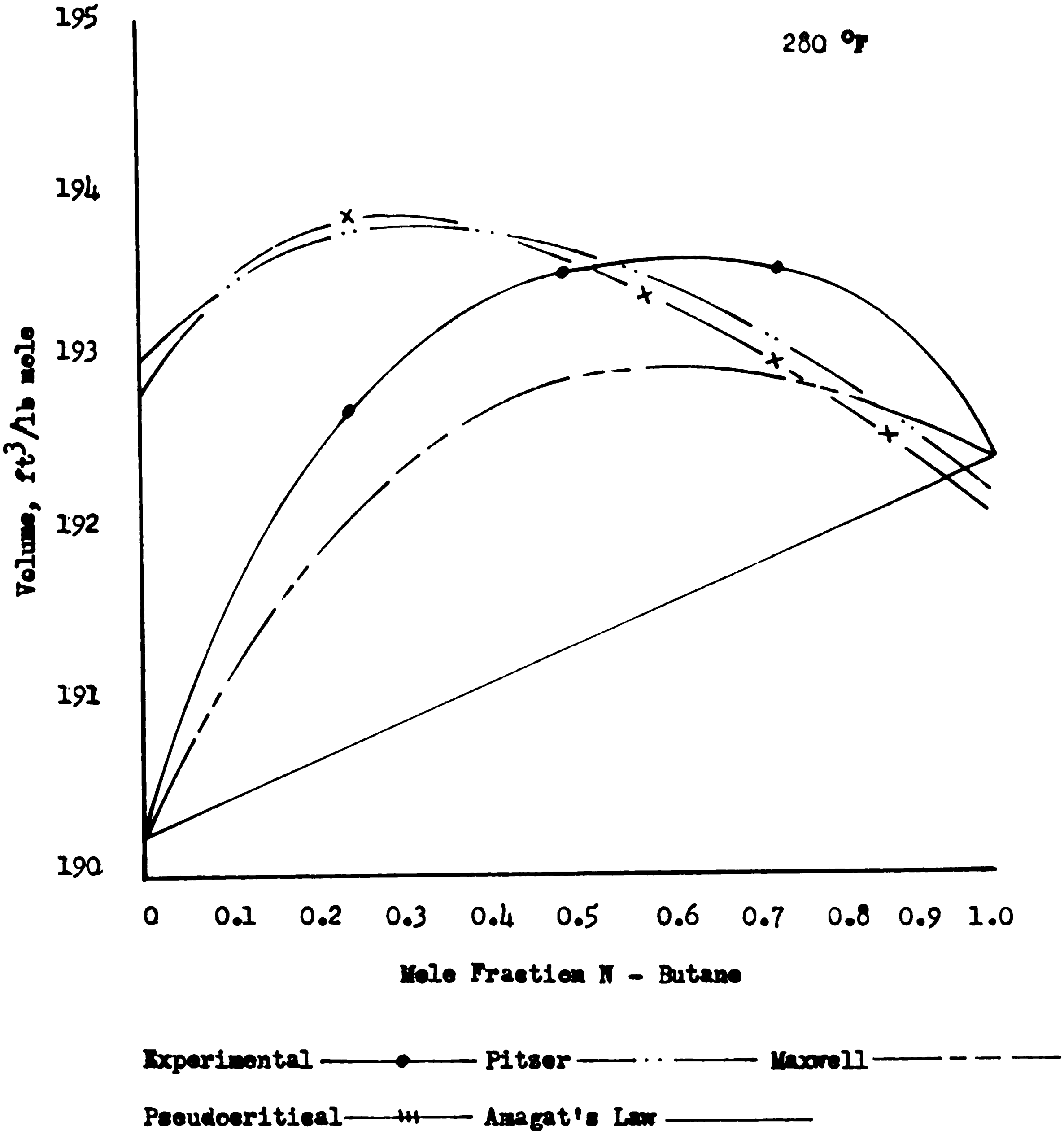


METHYL ALCOHOL - NORMAL BUTANE

Figure VI

40 Psia

280 °F

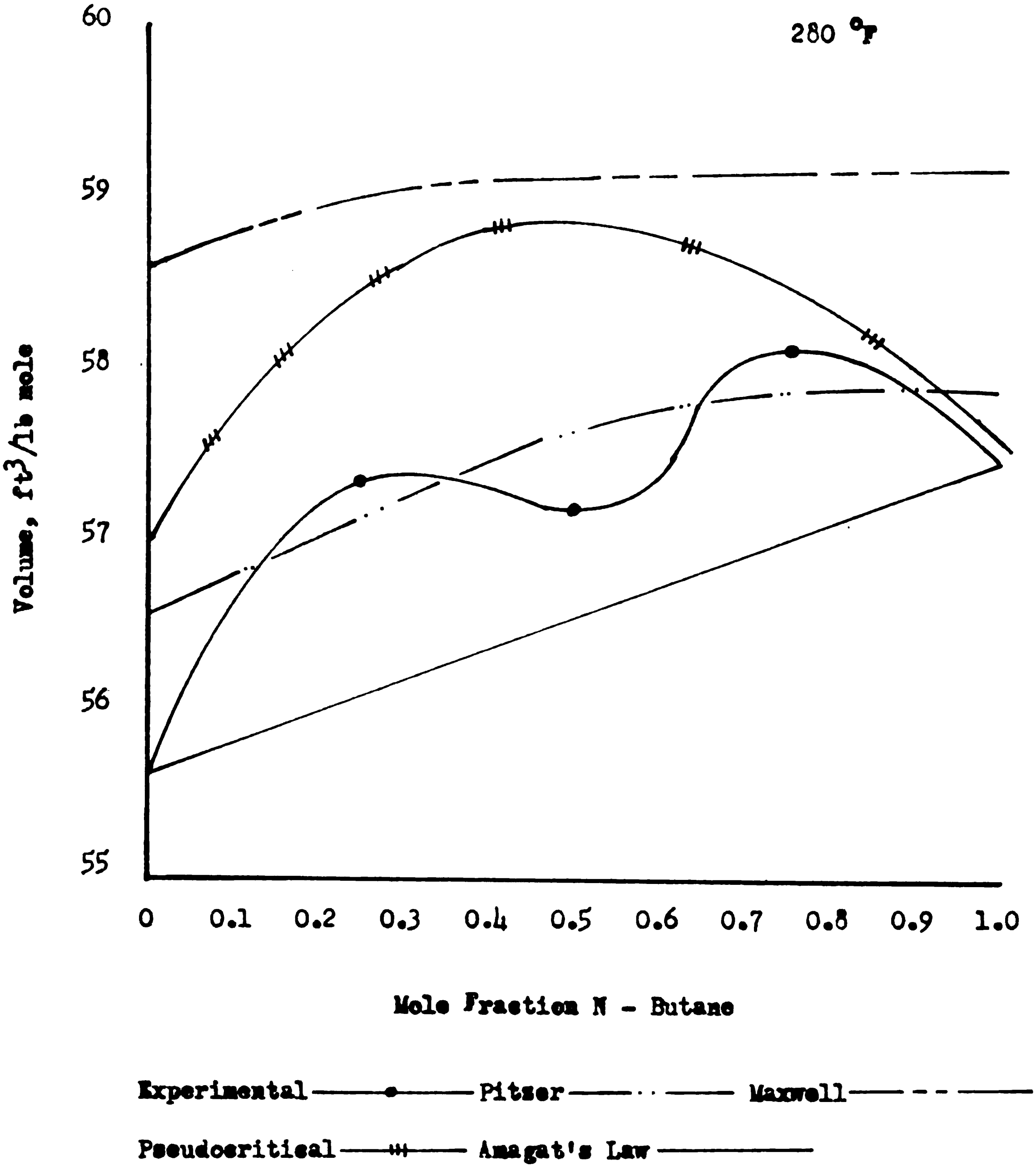


METHYL ALCOHOL - NORMAL BUTANE

Figure VII

125 Psia

280 °F



CONCLUSIONS

CONCLUSIONS

The following conclusions have been made as a result of this investigation:

1. Present methods of relating the properties of pure compounds to the properties of their mixtures are inadequate.
2. The Benedict-Webb-Rubin combinations, van der Waals' combinations, Kay's rule and the Prausnitz-Gunn correlation predict pseudocritical temperatures of the same magnitude.
3. These four methods predict pseudocritical pressures that show marked differences from one another.
4. The pseudocritical densities obtained with these four methods follow the same general pattern as the experimental actual critical densities.
5. Pitzer's correlation predicts vapor pressures of pure compounds within engineering accuracy but there are significant deviations when it is applied to the determination of the vapor pressures of azeotropic mixtures.
6. Pitzer's correlation is more accurate than Amagat's law, the pseudocritical method and the Maxwell method when employed to calculate the liquid volumes of mixtures.

RECOMMENDATIONS

RECOMMENDATIONS

It is suggested that the use of a high speed digital computer be considered for future work on the application of an equation of state to the prediction of vapor-liquid equilibria. This machine will enable engineers and scientists to extend their studies to innumerable mixtures and it will yield a degree of accuracy seldom achieved with manual calculations.

It might also prove to be beneficial to investigate the correlation of Lydersen, Greenkorn and Hougen (8) to determine its accuracy in describing the volumetric properties of mixtures.

NOMENCLATURE

NOMENCLATURE

A - Helmholtz work function

$\tilde{A}$ - Molal Helmholtz work function

A_o, B_o - Constants in Beattie-Bridgeman equation of
a, b, c state

A_o, B_o, C_o - Constants in Benedict-Webb-Rubin equation of
a, b, c, α, γ state

A_2, A_3, A_4 - Constants in Martin-Hou equation of state
B_2, B_3, B_5
C_2, C_3, S

a, b - Constants in van der Waals' equation of state

d - Molal density, moles/unit volume

d_c - Critical density

d_r - Reduced density

F - Free energy

$\tilde{F}$ - Partial molal free energy

f - Fugacity

K - Equilibrium ratio, y/x

N - Number of moles

P - Pressure

P_c - Critical Pressure

P_r - Reduced Pressure

P_o - Vapor pressure of pure component at temperature of system

R - Universal gas constant

r, s - Parameters in pseudocritical temperature equation of Prausnitz-Gunn correlation

T - Absolute temperature

T_c - Critical temperature

T_r - Reduced temperature

T_{c12} - Prausnitz-Gunn correction to characteristic critical temperature

V - Volume, unit volume/mole

V_c - Critical volume

V_r - Reduced volume

V_L - Molal volume of liquid phase at temperature and pressure of system

x - Mole fraction in the liquid phase

y - Mole fraction in the vapor phase

Z - Compressibility factor

Z_c - Critical compressibility factor

Z^o, Z' - Graphical functions of reduced pressure and
Z'' reduced temperature in Pitzer correlation

Greek Symbols

α - $\Sigma_{12} Y_1 Y_2 V_{c12}$ (Prausnitz-Gunn Correlation)

α_c - Riedel parameter

β - $\Sigma_{12} Y_1 Y_2 (V_c T_c)_{12}$ (Prausnitz-Gunn Correlation)

γ - Liquid phase activity coefficient to correct for deviations from ideal solution behavior

γ' - Gas phase activity coefficient to correct for deviations from Amagat's law

ν_{P_o} - Fugacity coefficient of pure component in liquid phase at vapor pressure which corresponds to the temperature of the system

ν_P - Fugacity coefficient of pure component in liquid phase at the temperature and pressure of the system

π - Total pressure

ω - Acentric factor

Subscripts

c - Critical state

i, j - Components i and j

L - Liquid phase

m - Property for a mixture and it signifies that the quantity is for mixtures as a whole

P_o - At vapor pressure of pure component

π - At total pressure of system

r - Reduced, dimensionless property

v - Vapor phase

BIBLIOGRAPHY

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1. Amagat, E. H., Ann. Chim. Phys., 5, 19, 384 (1880).
2. Beattie, J. A., and Bridgeman, O. C., Proc. Am. Acad. Arts Sci., 63, 229 (1928).
3. Beattie, J. A., Su, G. J., and Simard, G. L., Am. Chem. Soc., 61, 924 (1939).
4. Benedict, M., Webb, G. B., and Rubin, L. C., J. Chem. Phys., 8, 334-345 (1940) and 10, 747-758 (1942).
5. Benedict, M., Webb, G. B., and Rubin, L. C., Friend, L., Chem. Eng. Prog., 47, 419-422, 449-454, 571-578, 609-620 (1951).
6. Berthelot, P. E., Comp. rend., 126, 1703, 1857 (1898).
7. Cullen, E. J., and Kobe, K. A., A.I.Ch.E. J., 1, 452 (1955).
8. Dodge, B. F., "Chemical Engineering Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1944.
9. Galitzine, Wied. Ann. Physik, 41, 770 (1890).
10. Hirschfelder, J. O., Curtiss, C. F., Bird, R. B., "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, 1954.
11. Hougen, O. A., and Watson, K. M., "Chemical Process Principles Charts," John Wiley and Sons, Inc., New York, 1946.
12. Jordan, T. E., "Vapor Pressures of Organic Compounds," Interscience Publishers, Inc., New York, 1954.
13. Kay, W. B., Ind. Eng. Chem., 28, 1014 (1936).

14. Kay, W. B., Ind. Eng. Chem., 30, 459 (1938).

15. Keenan, J. H., and Keyes, F. G., "Thermodynamic Properties of Steam," John Wiley and Sons, Inc., New York, 1954.

16. Kendall, B. J., and Sage, B. H., "The Volumetric Behavior of Carbon Dioxide," Am. Petroleum Inst. Research Project 37.

17. Lorentz, H. A., Ann. Physik, 12, 127, 660 (1881).

18. Lydersen, A. L., Greenkorn, R. A., and Hougen, O. A., Generalized Thermodynamic Properties of Pure Fluids, Univ. Wisconsin, Eng. Expt. Sta. Rept. 4, 1955.

19. Martin, J. J., and Hou, Yu-Chun, A.I.Ch.E. J., 1, 142 (1955).

20. Maxwell, J. B., "Data Book on Hydrocarbons," D. Van Nostrand Company, 1951.

21. Nelson, L. C., and Obert, E. F., Trans. Am. Soc. Mech. Eng., 76, 1057 (1954).

22. Opfell, J. B., Schlinger, W. G., and Sage, B. H., Ind. Eng. Chem., 46, 1286 (1954).

23. Perry, J. H., "Chemical Engineers Handbook," 3rd ed., McGraw-Hill Book Company, New York, 1950.

24. Petty, L. B., and Smith, J. M., Ind. Eng. Chem., 47, 1258 (1946).

25. Pitzer, K. S., J. Am. Chem. Soc., 77, 3427, (1955).

26. Pitzer, K. S., Lippmann, D. Z., Curl, R. F., Huggins, C. M., and Peterson, D.E., J. Am. Chem. Soc., 77, 3433 (1955).

27. Prausnitz, J. M., and Gunn, R. D., A.I.Ch.E. J., 4, 430 (1958).

28. Riedel, L., Chem. Ing. Tech., 26, 679 (1954) and 27, 209 (1955).

29. Schiller, F. C., and Canjar, L. N., Chem. Eng. Prog. Symposium No. 7, 67 (1953).

30. Smith, K. A., and Watson, K. M., Chem. Eng. Prog., 45, 494 (1949).

31. Smith, L. B., Beattie, J. A., and Kay, W. J., J. Am. Chem. Soc., 59, 1587 (1937).

32. Stotler, H. H., and Benedict, M., Chem. Eng. Prog. Symposium No. 6, 25 (1953).

33. Van der Waals, J. D., Dissertation, Leiden 1873.

34. Van Laar, J., Z. Physik. Chem., 72, 723 (1910).

SAMPLE CALCULATIONS

SAMPLE CALCULATIONS

1. Liquid Volume Predications for Methanol - Normal Butane Mixtures

A. Pitzer Correlation

$\omega_m = X_i\omega_i + X_j\omega_j = (0.75)(0.201) + (0.25)(0.567) = \underline{0.293}$

$P_{cm} = X_iP_{ci} + X_jP_{cj} = (0.75)(37.47) + (0.25)(78.67)$

$= \underline{47.77 \text{ atm}}$

$T_{cm} = X_iT_{ci} + X_jT_{cj} = (0.75)(425.2) + (0.25)(513.1)$

$= \underline{447.2 \text{ °K}}$

$P_r = P/P_{cm} = 2.722 \div 47.77 = \underline{0.05698}$

$T_r = T/T_{cm} = 366.4 \div 447.2 = \underline{0.8195}$

$Z_c = Z^o + \omega Z' = 0.9605 - (0.293)(0.0239) = \underline{0.9535}$

$V = Z_cRT/P = (0.9535)(10.73)(660)/40 = \underline{168.81 \text{ ft}^3/\text{lb mole}}$

B. Pseudocritical Method

The temperatures and pressures are identical to those used for the Pitzer correlation since Kay's rule is used in both calculations for combining the pseudocritical constants.

$Z_c = 0.966$ (Page 103 - Chemical Process Principles Charts)

$V = Z_cRT/P = (0.966)(10.73)(660)/40 = \underline{171.03 \text{ ft}^3/\text{lb mole}}$

C. Maxwell Method

$P_{r_i} = P(Y_i)^{1/2}/P_{ci} = (2.722)(0.5)/78.67 = \underline{0.0173}$

$P_{r_j} = P(Y_j)^{1/2}/P_{cj} = (2.722)(0.866)/37.47 = \underline{0.0629}$

T_r = $\underline{0.8195}$ (Kay's rule)

Z_i = $\underline{0.985}$

(Page 152-3 - Maxwell's Data Book on Hydrocarbons)

Z_j = $\underline{0.951}$

$V = RT/P(Y_iZ_i + Y_jZ_j)$

$= (10.73)(660)/40 \quad (0.75)(0.985) + (0.25)(0.951)$

$= \underline{169.88 \text{ ft}^3/\text{lb mole}}$

2. Pseudocritical Properties of Ethane - Normal Heptane System

Arbitrary Constants

Constants	1.00 Mole Fraction Ethane	0.80 Mole Fraction Ethane	0.50 Mole Fraction Ethane	1.00 Mole Fraction n - Heptane
A_o	15670.7	22968.9	36524.0	66070.6
B_o	1.00554	1.44200	2.09668	3.18782
$C_o x 10^{-6}$	2194.27	7333.22	20684.5	57984.0
a	20850.2	59907.2	180710.3	626106
b	2.58539	5.95878	13.9056	38.9917
$c \times 10^{-6}$	6413.14	28540.1	114304.1	483427
$\alpha \times 10^{3}$	1000.44	2317.52	5911.58	17905.6
$\gamma \times 10^{2}$	302.790	553.755	1071.16	2309.42

Temperature and Density

$$(\partial P/\partial d)_T = 0$$

$$ce^{-\gamma d^2}(3d^2 - 3\gamma d^4 - 2\gamma^2 d^6) - 2dC_o + (-2A_od - 3ad^2 - 6a\alpha d^5)T^2 + (R + 3bRd^2 + 2B_oRd)T^3 = 0$$

(a)	d	0.30400	(n)	$-2\gamma^2 d^6$	-0.04841
(b)	d^2	0.09242	(o)	(l)+(m)+(n)	0.37072
(c)	d^3	0.02810	(p)	c(o)(k)	6342.4×10^6
(d)	d^4	0.00854	(q)	$-2dC_o$	4458.6×10^6
(e)	d^5	0.00260	(r)	(p)+(q)	1883.8×10^6
(f)	d^6	0.00079	(s)	$-2A_od$	-13965
(g)	d^7	0.00024	(t)	$-3ad^2$	-16609
(h)	γd^2	0.51176	(u)	$6a\alpha d^5$	2163
(i)	(h)/2.3026	0.22225	(v)	(s)+(t)+(u)	-28410
(j)	antilog (i)	1.66821	(w)	R	10.734
(k)	1/(j)	0.59945	(x)	$3bRd^2$	17.733
(l)	$3d^2$	0.27725	(y)	$2B_oRd$	9.411
(m)	$3\gamma d^4$	0.14188	(z)	(w)+(x)+(y)	37.878

$(\partial P/\partial d)_T = 0$

(aa)	log (r)	9.275035
(bb)	log (v)	4.453471
(cc)	log (z)	1.578387
(dd)	(aa) - (bb)	4.821564
(ee)	(cc) - (aa)	-8 + 0.303352
(ff)	-1.5 log (dd)	7.232346
(gg)	log 1.5	0.176091
(hh)	log 3.0	0.477121
(ii)	1.5 log 3.0	0.238561
(jj)	(ii) + (gg)	0.414652
(kk)	(ee)+(ff)+(jj)	9.950350 - 10
(ll)	Θ	63° 7' 18"
(mm)	$\Theta/3$	21° 2' 26"
(nn)	log sin $\Theta/3$	9.555129 - 10
(oo)	log 2.0	0.301030
(pp)	- 0.5 log (dd)	-2.410548
(qq)	(pp)+(nn)+(oo)-(ii)	2.793184
(rr)	antilog (qq)	621.132 °R
(ss)	T	71.943 °C

$$(\partial^2 P/\partial d^2)_T = 0$$

$$ce^{-\gamma d^2}(6d + 6\gamma d^3 - 18\gamma^2 d^5 + 4\gamma^3 d^7) - 2C_o + (6bRd + 2B_oR)T^3$$
$$+ (-2A_o - 6ad + 30\ a\alpha d^4)T^2 = 0$$

(a)	d	0.30400	(n)	$-18\gamma^2 d^5$	-1.43314
(b)	d^2	0.09242	(o)	$4\gamma^3 d^7$	0.16298
(c)	d^3	0.02810	(p)	(l)+(m)+(n)+(o)	1.48731
(d)	d^4	0.00854	(q)	c(k)(p)	25445.4×10^6
(e)	d^5	0.00260	(r)	$-2C_o$	14666.4×10^6
(f)	d^6	0.00079	(s)	(q)+(r)	10779.0×10^6
(g)	d^7	0.00024	(t)	$2A_o$	45938
(h)	γd^2	0.51176	(u)	$6ad$	109272
(i)	(h)/2.303	0.22225	(v)	$-30a\alpha d^4$	-35573
(j)	antilog (i)	1.66821	(w)	(t)+(u)+(v)	119637
(k)	1/(j)	0.59945	(x)	$6bRd$	116.67
(l)	$6d$	1.82400	(y)	$2B_oR$	30.96
(m)	$6\gamma d^3$	0.93347	(z)	(x)+(y)	147.63

$(\partial^2 P/\partial d^2)_T = 0$

(aa)	log (s)	10.032579
(bb)	log (v)	5.077866
(cc)	log (z)	2.169175
(dd)	(aa)-(bb)	4.954713
(ee)	(cc)-(aa)	- 8 + 0.136596
(ff)	- 1.5 log (dd)	7.432070
(gg)	log 1.5	0.176091
(hh)	log 3.0	0.477121
(ii)	1.5 log 3.0	0.238561
(jj)	(ii)+(gg)	0.414652
(kk)	(ee)+(ff)+(jj)	9.983318 - 10
(ll)	θ	74° 13' 15"
(mm)	$\theta/3$	24° 44' 25"
(nn)	log sin $\theta/3$	9.621701 - 10
(oo)	log 2.0	0.301030
(pp)	- 0.5 log (dd)	-2.477357
(qq)	(pp)+(nn)+(oo)+(ii)	2.793187
(rr)	antilog (qq)	621.136 °R
(ss)	T	71.946 °C

Pressure

$$P = RTd + (B_oRT - A_o - C_o/T^2)d^2 + (bRT - a)d^3 - \alpha a d^6$$
$$+ cd^3/T^2 \left[(1 + \gamma d^2)e^{-\gamma d^2}\right]$$

(a)	RTd	2026.8
(b)	B_oRT	9614.2
(c)	$-A_o$	-22968.9
(d)	$-C_o/T^2$	-19007.4
(e)	(b)+(c)+(d)	-32362.1
(f)	$(e)d^2$	-2990.8
(g)	bRT	39728.7
(h)	$-a$	-59907.7
(i)	(g)+(h)	-20179.0
(j)	$(i)d^3$	-566.9
(k)	$a\alpha d^6$	109.6
(l)	cd^3	801.8×10^6
(m)	$(l)/T^2$	2078.2
(n)	$1 + \gamma d^2$	1.51176
(o)	γd^2	0.51176
(p)	(o)/2.3026	0.22225
(q)	antilog (p)	1.66821
(r)	1/(q)	0.59945
(s)	(r)(n)(m)	1883.3
(t)	(s)+(k)+(j)+(a)+(f)	462.0 psia
(u)	P	31.44 Atm