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Phase Equilibria: An Informal Symposium

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NBS technical note

Phase Equilibria: An Informal Symposium

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PREFACE

Phase equilibria in fluid mixtures is a classical problem in the theory of liquids which is not properly resolved, even today. The problem is of special relevance because of current emphasis on synthetic fuels, the use of new feedstocks, and the need to conserve and increase productivity with existing fluid technology. However, the data base required for these new developments is deficient and, in any case, the task of measuring all data that might be required is prohibitive. One needs predictive procedures which can only be based on an understanding of fluid behavior backed up by the results of controlled experiments on well-defined systems.

One of the tasks of the Boulder Fluid Properties Group, National Engineering Laboratory, is to undertake such a program: namely, a study of mixtures via theory, experiment and data correlation. We felt that some of our theoretical ideas and approaches should be discussed and coordinated so an informal symposium was held in October 1980 to do this. This Technical Note reproduces the main presentations and is organized as follows: First, Ely reviews the state-of-the-art of phase equilibria of nonelectrolyte systems, McCarty then reports on his study of the procedure known as extended corresponding states with special emphasis on the nitrogen/methane system. This followed by a discussion by Rainwater on an alternative attack based on the approach of Griffith and Wheeler which addresses the prediction of VLE (vapor, liquid equilibrium) of mixtures near the critical locus. Finally, Eaton and coworkers discuss the calculation of the critical line itself and possible implications of the calculation to VLE in general.

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No claim is made that the symposium covered other than a limited segment of the total phase equilibria problem, but some themes and difficulties did emerge which are general. Perhaps the most important of these is the well-known dilemma between the strickly programmatic semi-empirical viewpoint, and the more systematic, more academic counterpart. In the long run, of course, the latter viewpoint is preferable, but one has to be realistic and appreciate the need for procedures which work for the systems of interest today. It was felt that the technique of extended corresponding states is an attractive compromise: it works well for nonpolar mixtures and is a systematic, soundly based, theory which can still be developed; it applies to the whole of the liquid phase diagram without parameter adjustment while most other techniques do not. However, the method is based on the concept that a mixture can be replicated by a hypothetical pure substance, and McCarty points out some subtle differences in mixture versus pure behavior which need to be discussed further. Clearly, too, the critical region has to be included in a systematic manner, and we are studying combining the extended corresponding states theory with that proposed by Rainwater. With respect to this, Rainwater points out that the logical variables for a phase equilibria study are the intensive set of pressure, temperature and chemical potential. The engineer, of course, prefers, say, pressure, temperature and mole fraction. It would be interesting and important to try to resolve this fundamental disagreement.

The problem of mixing rules and interaction parameters was discussed. The latter difficulty is serious. As pointed out by Eaton, even interaction parameters obtained by fitting the critical line, which is a sensitive task involving second and third derivatives of the chemical potential, have no significance away from the critical region. As of today, the parameters tend to obscure any unambiguous assessment of how well a theory can represent data. This is one more reason why it is important to understand the assumptions which go into a theory before the theory is developed and broadened.

Much of the work reported here was supported by the Office of Standard Reference Data, and we thank Dr. Howard White, who attended the meeting, for his interest and support. We also thank Mrs. Karen Bowie for typing and for other help in preparing this Technical Note.

H. J. M. Hanley

CONTENTS[*]

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[*] The occasional use of non-S.I. units in this document arose because the authors sought to compare their calculations directly with existing experimental measurements.

A REVIEW OF FLUID PHASE EQUILIBRIA PREDICTION METHODS

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The accurate prediction of phase equilibria plays an important role in the chemical process industries. A brief overview of fluid phase equilibria predictive techniques is presented with special emphasis on methods in current use in industry. Areas where better fundamental understanding will lead to improved models are discussed whenever possible.

Key words: activity coefficients; chemical potential; equations of state; fugacity; group contribution models; phase equilibria.

1. Introduction

The prediction of thermophysical properties of mixtures presents complications which are not encountered with pure fluids -- namely, that the composition as well as the temperature and pressure dependence of the property must be considered. This composition dependence introduces size and polarity difference effects in the properties of single phase mixtures. From a predictive point of view, however, the most difficult task is that of predicting the number and compositions of coexisting phases at a known temperature, pressure and bulk composition, e.g., the phase equilibria. Note that in predicting the properties of single phase mixtures we are concerned with the properties of the fluid as a whole. However, in the case of the phase equilibrium prediction, we are interested in the partial properties of the individual components which constitute the mixture.

Generally speaking, there is a vast base of experimental data for fluid phase equilibria, especially when compared to the available experimental mixture PVT, enthalpy and transport data. Partially due to this vast amount of phase equilibrium data, many simple, phenomenological models have been developed to predict and correlate the observed phase behavior. Frequently, the simple predictive models fail in a quantitative sense, especially when they are applied to systems which contain species which differ substantially in size and polarity.

In order to make accurate predictions on these systems, statistical mechanical models which can explicitly account for size and polarity effects must be used. Unfortunately, the potential of the molecular models to predict complex fluid phase equilibria has not been fully realized due to the mathematical complexity of the problem and, to some degree, ignorance concerning the interactions of chemically dissimilar molecules. For this reason, the engineering community is forced to use simple models to make predictions, regardless of the accuracy achieved.

The purpose of this chapter is to review the methods which are commonly used to predict fluid phase equilibria for engineering applications. Areas where fundamental research and further molecular understanding will improve our predictive models or perhaps lead to new models will be identified. Techniques which have a more fundamental basis and those which have been developed to deal with large size and polarity difference effects will be emphasized whenever possible. The review will be limited to nonelectrolyte systems with the exception being water-common inorganic (CO_2, H_2S,..) systems. Solid-liquid and solid-vapor systems will also be excluded.

The structure of this article is as follows: section 2 examines some binary mixture phase diagrams to illustrate some of the common types of fluid phase equilibria. In section 3, the thermodynamic criteria for phase equilibrium and mathematical methods for predicting the component equilibrium concentrations are discussed. Section 4 reviews mixture equation of state methods for predicting chemical potentials and section 5 reviews the liquid phase activity-vapor phase fugacity approach to phase equilibria, including the group solution methods.

2. Qualitative Phase Behavior in Mixtures

Phase diagrams for mixtures are considerably more difficult to visualize than those for pure components due to the fact that the composition must be considered. In addition to this added dimension, a casual inspection of different phase diagrams shows great disparity in behavior from one binary system to another. For example, some systems have azeotropes, isolated regions of immiscibility and three phase lines. Von Konynenburg and Scott [1,2] have proposed a convenient classification scheme which accounts for most of the possible types of behavior. Their method is based on the existence or absence of three phase lines, the number of critical lines and the manner in which the critical lines connect with the pure component critical points and three phase lines. Azeotropy gives rise to subclasses but does not change the qualitative structure of the classification scheme.

In this system there are six basic types of phase diagrams which are illustrated as p-T projections of their corresponding three dimensional space models in figure 1 [3]. In this diagram the dashed lines are critical loci and solid lines are either pure component vapor pressure curves, three phase lines or azeotrope lines. Type I systems are the simplest of those encountered and typically have a continuous critical locus which connects the critical points of the two pure fluids, a common example of which is methane/propane. As is shown in figure 1, the critical locus can be monotonically increasing or can have a maximum or minimum value. Figure 2 shows the three dimensional space model which is typical of a type I system and an isoplethal (constant composition) of the space model.

Phase behavior in the region of a mixture critical point is usually more complex than in a pure fluid because the two phase region can extend to pressures and temperatures which are higher than the critical values. This type of phenomenon is known as retrograde behavior and is very common in mixtures. It was first discovered and investigated by Kuenen in 1893 [4]. Figure 3 shows this behavior more clearly. In this figure the highest temperature and pressure at which the two phase exists (the maxcondentherm and maxcondenbar, respectively) do not correspond with the critical point. Moving in the direction of increasing temperature along the isobar $\overline{AB}$ in figure 3a, we see that we intersect the two phase region at the point B_1, where a less dense phase appears. Continuing along this line more and more of this phae forms until we reach a point where it begins to disappear and we emerge from the two phase region at B_2 into a single, dense liquid like phase. This process is called retrograde vaporization. Similar behavior is observed along the line isotherm $\overline{\alpha\beta}$ in figure 3b which is called retrograde condensation.

If this behavior is not complicated enough, figure 4 shows a relatively unknown type of behavior called double retrograde vaporization. This behavior has been seldom discussed in the literature [5,6] even though it has been experimentally observed in hydrogen/n-hexane mixtures [7]. In light of current technological interest in hydrogen mixtures (e.g., coal liquefaction) further experimental studies in this area seem warranted.

Figure 5 shows some isobaric cross sections of the type I space model projected on the T-X plane. The upper curves are called the dew point temperature curve which gives the temperatures as a function of composition at which liquid will condense at a fixed pressure. The lower curves are called bubble point curves and give the temperatures at which the liquids begin to vaporize. The sections at p_2 and p_4 show the mixture critical points which are extrema on these projections. Note that in the cross section at p_4 there are two critical points. This corresponds to a critical locus which has an extremum between the critical points of the two pure fluids. Similar projections can be made at constant temperature to obtain p-x curves as shown in figure 6.

In figures 5 and 6 the dew and bubble points were shown to be monotonic functions of composition. In reality, this is frequently not the case. It is very common to encounter chemical systems in which the pressure for an isothermal cross section or the temperature for an isobaric section attains a minimum or maximum value and the dew and bubble points become identical. These systems are called azeotropic mixtures and the different possibilities are shown in figure 7. At the azeotropic point, the liquid and vapor phase compositions become identical as is shown by the vertical, dashed line. From an industrial point of view this means that the components cannot be separated by simple distillation. There are occasions where the formation of an azeotrope is desired, e.g., azeotropic distillation in a multicomponent mixture, so that an otherwise difficult secondary separation may be made. It is also relatively common for the azeotropic line in a binary mixture to intersect the critical locus thereby giving rise to a critical azeotrope as is shown in figure 8.

Another variation in the behavior of mixtures is that of a miscibility gap. Usually this type of behavior is only observed for liquid or solid phases, but it can also occur in the high pressure vapor phase giving rise to the so-called gas-gas or fluid-fluid equilibria. This type of behavior is shown in the types II-VI examples in figure 1. Usually the components are partially miscible as is shown in figure 9. Within the closed loop shown in figure 9, two liquid phases exist with compositions being given by the ends of the tie lines. The temperatures and pressures labeled T_u, T_L, P_u and P_L are called the upper and lower critical solution or consolute temperatures and pressures, respectively. Above or below these points the components are completely miscible and form a single liquid phase.

Many systems only exhibit an upper or lower consolute point in which case the miscibility gap can intersect a two phase liquid-vapor region. This is shown in figure 10. To further complicate matters azeotropic systems can also exhibit partial miscibility as is shown in figure 11.

This brief description of qualitative fluid phase behavior has been included to present a picture of the vast possibilities. For a more complete qualitative discussion of different types of phase behavior see references [8-10].

3. Prediction of Phase Equilibria

The basic problem that we are faced with in mixture thermodynamics is to predict the composition of the various phases which are in equilibrium. Once we have obtained the compositions of these phases we are then faced with the secondary problem of predicting the thermophysical properties (e.g., entropy, viscosity, enthalpy, etc.) of those phases. Normally the temperature and pressure are specified along with the total, bulk composition of the system, but frequently we must also calculate the dew or bubble point temperature or pressure given only the overall composition and another variable. Certainly part of this general problem is to be able to know how many and what types of phases coexist at certain conditions. Even though this problem is quite complex, both mathematically and conceptually, thermodynamics gives us some extremely powerful tools for tackling it.

From thermodynamics we know that the condition for equilibrium in a closed system is that at constant entropy and volume, for any infintesimal change in state

$$dU_{s,v} = 0 \tag{1}$$

Since we can always consider a multiphase system to be one large closed system we are thereby led to the conclusion that for equilibrium to exist we must have the conditions

$$T^{(1)} = T^{(2)} = \ldots = T^{(\pi)} \tag{2}$$

$$p^{(1)} = p^{(2)} = \ldots = p^{(\pi)} \tag{3}$$

$$\hat{\mu}_i^{(1)} = \hat{\mu}_i^{(2)} = \ldots = \hat{\mu}_i^{(\pi)} \quad i = 1, N \tag{4}$$

where $T^{(j)}$, $p^{(j)}$ and $\hat{\mu}_i{}^{(j)}$ are the temperature, pressure and chemical potential of the i^{th} component in the j^{th} phase. The super "^" denotes a property of a component in solution. Physically these equations mean that there is no heat transfer between phases, no boundary expansion and no potential for mass transfer. The chemical potential is an intensive parameter which, in general, a function of temperature, pressure and composition. From a predictive viewpoint we can assume that the temperature and pressure of the coexisting phases are equal, so the prediction of phase equilibrium reduces to the problem of predicting the chemical potential at some specified temperature and pressure and (to be determined) composition.

Most engineers do not, however, work directly with the chemical potential but rather with a related quantity, the <u>fugacity</u>. The fugacity was defined by G. N. Lewis [11] by the differential relation

$$d\hat{\mu}_i = RT \, d \, \ell n \, \hat{f}_i \tag{5}$$

and has the units of pressure. Mathematically the fugacity is easier to work with than the chemical potential for two reasons: (1) it approaches the pressure as the fluid approaches the ideal gas state whereas the chemical potential approaches minus infinity and (2) unlike the chemical potential it can be calculated without a knowledge of thermal properties of the component, e.g., ideal gas heat capacities. The use of fugacity does not affect the criteria for equilibrium -- eq (4) is merely transformed to be

$$\hat{f}_i^{(1)} = \hat{f}_i^{(2)} = \ . \ . \ . \ = \hat{f}_i^{(\pi)} \quad i = 1, N \tag{6}$$

e.g., the fugacity merely replaces the chemical potential.

Fugacity is frequently referred to as the escaping tendency and in order to get a better feel for eq (6), it is appropriate to consider some qualitative molecular aspects of phase equilibrium. In a system which is capable of existing in two phases at some pressure and temperature, the molecules will have a tendency to "escape" from the phases in which they exist to another phase because of their thermal energy. Unless this escaping tendency is exactly balanced by the tendency of molecules to return to the given phase by escaping from another coexisting phase [e.g., no potential for mass transfer], the phase in which the escaping tendency is greater will disappear in favor of the phase of smaller escaping tendency. The fugacity (and chemical potential) is a measure of this escaping tendency and thus we can grasp the meaning of the criteria that $\hat{f}_i^{(1)} = \hat{f}_i^{(2)} = \ldots = \hat{f}_i^{(\pi)}$.

As was mentioned previously, the prediction of phase equilibrium reduces to the prediction of fugacity. There are basically two ways of achieving this goal: (1) equations of state which incorporate a corresponding states principle and (2) specific correlations or models for fugacity.

3.1 Mathematical Considerations for Calculating Phase Equilibria

Before proceeding to discuss specific means of calculating phase equilibria, let's briefly consider the philosophy of how one actually performs the calculations. From thermodynamics we know that at equilibrium the Gibbs energy of the entire system is at a minimum, i.e., at constant temperature and pressure

$$dG_{T,P} \leq 0 \qquad (7)$$

Since for a composite system comprised of several phases in equilibrium we have

$$\eta_T G_T = \sum_{j=1} \eta_T^{(j)} G^{(j)} \qquad (8)$$

and for every phase in equilibrium

$$G^{(j)} = \sum_{i=1}^{N} \eta_i^{(j)} \hat{\mu}_i^{(j)} \qquad (9)$$

we can use a non-linear minimization routine to find the absolute minimum of the Gibbs energy of the system, subject to the material balance constraints that

$$\eta_T = \sum_{j=1}^{\pi} \eta_T^{(j)} \quad \text{and} \quad \eta_{i}, = \sum_{j=1}^{\pi} \eta_i^{(j)} \qquad (10)$$

i.e., material balance. In these equations $G^{(j)}$ is the molar Gibbs energy of the ith phase, $\hat{\mu}_j^{(i)}$ is the chemical potential of the jth component in the ith phase and $\eta_i^{(j)}$ is the number of moles of the ith component in the jth phase and the subscript "T" denotes the total, composite system.

This procedure, which is conceptually simple, is time consuming from a numerical point of view and is susceptible to the usual problems of non-linear optimization, i.e., local minima. In addition, in order for the procedure to be perfectly general it requires a "phase splitting" algorithm which is capable of deciding when another phase will form and what its major components will be. This is obviously a very difficult task and only recently has there been an algorithm proposed which shows promise of being successful. This method was developed by Guatam and Seider [12,13] and has been included in the project ASPEN simulation program. Several other Gibbs energy minimization algorithms have also been proposed [14-16].

Because of the difficulties with direct minimization, most investigators use what is called a multiphase flash algorithm for phase equilibria calculations. The basic limitation of this type of calculation is that it is not easily expanded to more than three phases and can be unstable near a critical point. Nonetheless this method is applicable to a wide range of phase behavior and is probably used in 99 percent of all phase equilibrium calculations.

A flash calculation is essentially a direct solution of the material balance eq (10) for the coexisting phases. Its name is derived from what is called a flash separator or single stage distillation in chemical engineering. The general scheme of a 2-phase flash calculation is as follows. If there are n_i moles of a component in a mixture which potentially could be two-phased, we can write without loss of generality a material balance equation

$$x_i L + y_i V = Z_i F = n_i \qquad i=1, N \tag{11}$$

where L, V and F are the total number of moles in the liquid, vapor and bulk mixture phases and x_i, y_i and Z_i are the mole fractions of component i in the liquid, vapor and feed phases respectively. By overall material balance for the mixture

$$F = L + V \tag{12}$$

and we may write

$$Z_i = [(1 - R) K_i + R] x_i \tag{13}$$

and

$$Z_i = [(1 - R) + R/K_i] y_i \tag{14}$$

where R is the so-called liquid to feed distribution ratio, L/F, and k_i is the equilibrium K-value y_i/x_i. The K-value is very common in engineering distillation calculations and gives the equilibrium distribution of a component between coexisting phases (in this case liquid and vapor). By rearranging these equations and summing over all components we find that

$$\sum_{i=1}^{N} Z_i [(1 - R)K_i + R]^{-1} = \sum_{i=1}^{N} Z_i K_i [(1 - R)K_i + R]^{-1} = 1 \tag{15}$$

Subtracting, we find that our material balance equation takes the form

$$Z_i \; (1 - K_i)[(1 - R)K_i + R]^{-1} \;=\; 0 \qquad (16)$$

The method of calculating phase compositions is then to make an initial guess at the K-values (typically Raoult's law) for every component in the system and then numerically solving the material balance equation for R. Then, new phase compositions are calculated using the relations

$$x_i \;=\; Z_i/[(1 - R)K_i + R] \qquad (17)$$

$$y_i \;=\; Z_i k_i/[(1 - R)K_i + R] \;. \qquad (18)$$

These new compositions are then used in the calculation of the component fugacities. If the fugacities of the components do not match, new K values are calculated from the expression $K_i = \phi_i^{(\ell)}/\phi_i^{(v)}$ where $\phi_i^{(\ell)} = f_i^{(\ell)}/x_i p$ and $\phi_i^{(v)} = f_i^{(v)}/y_i p$, i.e., the fugacity coefficients in each phase, and a new and set of compositions are calculated. The iteration stops when two successive values of R match and the fugacities of all components satisfy the criteria delineated earlier.

There are also some variations of this procedure, namely dew and bubble point calculations which are performed by forcing R to be either 0 or 1, respectively, and searching for the temperature and pressure that make the fugacities match. For extensions of this method to three phases see [17-20].

4. Mixture Equations of State

As mentioned previously, the first method of calculating fugacities for phase equilibrium uses an equation of state. Given an equation of state and the ideal gas heat capacities for the mixture, it is possible via straightforward thermodynamics to calculate all of the thermophysical properties of interest, e.g., enthalpy, entropy, energy, etc. In order to calculate the fugacity, one uses the relationship

$$RT \,\ell n \frac{\hat{f}_i}{x_i P} \;=\; \int_0^{\rho} \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \rho RT \right] \frac{d\rho}{\rho^2} - RT \,\ell n\, Z \qquad (19)$$

As of today, no investigator has reported a perfectly general equation of state which can be applied to a wide spectrum of mixtures whose components differ greatly in polarity and size. Instead, specialized equations have been developed which apply to limited ranges of mixtures, for example, natural gases and gas liquids, and perhaps mixtures of aliphatic alcohols. The primary hinderance to the development of what might be called a master equation of state is rooted in our level of understanding concerning the interactions of chemically dissimilar molecules. Nevertheless equation of state methods for predicting phase equilibria in nonpolar mixtures have developed rapidly during the last ten years. Generally speaking these equations may be classified as being a member of one of four possible families [21]: (1) van der Waals; (2) Benedict-Webb-Rubin; (3) Reference Fluids Equations or (4) Augmented Rigid Body Equations.

4.1 van der Waals Family

Equations of state within this family are probably the most widely used for engineering calculations. This popularity arises from the simplicity of the equations which enables them to be expressed in terms of dimensionless two or three parameter corresponding states functions [21]. Generically these equations have a cubic volume dependence and may be written as

$$p = \frac{RT}{V-b\ (T_r,\omega)} - \frac{a(T_r\omega)}{g(V,T_r,\omega)} \tag{20}$$

where g is a function of volume which typically depends on the b parameter and, perhaps another parameter. The most important variants of this equation are summarized in table 1. These equations are typically written for pure fluids and then extended to mixtures as discussed below. Before proceedings to that discussion it should be noted that once the pure fluid critical point constraints have been imposed

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0$$

only the values of $b(1,\omega)$ $a(1,\omega)$ and $g(V_c,1,\omega)$ are fixed. This means then that the temperature dependence of these functions may be adjusted to obtain optimal agreement which some selected properly. The members of this family which are the most successful in predicting phase equilibria (Soave, Peng-Robinson and Harmens-Knapp) adjust this temperature dependence so as to provide good agreement with pure component vapor pressures. For example, with the Peng-Robinson equation

$$p = \frac{RT}{V-b} - \frac{a(T_r,\omega)}{V(V-b) - b(V+b)}$$

the constant b is given by $\Omega_b b_c$ where Ω_b is a universal constant and

$b_c = RT_c/p_c$, $a(T_r,\omega) = a_c\alpha(T_r,\omega)$ where $a_c = \Omega_a(RT_c)^2/p_c$ and

$$\alpha(T_r,\omega) = [1 + m(\omega)(1 - T_r^{1/2})]^2$$

$$m(\omega) = m_1 + m_2\omega + m_3\omega^2$$

The function α was chosen to fit vapor pressures for a series of compounds including the normal paraffins in the temperature range $0.7 \leq T_r \leq 1$ and generally gives good phase equilibria predictions for mixtures containing those fluids.

Table 1. Summary of Common van der Waals Family Equations

Equation	Reference	$g(V,T,\omega)$
van der Waals	[96]	V^2
Redlich-Kwong	[97]	$T^{1/2}\ V(V + b)$
Soave	[98]	$V(V + b)$
Peng-Robinson	[99]	$V(V + b) - b(V - b)$
Fuller	[100]	$V(V + cb)$
Harmens	[101]	$V^2 + Vcb - (c - 1)b^2$
Usdin	[102]	$V(V + d)$

As pointed out by Leland [21] the selection of $\alpha(T_r,\omega)$ to fit pure component vapor pressures results in poorer representation of other features of the PVT surface, e.g., enthalpy. This arises because of theoretical flaws in the van der Waals family of equations, primarily in the repulsive, hard sphere pressure term RT/(V-b) [23].

In order to apply these equations to mixtures, mixing rules must be introduced. For the van der Waals family, the appropriate mixing rules can be deduced on theoretical grounds by considering the conformal interactions between different molecular species and the proportionality between the intermolecular potential parameters and critical constants [24]. The end result is

$$a_m = \sum_i \sum_j x_i x_j\ a_{ij} \tag{21}$$

$$b_m = \sum_i \sum_j x_i x_j\ b_{ij} \tag{22}$$

These are called the van der Waals one-fluid mixing rules. In order to apply them to a mixture, combining rules which relate the binary parameters a_{ij} and b_{ij} to the pure component parameters. For this family they are defined by

$$a_{ij} = (a_i a_j)^{1/2} (1 - k_{ij}) \tag{23}$$

$$b_{ij} = \frac{1}{8} \left(b_i^{1/3} + b_j^{1/3}\right)^3 (1 - \ell_{ij}) \tag{24a}$$

or

$$b_{ij} = \frac{1}{2} (b_i + b_j)(1 - \ell_{ij}) \tag{24b}$$

where k_{ij} and ℓ_{ij} are called binary interaction coefficients which must be determined from experimental data. Usually the volume interaction coefficient, ℓ_{ij}, is taken as being zero. Compilations of k_{ij} values applicable to the van der Waals and other families of equations of state have been reported [25,26]. In addition, several correlations for k_{ij} have been given in the literature [27-31].

As mentioned previously, recent members of the van der Waals family have been very successful in predicting the phase behavior of hydrocarbon mixtures which possibly include common inorganics such as CO_2, N_2, etc. Many comparisons of predicted and experimental phase equilibria have been given in the literature for these equations [32-40]. For our purposes figure 12, which was taken from the original Peng-Robinson (PRS) [32] paper suffices. This figure compares the equilibrium K-values for a six-component mixture as a function of pressure. In general the results are excellent with the only serious errors being in the heaviest component at low pressures. The Soave equation (RKS) gives similar results for this system. Both equations give results which are accurate to within ± 5.8 percent which in many cases corresponds to the uncertainty in the experimental data. The PRS equation has the advantage of being more accurate in its predictions of the liquid phase density.

More recent activity related to this family of equations has dealt with extending them to water/hydrocarbon systems. Application of these equations to this type of system without modification tends to overpredict the solubility of water in the hydrocarbon rich phase and underpredict the hydrocarbon solubility in the water rich phase. This can be explained intuitively by observing that these equations use the critical constants of the pure fluids as a measure of the strength of intermolecular interactions and further, have no measure of induction effects (e.g., induced dipoles in hydrocarbons due to strong electric fields in water) or of structure breaking effects on water. Thus, the critical constants of water in a hydrocarbon phase are too large since its hydrogen bonded structure has been broken (predicted solubility is too high) and the hydrocarbon criticals in a water phase are too small since they have induced dipoles which interact strongly with the water (predicted solubility is too small).

There have been three basic approaches to this problem. The first method which has been proposed [41,42] is to use temperature dependent binary interaction coefficients in the water rich phases, i.e.,

$$a_{ij} = (a_i a_j)^{1/2}(1 - \tau_{ij}^{W}(T))$$

and in a hydrocarbon rich phase

$$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij})$$

This method although highly correlative in nature has been very successful. Figures 13 and 14 demonstrate some typical results which were reported by Robinson [41].

The second approach concentrates primarily on the wter solubility in the hydrocarbon phase and amounts dividing the attractive a parameter into a polar and nonpolar contribution and allowing them to interact tensorially, e.g.,

$$a_{ij} = \sqrt{a_i^N a_j^N}\,(1 - k_{ij}) + \sqrt{a_i^P a_j^P}$$

where the superscripts "P" and "N" denote polar and nonpolar. By allowing a_i^P to have an induced contribution from the water it is also possible to obtain an improved representation of the hydrocarbon solubility in the polar phase. This approach was proposed in some form by Chueh [43], Nakamura, et al. [44] and Won [45] and has been moderately successful. Figures 15 and 16 show some typical results.

The third approach which has been proposed handle polar-nonpolar systems with cubic equations of state has been to use a binary interaction coefficient with the repulsive, b parameter, as indicated in eq (24). This approach, which has been proposed by Heidemann [46] and Erbar [47] is also reasonably successful. Figures 17 and 18 demonstrate some of their results.

In spite of the relative success of these modifications in correlating polar/nonpolar phase equilibria, they still leave much to be desired. For example, it is not generally possible to a priori predict the required binary interaction coefficients nor is it possible to determine the polar/nonpolar separation of the attractive coefficients. In addition, this type of model is merely correcting a model which is basically too simple and incorrect in detail to make it work for more complicated systems.

Another approach to the correlation and prediction of phase equilibrium based on a van der Waals family equation has been proposed by several investigators. It is based on modifying the composition dependence of the mixing rule, eq (21). This method enables one to correlate data for complex mixtures but the equation of state parameters can no longer be identified with critical constants. In addition, these models do not give the theoretically correct composition dependence of the second virial coefficient. For details of this method see references [48-51].

4.2 Benedict-Webb-Rubin Family

The second class of equations which are commonly used in engineering phase equilibria are those of the Benedict-Webb-Rubin (BWR) family. The original BWR [52] equation contains eight adjustable constants and is given by

$$P = \rho RT + (B_0RT - A_0 - C_0/T^2)\rho^2 + (bRT - a)\rho^3 + a\alpha\rho^6 + (c\rho^3/T^2)(1 + \gamma\rho^2)e^{-\gamma\rho^2} \qquad (25)$$

In order to use this equation for mixtures, mixing rules such as those used for the van der Waals equations are used. In general they are given by

$$a_m = \left(\sum_j x_j\, a_j^{1/r}\right)^r$$

Values of r for each coefficient are given in table 2. It should be noted, however, that unlike the van der Waals equation, these mixing rules have no theoretical basis. This type of equation offers vastly improved thermodynamic property predictions but does not offer any better results for the phase equilibria. It suffers from a second short coming in that it requires a large number of coefficients for every component in the mixture and it tends to fail at low reduced temperatures.

Table 2. Benedict-Webb-Rubin Mixing Rules

$$a_m = \left(\sum_j x_j \, a_j^{1/r} \right)^r$$

Constant (a_m)	r
B_o	1
A_o	2
C_o	2
a	3
b	3
c	3
α	3
γ	2

Starling [53,54] addressed these latter two shortcomings and thereby greatly expanded the use of this type of equation. The basic form of his equation (BWRS) is as follows

$$P = \rho RT + (B_o RT - A_o - C_o/T^2 + D_o/T^3 - E_o/T^4)\rho^2 + (bRT - a - d/T)\rho^3 \\ + \alpha(a + d/T)\rho^6 + (c\rho^3/T^2)(1 + \gamma\rho^2) \exp(- \gamma\rho^2) \tag{26}$$

which has eleven adjustable constants. In its original formulation, mixing rules such as those for the BWR were used except geometric means were recommended for the A_o, C_o, D_o and E_o coefficients. These mixing rules are summarized in table 3. Later however Han and Starling [55] generalized the BWRS constants in terms of the critical constants and Pitzer's acentric factor, for example

$$\rho_{c_i} B_{o_i} = A_1 + B_1 \omega_i$$

The appropriate equations and coefficients are summarized in table 4.

Table 3. Benedict-Webb-Rubin Starling Equation of State Mixing Rules

$$a_m = \left(\sum_j x_j a_j^{1/r}\right)^r \qquad a_m = \sum_i \sum_j x_i x_j a_i^{1/2} a_j^{1/2} (1 - k_{ij})^n$$

Constant (a_m)	r
B_o	1
a	3
b	3
c	3
d	3
α	3
γ	2

Constant (a_m)	n
A_o	1
C_o	3
D_o	4
E_o	5

Table 4. Generalized Coefficients for the BWRS Equation

$$\rho_{ci}B_{oi} = A_1 + B_1\omega_i$$

$$\frac{\rho_{ci}A_{oi}}{RT_{ci}} = A_2 + B_2\omega_i$$

$$\frac{\rho_{ci}C_{oi}}{RT^3_{ci}} = A_3 + B_3\omega_i$$

$$\rho^2_{ci}\gamma_i = A_4 + B_4\omega_i$$

$$\rho^2_{ci}b_i = A_5 + B_5\omega_i$$

$$\frac{\rho^2_{ci}a_i}{RT_{ci}} = A_6 + B_6\omega_i$$

$$\rho^3_{ci}\alpha_i = A_7 + B_7\omega_i$$

$$\frac{\rho^2_{ci}c_i}{RT^3_{ci}} = A_8 + B_8\omega_i$$

$$\frac{\rho_{ci}D_{oi}}{RT^4_{ci}} = A_9 + B_9\omega_i$$

$$\frac{\rho^2_{ci}d_i}{RT^2_{ci}} = A_{10} + B_{10}\omega_i$$

$$\frac{\rho_{ci}E_{oi}}{RT^5_{ci}} = A_{11} + B_{11}\omega_i \exp(-3.8\,\omega_i)$$

This equation has been extremely successful in predicting the properties of natural gas mixtures and has been used to design a substantial number of pipepipelines and gas processing plants. Recently, Starling and coworkers [56] have given this model a face-lift by essentially making the acentric factor an adjustable variable and by using molecular-size and energy parameters for reduction of the density and temperature. In the generalization in terms of the critical constants, the acentric factor has been eliminated in favor of a parameter labelled as γ which is usually close to ω. Generally speaking this equation offers only marginal improvement over the original BWRS. Other modifications of the BWR equation have been proposed and the interested reader should consult references [57-60].

The BWR family of equations has not been successfully extended to mixtures containing highly polar components such as water. The primary problem in this area lies in the large number of parameters used in this equation and the lack of any theoretical guidelines. In fact, the BWRS has never been successfully fitted to pure water so the parameters required for the mixing rules are not available. This problem is under current investigation by Starling and his coworkers [61].

4.3 Reference Fluid Equations of State

During the past 15 years large quantities of highly precise (and accurate) PVT and thermodynamic property data have been measured by various laboratories. With the advent of these data, complex equations of state have been developed to represent these data without regard to mathematical simplicity or eventual generalization to other fluids. Notable examples of this class of equations are the 32 term BWR proposed by Stewart and Jacobsen [62] and the nonanalytic equation developed by Goodwin [63].

In order to apply this type of equation of state to other pure fluids or mixtures, conformal solution theory must be used. This theory is based on the assumption that within classes (e.g., homologous series) of fluids the intermolecular potentials are given by

$$u_j\,(r) = \varepsilon_j\, f(r/\sigma_j)$$

for a pure fluid and

$$u_{ij}\,(r) = \varepsilon_{ij}\, f(r/\sigma_{ij})$$

for an unlike binary pair. This leads to the conclusion [64,65] for this class of fluids that

$$Z_i(V,T) = Z_o(V/h_i,\, T/f_i) \tag{27a}$$

and

$$A_i^R = f_i\, A_o^R(V/h_i,\, T/f_i) \tag{27b}$$

where Z is the compressibility factor, A^R is the residual Helmholtz free energy and f_i and h_i are called equivalent substance reducing ratios which are defined by

$$h_i = V_i^c/V_o^c \quad \text{and} \quad f_i = T_i^c/T_o^c \quad .$$

The subscript "o" denotes the reference fluid. Leland and coworkers [66,67] further extended this two parameter corresponding states model to fluids having assymetric, but not dipolar interactions by introducing shape factors in the equivalent substance reducing ratios, viz.

$$h_i = (V_i^c/V_o^c)\ \phi_i\ (T_{r_i}, V_{r_i}, \omega_i) \tag{28}$$

$$f_i = (T_i^c/T_o^c)\ \theta_i\ (T_{r_i}, V_{r_i}, \omega_i) \tag{29}$$

The shape factors have been fit to a generalized mathematical form and are given in reference [67]. Given eqs (27-29) it is possible to calculate all of the thermodynamic properties of a pure fluid belonging to the same conformal class. In order to extend this method to mixtures, mixing and combining rules must be introduced for the parameters f and h. Usually they are chosen in accordance with the van der Waals one-fluid theory [68]

$$f_x = h_x^{-1} \sum_\alpha \sum_\beta x_\alpha x_\beta\ f_{\alpha\beta}\ h_{\alpha\beta} \tag{30}$$

and

$$h_x = \sum_\alpha \sum_\beta x_\alpha x_\beta\ h_{\alpha\beta} \tag{31}$$

although other choices are possible. The combining rules used with this model are

$$f_{\alpha\beta} = (f_\alpha f_\beta)^{1/2}\ (1 - k_{\alpha\beta}) \tag{32}$$

and

$$h_{\alpha\beta} = \frac{1}{8}\ (h_\alpha^{1/3} + h_\beta^{1/3})^3\ (1 - \ell_{\alpha\beta}) \tag{33a}$$

or

$$h_{\alpha\beta} = \frac{1}{2}(h_\alpha + h_\beta)(1 - \ell_{\alpha\beta}) \qquad (33b)$$

Using eqs (30-33) in conjunction with (27-29) enables one to calculate any mixture property of interest. For example, for the fugacity of a component in solution

$$\ell n(f_\alpha/x_\alpha p) = \frac{U_0^r}{RT_0}\frac{n}{f_x}\frac{\partial f_x}{\partial n_\alpha} + (Z_0 - 1)\frac{n}{h_x}\frac{\partial h_x}{\partial n_\alpha} + \ell n(f_0/P) \qquad (34)$$

where U_0^r and Z_0 are the residual internal energy and compressibility factor of the reference fluid. Several authors [69-72] have explored the predictions of this method using a methane reference and figures 19 and 20 show some typical results. In general, results obtained with this method using a methane reference are very accurate if the system doesn't contain components with molecular weights greater than C_7 or associating components [69]. Furthermore, the method suffers from being mathematically complex which historically hinders industrial acceptance.

A second reference fluid equation of state method has been proposed by several authors [73-76]. It is based on the original Pitzer corresponding states model [75], but uses more than one reference fluid. For a two-fluid model [74] it takes the form

$$Z(P_r,T_r) = Z^{(1)} + \frac{\omega - \omega^{(1)}}{\omega^{(2)} - \omega^{(1)}}[Z^{(2)} - Z^{(1)}]$$

where the superscripts (1) and (2) denote the reference fluid values. In order to apply this method to mixtures, pseudocritical parameters must be defined via mixing rules such as

$$T_{cm} V_{cm} = \sum_i \sum_j x_i x_j T_{c_{ij}} V_{c_{ij}}$$

$$\omega_m = \sum_i x_i \omega_i \quad , \text{etc.}$$

most applications of this method have dealt with prediction of mixture density and enthalpy and the results are very good [75]. Current work with this approach deals with phase equilibria and critical lines [77].

4.4 Augmented Rigid Body Equations of State

The final category of equations of state is similar in some respects to the van der Waals family, but is set apart because of the abandonment of the van der

Waals repulsion term RT/(V-b). These equations start with theoretically based rigid body equations of state and add terms to account for the effect of molecular attraction. The rigid body terms are the Wertheim-Thiele [82], Carnahan-Starling equation of state for hard spheres [78] and the equations of Gibbons [79], Boublik [80] or Nezbeda and Leland [81] for rigid nonspherical bodies. Examples of this class of equations are the perturbed hard chain theory [83,84], augmented van der Waals theory [85-87] and the Hlavaty equation of state [88,89] among others [99-94].

Of particular interest in this class are the augmented van der Waals equation developed by Kregleski and coworkers [85-87] and the perturbed hard chain theory of Prausnitz, et al. [83,84]. These two models have been applied to polar/nonpolar systems with moderate success. Recently [95] the Prausnitz model has been successfully applied to water and water/alcohol/hydrocarbon containing mixtures. Generally speaking, this family of equations of state is in a developmental stage and has not yet found widespread industrial use. They appear, however, to offer the most economical route to phase equilibria in polar/nonpolar systems.

4.5 Critical Loci From Cubic Equations of State

Latter portions of this report deal with the prediction of critical loci using the reference fluid equation of state approach and the Leung-Griffiths model [103-105]. It should be pointed out in passing that a considerable amount of effort has been made in predicting these loci using members of the van der Waals (cubic) family of equations of state. Scott and von Konynenburg [1,2] have shown that with the appropriate choice of parameters in the original van der Waals equation, all known types of critical lines in binary mixtures may be qualitatively predicted. More recently, Peng and Robinson [106] have developed a numerical method for predicting critical lines in multicomponent mixtures. They applied this method using their equation of state to both binary and multicomponent liquid-vapor mixtures having up to 12 components. Their comparisons showed prediction of the mixture critical temperature to within an average absolute error of 4 K ($\sim$ 1.3 percent) and pressures to within 173 kPa ($\sim$ 2.3 percent). Predictions of the critical volumes were substantially worse ($\sim$ 12 percent error) which is not surprising since cubic equations of state are not very accurate for density prediction.

The main advances in this area have been in the computational methods that can be used with cubic equations of state. In particular the algorithm of Heidemann and Khalil [107] which is based on the Helmholtz (rather than Gibbs) free energy. This method used with a cubic equation of state requires only a few milliseconds computational time regardless of the number of mixture components [107].

5. Phase Equilibria From Liquid Phase Activity Methods

As was stated in section 3 there are two methods of predicting and/or correlating phase equilibria -- equations of state and activity coefficient methods. By and large, equation of state methods are primarily limited to hydrocarbon systems with some current methods being directed towards polar/nonpolar systems such as water hydrocarbon systems. Obviously there is a wide spectrum of other mixtures which are routinely processed and for which phase equilibria are predicted for engineering design purposes. The technique which is used for these calculations is not new and is what is called classical solution thermodynamics. It amounts to defining an idealized model of a mixture called an ideal solution and describing deviations from this model in terms of excess functions.

The necessary and sufficient condition for phase equilibrium is that the temperature and pressures of all phases are equal and that

$$\hat{f}_i^{(1)} = \hat{f}_i^{(2)} = \ldots = \hat{f}_i^{(\pi)} \qquad i = 1, N$$

Ideally it would be nice if a solution behaved like a group of individual pure components weighted by some measure of their concentration. In other words, we would like for a liquid

$$\hat{f}_i^{(\ell)} = x_i f_i^0$$

where f_i^0 is the pure component fugacity and for a vapor

$$\hat{f}_i^{(v)} = y_i p$$

i.e., ideal gas. The combination of these leads to a definition of an ideal solution, i.e.,

$$y_i p = x_i f_i^o$$

Considering the case of a low temperature, low pressure liquid $f_i^o = p_i^\sigma(T)$, e.g., the vapor pressure and we find

$$y_i p = p_i = x_i p_i^\sigma$$

which is Raoult's law. Given this definition one can define all of the thermodynamic functions of interest in the ideal solution which are given in table 5.

Table 5. Thermodynamic Properties of an Ideal Solution

Property	Dependence on Pure Component Properties	Mixing Contribution
Gibbs Energy	$G = \Sigma n_i \mu_i^o + RT\, \Sigma n_i\, \ell n\, x_i$	$RT\, \Sigma n_i\, \ell n\, x_i$
Enthalpy	$H = \Sigma n_i h_i^o$	0
Entropy	$S = \Sigma n_i s_i^o - R \Sigma n_i\, \ell n\, x_i$	$- R \Sigma n_i\, \ell n\, x_i$
Volume	$V = \Sigma n_i v_i^o$	0
Heat Capacity	$C_p = \Sigma n_i c_{pi}{}^o$	0
K Value	$K_i = p_i^\sigma(T)/p$	
Relative Volatility	$\alpha_{ij} = p_i^\sigma(T)/p_j^\sigma(T)$	

The superscript o refers to a pure component value -- <u>not</u> an ideal gas. Also, lower case symbols for extensive properties refer to molar values.

Just as no real gas behaves ideally no real solution behaves ideally. What we do, therefore, is to define thermodynamic excess functions which are over and above those of the ideal mixture, e.g.,

$$M^E = M - M^{id}$$

where M is any thermodynamic property. Obviously the excess functions satisfy the same thermodynamic relations that the total functions satisfy. Next without any loss of generality

$$f_i^{(v)} = \phi_i(T,p, \{y_j\})y_i p$$

and

$$f_i^{(\ell)} = \gamma_i(T,p, \{x_j\})x_i f_i^0$$

where ϕ_i is called the vapor phase fugacity coefficient and γ_i is called the liquid phase activity coefficient.

Normally one calculates ϕ_i from a simple vapor phase equation of state such as the PRS, RKS or virial equation of state via the integral relationship presented in our discussion of equations of state. Even though this leads to some inaccuracies (pressures lower than 10-20 atm) the quantities seldom deviate from unity by more than 10 percent. On the other hand, liquid phase nonidealities as reflected in activity coefficients can be and frequently are very large and in fact can change by many orders of magnitude. For example γ for a hydrocarbon in water may be around 10^9 whereas for methane in ethane it is around 2.

Thus in this formulation the approach to phase equilibria is to develop predictive and correlative methods for the liquid phase activity coefficient. This, in effect, is to develop models for the excess Gibbs energy since from thermodynamics

$$G^E = G - G^{id}$$

$$\mu^E = \left(\frac{\partial G^E}{\partial n_i}\right)_{T,p,n_j} = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} - \left(\frac{\partial G^{id}}{\partial n_i}\right)_{T,p,n_j}$$

$$\overline{G}_i^E = RT \ \ell n \ (f_i/f_i^{ideal})$$

or

$$\overline{G}_i^E = RT \, \ell n \, \gamma_i$$

where the bar indicates a partial molar quantity. This partial molar excess Gibb's energy is simply the log of the activity coefficient. Since

$$G^E = \sum_i n_i \overline{G}_i^E$$

we see that

$$G^E = RT \sum_i n_i \, \ell n \, \gamma_i$$

In this overview consideration will be given to four of the most popular models for excess Gibbs energy in liquids which are correlative and two predictive models which are based on a group contribution concept. The first of these is the Margules model. Before doing that, however, let us consider some general points about activity coefficients.

Figure 21 illustrates the different kinds of deviations from ideality that are commonly encountered in vapor-liquid systems in terms of partial pressures, activity coefficients, and y-x diagrams. There are two important features that are shown in this figure. The first, and most important, is that the activity coefficient of any component approaches a finite limiting value as the concentration of that component approaches zero. This limiting value is of upmost importance in activity coefficient correlations (or G_E correlations) and is given the symbol of γ_i^o or γ_i. It is called the infinite dilution activity coefficient

$$\lim_{x_i \to o} \gamma_i = \gamma_i^o$$

As will be shown, a knowledge of only the infinite dilution activity coefficients enables us to calculate the activity coefficient over the entire composition range. It will also be shown that infinite dilution activity coefficients follow very systematic trends within a homologous series which enables one to predict γ_i's for many compounds based on experimental measurement of a few key members of a homologous series.

The second point which is of interest with regard to figure 21 has to do with azeotrope formation and miscibility gaps. In the case labeled "large positive deviations" we see in the y-x diagram the vapor and liquid compositions actually become identical at x = .85. This corresponds to azeotrope formation, which as you can see by comparison is not possible in an ideal solution. In the system with very large positive deviations, the dotted lines indicate a miscibility gap, which also is not possible in an ideal mixture. Thus, it would not be possible to do azeotropic distillation or liquid-liquid extractions if it were not for liquid phase non-idealities.

Returning to the expression for k-values in non-ideal systems, it is convenient from a computational point of view to separate the pressure dependence of the pure component fugacity and activity coefficient. Normally, the greatest contribution to the pure component liquid fugacity comes from the vapor pressure, therefore it is convenient to rewrite this term to make that dependence explicit. Since

$$\left(\frac{\partial \ln f_i^o}{\partial p}\right)_{T,n} = \frac{V_i^o}{RT}$$

the change in the fugacity in compressing the pure fluid from vapor pressure p_i^σ to the system pressure p is

$$\ln f_i^o(T,p)/f_i^o(T,p_i^\sigma) = \int_{p_i^\sigma}^{p} \frac{V_i^o}{RT}\, dp$$

Since for the pure component at p_i^σ, $f_i^o = \phi_i(p_i^\sigma,T)p_i^\sigma$, we have

$$f_i^o(T,p) = p_i^\sigma\, \phi_i(p_i^\sigma,T) \exp \int_{p_i^\sigma}^{p} \frac{V_i^o}{RT}\, dp \tag{35}$$

There is also pressure dependence in the activity coefficient. Most correlations of excess Gibbs energy (i.e., activity coefficients) are for a standard or reference pressure, p . The pressure dependence is then separated in the same manner that we separated the pressure dependence of the pure component liquid fugacity, only using the equation

$$\frac{\partial \ell n \hat{f}_i}{\partial p} = \frac{\overline{V}_i}{RT}$$

After performing all the appropriate integrations and manipulations we find that

$$\gamma_i(p,T,\{x_j\}) = \gamma_i(p^*,T,\{x_j\}) \exp \int_{p^*}^{P} \frac{\overline{V}_i - V_i}{RT} \, dp \quad . \tag{36}$$

As was mentioned earlier, one of the key quantities in VLE is the k value y_i/x_i. Using the solution thermodynamics formulation of fugacities we find for the k value

$$k_i = \frac{\gamma_i f_i^0}{\phi_i P}$$

substituting in the results from eqs (35-36) we find

$$k_i = \frac{\gamma_i p_i^\sigma}{\theta_i P}$$

where θ_i is defined as

$$\theta_i = \frac{\phi_i(T,p,\{y_i\})}{\phi_i(T,p_i^\sigma)} \exp \left\{ - \int_{p^*}^{P} \frac{\overline{V}_i - V_i}{RT} \, dp - {}_{p_i^\sigma}^{P} \frac{V_i}{RT} \, dp \right\}$$

and is called the "vapor imperfection coefficient" by some authors. Normally the reference pressure, p^*, is chosen as one atmosphere. Also, at low operating pressures, the integral terms are small and may be neglected so that θ_i reduces to ϕ_i/ϕ_i^σ which below 2 atm is also close to unity. Table 6 summarizes the important thermodynamic relationships for non-ideal solution thermodynamics. The expressions given in this table coupled with those in table 5 enable one to calculate all the thermodynamic properties of mixtures. The important thing to remember is that once one has the activity coefficients of all the mixture components as a function of temperature and pressure, one can calculate all of the mixture thermodynamic properties.

Table 6. Relations Between the Activity Coefficient and Thermodynamic Functions Which are Useful in Vapor-Liquid Equilibria

Function or Variable	Relation to the Activity Coefficient
Excess Gibbs Energy, G^E	$G^E = RT\,\Sigma n_i \,\ln \gamma_i$
Excess Enthalpy, H^E	$H^E = RT^2 [\partial(G^E/T)/\partial T]_{p,n}$ $= -RT^2\,\Sigma n_i(\partial \ln\gamma_i/\partial T)_{p,n}$
Excess Entropy, S^E	$S^E = -(\partial G^E/\partial T)_{p,n}$ $= -R\,\Sigma n_i[\ln\gamma_i - T(\partial \ln\gamma_i/\partial T)_{p,n}]$
Excess Volume, V^E	$V^E = (\partial G^E/\partial p)_{T,n}$ $= RT\,\Sigma n_i(\partial \ln\gamma_i/\partial p)_{T,n}$
Activity	$a_i = \gamma_i x_i$
k-value	$K_i = \gamma_i p_i^o(T)/\phi_i p$
Relative Volatility	$\alpha_{ij} = \gamma_i p_i^o(T)\,\phi_j/\gamma_j p_j^o(T)\,\phi_i$

$$\theta_i = [\phi_i/\phi_i^o] \exp \int_p^{p_i^\sigma} \frac{(v_i^o - v_i)}{RT}\,dp - \int_{p_i^o}^{p} \left(\frac{v_i}{RT}\right) dp$$

5.1 Azeotropes and Miscibility Gaps

Before going on to specific correlations for the excess Gibbs energy, we need to briefly consider the circumstances under which azeotropes and multiple liquid phases are formed. For the sake of simplicity, let's only consider a binary mixture.

Azeotropes occur whenever the relative volatility becomes unity, i.e., the k values of the two components are identical. There really is not anything magical about this type of behavior, it just so happens that

$$\frac{\gamma_1 p_1^\sigma}{\phi_1 p} = \frac{\gamma_2 p_2^\sigma}{\phi_2 p}$$

at some temperature, pressure and composition. If the pressure is low enough so that $\phi_i = 1$ (say one atmosphere for most systems), this identity reduces to

$$\gamma_1 p_1^\sigma = \gamma_2 p_2^\sigma$$

The term $\gamma_i p_i^\sigma$ is frequently called the volatility and is like a corrected vapor pressure of a component in a liquid mixture.

Given the infinite dilution activity coefficients and the assumption that the vapor phase behaves ideally, it is possible to predict from the pure component vapor pressures whether or not an azeotrope will form. Consider, for example, an isothermal system which exhibits positive deviations from ideality. In this case both activity coefficients are greater than unity. If we number the components such that "1" indicates the more volatile component, the maximum value the relative volatility $\alpha_{12} = K_1/K_2$ can attain is

$$(\alpha_{12})_{max} = \lim_{x_1 \to o} (\gamma_1 p_1^\sigma/\gamma_2 p_2^\sigma)$$

$$= \gamma_1^\infty (p_1^\sigma/p_2^\sigma)$$

At the other end of the composition range ($x_1 = 1$), we find that the other limiting value of the relative volatility is given by

$$(\alpha_{12})_{min} = (p_1^\sigma/p_2^\sigma)/\gamma_2^\infty$$

Thus, the total range of α_{12} is given by

$$\frac{p_1^\sigma}{p_2^\sigma}\,\frac{1}{\gamma_2^\infty} \leq \alpha_{12} \leq \frac{p_1^\sigma}{p_2^\sigma}\,\gamma_1^\infty$$

If α_{12} is unity (azeotrope formation), we find that by multiplying this inequality by p_2^σ/p_1^σ that

$$\frac{1}{\gamma_2^\infty} < (p_2^\sigma/p_1^\sigma) < \gamma_1^\infty \qquad \text{(positive deviations)}$$

If this criterion is satisfied, there will be a minimum boiling azeotrope.

In a similar fashion one can show that for systems in which there are negative deviations from ideality, a maximum boiling azeotrope will form if

$$\gamma_1^\infty < (p_2^\sigma/p_1^\sigma) < 1/\gamma_2^\infty \qquad \text{(negative deviations)}$$

The main thrust of this discussion is to point out that there are no fundamental behavioral differences between systems which are azeotropic and those which are not. It just so happens that in the former case, the vapor pressures and activity coefficients have magnitudes such that $\gamma_1 \, p_1^\sigma = \gamma_2 \, p_2^\sigma$.

One last point concerning azeotropes is that if the vapor phase is ideal, $\gamma_i x_i p_i^\sigma/\phi_i y_i p = 1$, or since $x_i = y_i$, $\gamma_i = (p/p_i^\sigma)$. Thus, azeotropic data give activity coefficients directly.

Now let us briefly turn our attention to immiscibility. At a fixed temperature and pressure, a stable state is one in which the Gibbs energy is a minimum, i.e., for any infintesimal change in state, $\delta G \leq 0$. This means that a liquid mixture will only split into two distinct phases if upon doing so, it can lower its Gibbs energy. If we were to expand the Gibbs energy of mixing in a Taylor series, we would find that mathematically the criterion for immiscibility is that

$$\frac{\partial^2 \Delta G}{\partial x^2} < 0 \qquad \text{(constant, T,p)}$$

For a binary mixture, this amounts to the criterion that

$$\frac{\partial^2 G^E}{\partial x_1^2} + RT\left(\frac{1}{x_1} + \frac{1}{x_2}\right) < 0$$

where the second term on the left hand side comes from the ideal Gibbs energy of mixing. Thus, if a mixture is to split into two liquid phases, it must "overcome" the ideal mixing contribution. Since G^E is only a function of temperature and the magnitudes of the activity coefficients, we see again that immiscibility does not represent any abnormal behavior, but rather is a consequence of the non-ideality of the system.

Finally, the equilibrium criteria for phase equilibrium require that for a system which exhibits two liquid phases

$$f_i^{(\ell_1)} = f_i^{(\ell_2)}$$

or, using our definition of liquid fugacity in terms of activity coefficients

$$\gamma_i^{(\ell_1)} x_i^{(\ell_1)} = \gamma_i^{(\ell_2)} x_i^{(\ell_2)}$$

Thus, a knowledge of the liquid phase compositions (also called the solubility limits) gives the ratio of the activity coefficients directly.

5.2 Excess Gibbs Energy Correlations

Thus far, statistical mechanics has not provided us with an adequate theoretical basis on which we can develop prediction or correlation techniques for liquid mixture properties containing chemically dissimilar species. Whenever there is a lack of a definitive theory, there are always many seemingly different correlations for the same property and the excess Gibbs energy is no exception.

5.2.1 Margules Equation

At a fixed temperature, the excess Gibbs energy of a mixture depends on the composition of the mixture and, to a lesser extent, the pressure. If we consider a binary mixture where the excess properties are taken with reference to an ideal solution where the standard state is the pure component fugacity at p and T, the molar excess Gibbs energy, $g^E = G^E/n$ must satisfy two boundary conditions:

$$g^E = 0 \quad \text{when} \quad x_1 \text{ or } x_2 = 0$$

The simplest non-trivial expression which obeys these conditions is

$$g^E = A\, x_1 x_2$$

where A is a function of temperature, but is independent of composition. Since $(\partial G^E/\partial n_i)_{n_j,T,p} = RT\,\ell n\,\gamma_i$, we have upon differentiation

$$RT\,\ell n\,\gamma_1 = A\, x_2^2$$

and

$$RT \ \ell n \ \gamma_2 = A \ x_1^2$$

These equations are called the two-suffix Margules equations [109] and are reasonable representations of simple (nearly ideal) liquid mixtures. Notice that the predicted activity coefficients are symmetrical. Also, this correlation implies that both infinite dilution activity coefficients are equal, i.e.,

$$\gamma_1^\infty = \gamma_2^\infty = \exp \ (A/RT)$$

The two suffix Margules equation is very simple and requires only one piece of data (γ_1 or γ_2) for its application. A convenient extension of this equation due to Redlich and Kister [110] is given by

$$g^E = x_1 x_2 \sum_{n=0}^{N} a_n \ (x_1 - x_2)^n$$

This type of expansion leads to power series expansions for the activity coefficients of the form

$$RT \ \ell n \ \gamma_1 = x_2^2 \sum_{n=0}^{N} \alpha_n^{(1)} \ x_2^n$$

$$RT \ \ell n \ \gamma_2 = x_1^2 \sum_{n=0}^{N} \alpha_n^{(2)} \ x_1^N$$

which are called N + 2 suffix margules equations. [A k-suffix Margules equation gives $\ell n \ \gamma_1$ (or $\ell n \ \gamma_2$) as a polynomial in x_2 (or x_1) of degree K.] Since, in general, $\alpha_n^{(1)} = \alpha_n^{(2)}$, these relations do not predict symmetrical activity coefficient curves.

Most physical models for g^E have in them an implicit assumption concerning the structure of the liquid phase, i.e., they imply that the local structure of the liquid is determined solely by the interactions of binary pairs. This certainly is not the case in reality, but it is a necessary simplifying assumption. If we make this assumption, it is a trivial matter to extend the two-suffix Margules equation to multicomponent systems. We find

$$g^E = \frac{1}{2} \sum_i \sum_j A_{ij} \ x_i x_j$$

where both sums extend over the number of components in the solution, $A_{ii} = A_{jj} = 0$, and the factor of 1/2 is included to avoid double counting. Upon differentiation with respect to one of the mole numbers, we find that

$$RT \ln \gamma_k = \sum_i \sum_j (A_{ik} - \frac{1}{2} A_{ij}) x_i x_j$$

where all the A_{ij} are determined from binary data.

5.2.2 van Laar Equation

One of the earliest attempts to form a rational physical model for liquid phase mixtures is due to van Laar [111]. van Laar considered a mixture of two liquids and assumed that they mixed at constant temperature and pressure such that V^E and S^E were identically zero, in which case $G^E = \;^E$. He then devised a thermodynamic cycle for the mixing process and used the van der Waals equation of state to calculate the energy changes during the cycle. The net result was the expression:

$$\frac{g^E}{RT} = \frac{A_{12} A_{21} x_1 x_2}{(A_{12} x_1 + A_{21} x_2)}$$

Differentiating, we find for the activity coefficients

$$\ln \gamma_1 = A_{12} [1 + (A_{12}/A_{21})(x_1/x_2)]^{-2}$$

and

$$\ln \gamma_2 = A_{21} [1 + (A_{21}/A_{12})(x_2/x_1)]^{-2}$$

These equations provide a direct relationship between the equation parameters A_{12} and A_{21} and the infinite dilution activity coefficients, viz.

$$\ln \gamma_1^\infty = A_{12}$$

and

$$\ln \gamma_2^\infty = A_{21}$$

The van Laar equation is extremely easy to work with and can adequately represent moderately non-ideal systems. In general, however, it is not capable of representing strongly non-ideal systems, especially those which exhibit association or strong physical interactions.

5.2.3 Wilson Equation

For mixtures which have no excess enthalpy (athermal solutions) but whose components do differ in size, Flory and Huggins [112] derived the following expression for the excess Gibbs energy

$$\frac{g^E}{RT} = \sum_i x_i \ \ell n \ (X_i/x_i)$$

where X_i is some measure of the size of the molecules, e.g., a volume fraction. Wilson considered the case where the molecules not only differed in size but also in the intermolecular interactions. These differences in intermolecular interactions lead to microscopic deviations from the random mixing notion which is inherent in many phase equilibrium models. Viewed microscopically a solution is not homogeneous but has local domains which differ in composition. This is illustrated in figure 22 which was taken from Prausnitz's review on phase equilibrium [113]. There is no easy way to relate the local composition to the bulk composition but Wilson proposed a Boltzmann factor type approach, i.e.,

$$\frac{x_{21}}{x_{11}} = \frac{x_2 e^{-\lambda_{12}/RT}}{x_1 e^{-\lambda_{11}/RT}}$$

and

$$\frac{x_{12}}{x_{22}} = \frac{x_1 e^{-\lambda_{12}/RT}}{x_2 e^{-\lambda_{22}/RT}}$$

where x_{21} is the concentration of molecules of type "1" around a central "2," etc., and λ_{ij} is an unspecified parameter. Wilson then defined a local volume fraction by

$$X_1 = \frac{\nu_1 x_{11}}{\nu_1 x_{11} + \nu_{21}}$$

where ν_i is a measure of size and with an analogous equation for X_2. Wilson then substituted his volume fraction into the Flory-Huggins expression for G^E. By defining

$$A_{12} = \frac{\nu_2}{\nu_1} \exp - \frac{\lambda_{12} - \lambda_{11}}{RT}$$

$$A_{21} = \frac{\nu_1}{\nu_2} \exp - \frac{\lambda_{12} - \lambda_{22}}{RT}$$

he found for a binary mixture

$$\frac{g^E}{RT} = - x_1 \ln (x_1 + A_{12}x_2) - x_2 \ln (x_2 + A_{21}x_1) \ .$$

The activity coefficients obtained from this expression are

$$\ln \gamma_1 = - \ln(x_1 + A_{12}x_2) + x_2 \left[\frac{A_{12}}{x_1 + A_{12}x_2} - \frac{A_{21}}{A_{21}x_1 + x_2}\right]$$

and

$$\ln \gamma_2 = - \ln(x_2 + A_{21}x_1) + x_1 \left[\frac{A_{12}}{x_1 + A_{12}x_2} - \frac{A_{21}}{A_{21}x_1 + x_2}\right] .$$

$$\ln \gamma_1^\infty = 1 - \ln A_{12} - A_{21}$$

and

$$\ln \gamma_2^\infty = 1 - \ln A_{21} - A_{12} \ .$$

The extension of Wilson's equation to multicomponent mixtures is very simple, viz.

$$\frac{g^E}{RT} = - \sum_i x_i \left[\ln \sum_j x_j A_{ij}\right]$$

and the corresponding activity coefficients are given by

$$\ln \gamma_k = - \ln \left[\sum_j x_j A_{kj}\right] + 1 - \sum_i \left[x_i A_{ik} / \sum_j x_j A_{ij}\right]$$

The Wilson equation has proved to be an extremely valuable tool in correlating highly non-ideal vapor-liquid equilibria data. As written, however, this equation is not capable of predicting miscibility gaps. This problem has been overcome, however, but we will not go into the details here. An important point relating to this equation is that it forms the basis for a predictive method of calculating vapor-liquid equilibria known as ASOG (Analytical Solution of Groups) which has been developed by E. L. Derr. This method along with another predictive method for activity coefficients will be discussed in section 5.3.

5.2.4 NRTL Equation

In the discussion of the equation of state methods for predicting phase equilibria we alluded to a one-fluid model which simply stated implies that the properties of a mixture can be related to those of a hypothetical pure fluid. There are also n-fluid theories of mixtures which state that the properties of a mixture can be related to those of an ideal mixture of several fluids of different behavior. For example, a two fluid theory says that the residual Gibbs energy of a mixture is given by

$$G^R = x_1 G_1^R + x_2 G_2^R$$

where the "R" refers to a residual value. The procedure then is to identify all components of the mixture with either of the two fluids via a one-fluid corresponding states principle and then mix them ideally.

Renon [114] combined the two-fluid approach with the local mole fraction ideas of Wilson except he used the quasi-chemical approximation rather than the Flory-Huggins term. He found that for the local mole fractions

$$\frac{x_{21}}{x_{11}} = \frac{x_2 \exp(-\alpha_{12} g_{21}/RT)}{x_1 \exp(-\alpha_{12} g_{11}/RT)}$$

Proceeding as in Wilson's case he found that

$$g^E = x_1 x_2 \left[\frac{\alpha_{21} A_{21}}{x_1 + x_2 A_{21}} + \frac{\alpha_{12} A_{12}}{x_2 + x_1 A_{12}} \right]$$

where $A_{ij} = \exp(-\alpha_{ij} \tau_{ij})$, $\tau_{ij} = \beta_{ij}/RT$ and $\alpha_{ij} = \alpha_{ij}$. This equation has three parameters per binary pair, β_{12}, β_{21} and α_{12}, unlike the Wilson equation which has only two parameters per pair. This equation does, however, appear to adequately represent strongly non-ideal systems, including those which exhibit liquid-liquid immiscibility. The activity coefficients for the NRTL equation for a binary mixture are

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{A_{21}}{x_1 + x_2 A_{21}} \right)^2 + \frac{\tau_{12} A_{12}}{(x_2 + x_1 A_{12})^2} \right]$$

and

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{A_{12}}{x_2 + x_1 A_{12}} \right)^2 + \frac{\tau_{21} A_{21}}{(x_1 + x_2 A_{21})^2} \right]$$

At infinite dilution we find the relations

$$RT \ln \gamma_1^\infty = \beta_{21} + \beta_{12} \exp(- \alpha_{12}\beta_{12}/RT)$$

and

$$RT \ln \gamma_2^\infty = \beta_{12} + \beta_{21} \exp(- \alpha_{12}\beta_{21}/RT) \quad .$$

Notice that unless we arbitrarily assign some value to α_{12}, knowledge of the infinite dilution activity coefficients alone is insufficient for the determination of the equation parameters.

This equation, like the Wilson equation, may be readily extended to multicomponent mixtures, for which we have the following relations:

$$\frac{g^E}{RT} = \sum_i x_i \frac{\sum \tau_{ji} A_{ji} x_j}{\sum_k x_k A_{ki}}$$

and

$$\ln \gamma_i = \sum_j x_j A_{ji} \, {}_{ji}/S_i + \sum_j (x_j A_{ij}/S_j) \left[\tau_{ij} - \sum_m x_m A_{mj} \, {}_{mj}/S_j \right]$$

where

$$S_k = \sum_j x_j A_{jk} \quad .$$

5.2.5 UNIQUAC

Recently, another correlation for the excess Gibbs energy called UNIQUAC, (UNIversal QUAsi-Chemical), has been proposed by Prausnitz and his co-workers [115]. This correlation is also based on semi-theoretical arguments and divides the excess Gibbs energy into a combinatorial part and what Prausnitz calls a residual part, i.e.,

$$g^E = g^E\ (\text{combinatorial}) + g^E\ (\text{residual})$$

The combinatorial part comes from considering the fluid to be described by a statistical mechanical lattice model to which the quasi-chemical approximation has been applied. The residual part was obtained by considering interaction energies, much in the same way as Wilson and Renon.

This equation is quite complex, although it only uses two adjustable parameters per binary pair. Preliminary indications from other investigators are that it is capable of correlating highly non-ideal systems, including those which are immiscible. For the sake of brevity, we will only give the multicomponent form of this equation and the activity coefficients derived from it.

$$g^E/RT = \sum_i x_i \ell n(\Phi_i/x_i) + 5 \sum_i \theta_i x_i \ell n(\Theta_i/\Phi_i) - \sum_i \theta_i x_i \ell n \left(\sum_j \Theta_j A_{ji} \right)$$

where $\Phi_i = x_i \phi_i / \sum x_i \phi_i$ and $\Theta_i = \theta_i x_i / \sum \theta_i x_i$. The adjustable parameters in this equation are the $A_{ij} = \exp(-\beta_{ij}/RT)$. The terms ϕ_i and θ_i are pure component parameters which are measures of the molecular volumes and surface areas, respectively.

The activity coefficients for this equation are given by

$$\ell n\ \gamma_i = \ell n(\Phi_i/x_i) + 5 \ell n(\Theta_i/\Phi_i) + \ell_i - (\Phi_i/x_i) x_j \ell_j$$

$$- \theta_i \ell n \sum_j \Theta_j A_{ji} + \theta_i - \theta_i \sum_j \Theta_j A_{ij} / \sum_k \Theta_k A_{kj}$$

where

$$\ell_i = 5(\phi_i - \theta_i) - (\phi_i - 1) \quad .$$

5.3 Group Contribution Models

All of the activity coefficient expressions that we have considered thus far are correlative in nature. They require specific data (at least the infinite dilution activity coefficients) to determine the parameters of the correlation. Derr and his coworkers [116-118] have developed an empirical method of predicting molecular activity coefficients given only the molecular structure of the mixture components which is known as the analytical solution of Groups or ASOG. The general idea is that there are many less functional groups, e.g., CH_3-,-OH,-NH_2, etc. than there are molecules. Thus if it is possible to correlate activity coefficients in terms of groups it is possible to cross correlate or predict activity coefficients in many molecular systems.

Initial efforts in predicting activity coefficients on the basis of structural groups were performed by Pierotti, Deal and Derr [108] and consisted of studying the infinite dilution activity coefficient of a homologous series of solutes in some solvent. Some typical results are shown in figure 23. As one can see from this figure there is a regular behavior as the number of (CH_2) groups increase in the polute. Pierotti, et al. performed this type of analysis on many types of systems and found that the results could be correlated by the equation

$$\ell n\ \gamma_1 = A_{12} + \frac{B_2 n_1}{n_2} + \frac{C_1}{n_1} + D(n_1 - n_2)^2 + \frac{F_2}{n_2}$$

where n is the number of -CH - groups. A-F are parameters and the subscript "1" denotes the solute. The coefficients for various binary systems have been summarized elsewhere [122,123] and will not be repeated here.

The study on infinite dilution activity coefficients led to an investigation of whether the group method could be applied to the entire range of composition. To do this we define group concentrations by the equation

$$X_k = \sum_j n_{jk} x_j / \sum_j n_j x_j$$

where X_k is the concentration of group k, n_{jk} is the number of k groups in the j^{th} molecular species, viz.,

$$n_j = \sum_k n_{jk}$$

The group activity coefficient model has four basic assumptions [123]:

1) The molecular activity coefficient is made up of two contributions, one due to size differences $\ell n\ \gamma^S$ and the other due to interactions of the groups, $\ell n\ \gamma^G$.

$$\ell n\ \gamma_i = \ell n\ \gamma_i^S + \ell n\ \gamma_i^G$$

2) The size difference term may be obtained from an idealized model such as the Flory-Huggins athermal solution or Gugenheim's lattice model [124]. For example for the Flory-Huggins term

$$\ell n \ \gamma_i^S = \ell n \left(\frac{\nu_i}{\sum\limits_j x_j \nu_j} \right) - \frac{\nu_i}{\sum\limits_j x_j \nu_j} + 1$$

where ν_i is some measure of the molecular size.

3) The contribution from the interactions of the groups is given by the term

$$\ell n \ \gamma_j^G = \sum_k n_{jk} \ (\ell n \ \Gamma_k - \ell n \ \Gamma_{kj}^*)$$

where Γ_{kj}^* is the standard state activity coefficient of the k group in the j molecular and Γ_k is the activity coefficient of the k group in the mixture. The standard state group coefficients must be included to ensure that γ_j^G approaches unity when $x_j \rightarrow 1$.

4) The final assumption is that the group activity coefficients may be obtained from a correlation like the Wilson equation except that group concentrations and parameters are used, e.g.,

$$\ell n \ \Gamma_k = 1 - \ell n \left[\sum_j X_j \ a_{ij} \right] - \sum_k \frac{X_k \ a_{ki}}{\sum\limits_j X_j \ a_{ki}} \quad .$$

There have been two very successful group contribution models -- ASOG [116-118] (Analytical Solution of Groups) which uses the Flory-Huggins size term and the Wilson equation, and UNIFAC [121] which uses the Gugenheim lattice model and the UNIQUAC equation. Tables of group parameters are available for both of these models which allow extensive predictions. Both of these models are accurate to within 10-20 percent for systems where the group parameters are available. This is usually sufficient for engineering screening design calculations.

5.4 Comments on Excess Gibbs Energy Correlations

A few comments are in order with regard to the activity coefficient correlations which we have presented. First of all, by design we have removed the pressure dependence of γ_i and placed it in the "vapor imperfection coefficient," θ_i. Although this is formally correct, we still need to know V_i and V_i as a function of pressure to accurately calculate the liquid fugacity. Normally, V_i is known with sufficient accuracy, but V_i is not. In fact,

. experimental data for $\overline{V}_i$ are scarcer than those for the activity coefficients themselves. In this case, a common assumption is that $\overline{V}_i = V_i$, in which case we only have to worry about the pressure dependence of the latter term. At low pressures, however, the activity coefficient is very insensitive to the pressure and the errors caused by these approximations are negligible. At higher pressures, however, especially in the critical region of a component, these approximations can lead to serious errors.

Secondly, and much more importantly, all of the excess Gibbs energy correlations that we presented are for only one temperature, including those which show an explicit temperature dependence. This is a particularly troublesome problem, since we may require activity coefficients at temperatures where we do not have experimental data. Since $(\partial G^E/\partial T) = -S^E$, the problem of predicting the temperature dependence amounts to predicting or knowing the excess entropy as a function of temperature. Since this type of data is also seldom available we are forced into a situation where we have to make some serious approximations.

Two possible approximations are that the solution is athermal or that it is regular. In the athermal case (i.e., $H_E = 0$), we are lead to the conclusion that at constant composition, the activity coefficients are independent of temperature. Generally this is a very poor approximation. The second choice is to assume that we have a regular solution (i.e., $S^E = 0$) which leads us to the conclusion that the activity coefficient varies as 1/T. Normally this assumption is better than the first, but both are far from adequate.

The optimal situation (other than having data at the temperatures that we want) is to have experimental data at two or more other temperatures which we can use to fit the Gibbs energy correlation coefficients or the activity coefficients themselves, to some polynomial in temperature. For example

$$\ell n \, \gamma_i = a + bT + c/T^n$$

where a_i, b_i, c_i and possibly even n, are determined by curve fitting experimental data at known temperatures.

6. Conclusions

This completes our brief overview of phase equilibria prediction methods. Although equation of state methods have developed rapidly during the past few years, there is still a definite need for models which represent systems which have large size and polarity differences. Activity coefficient methods which are predictive, e.g., ASOG, lack a sound theoretical basis upon which they may be improved. Further work in this area is needed.

7. References

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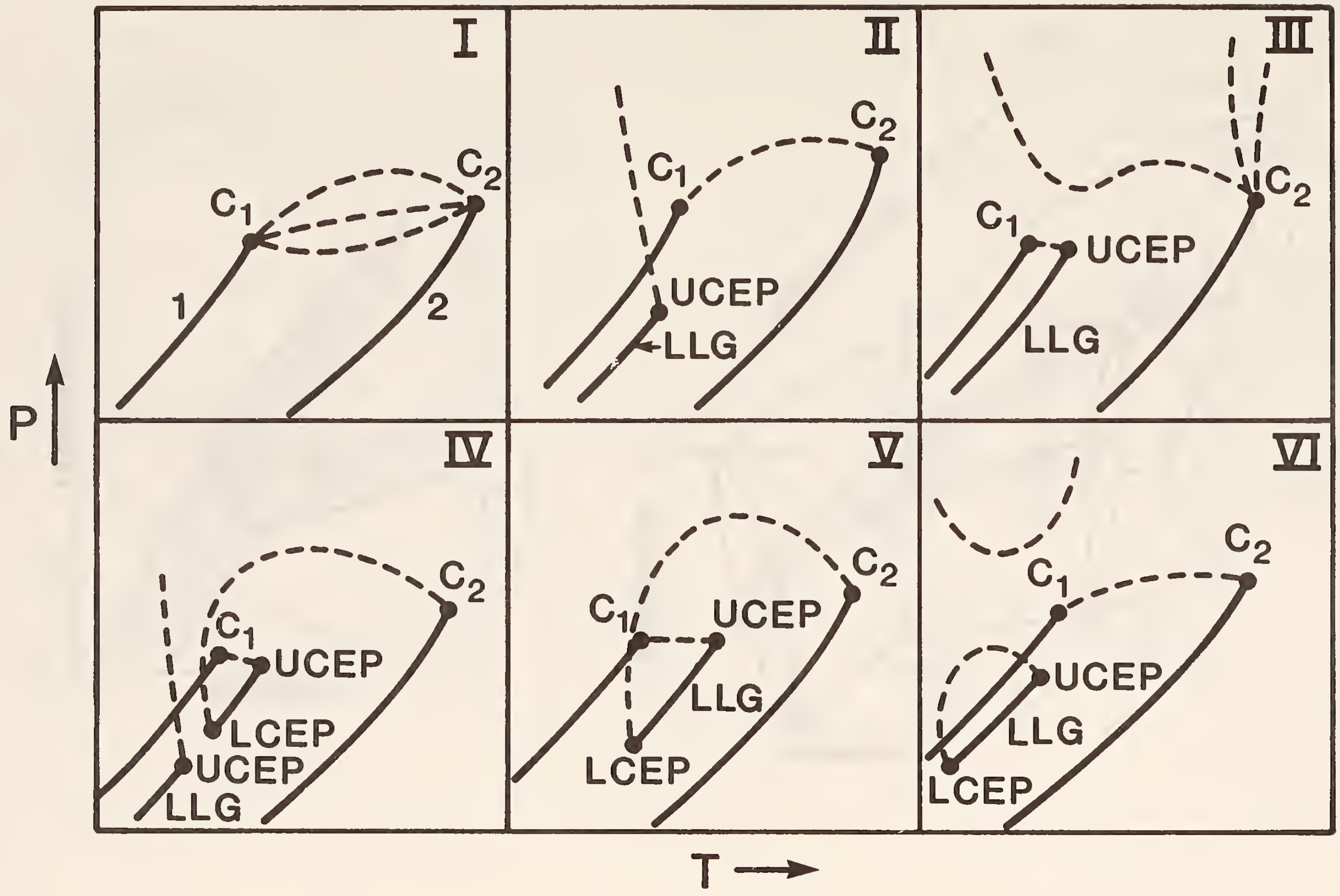


Figure 1. p-T projections of different classes of binary mixture phase behavior [3].

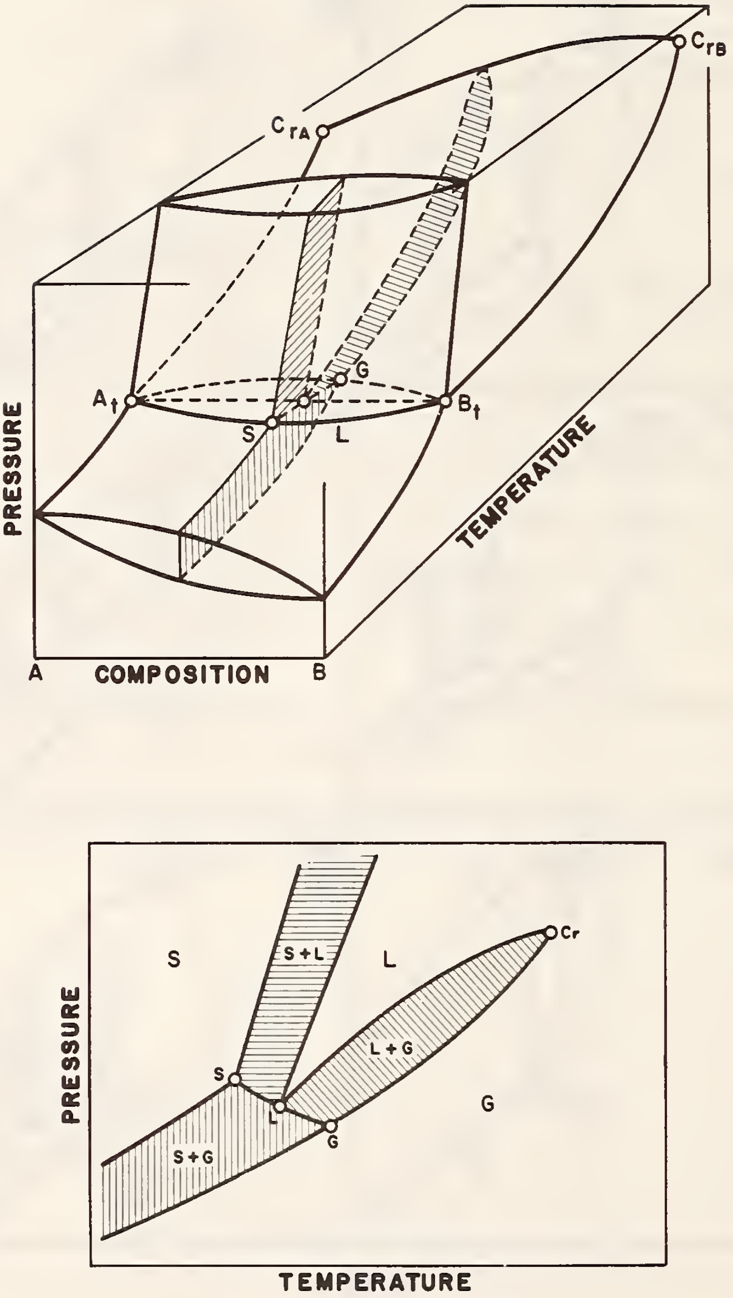


Figure 2. Three dimensional space model for a type I system and corresponding isoplethel cross section [8].

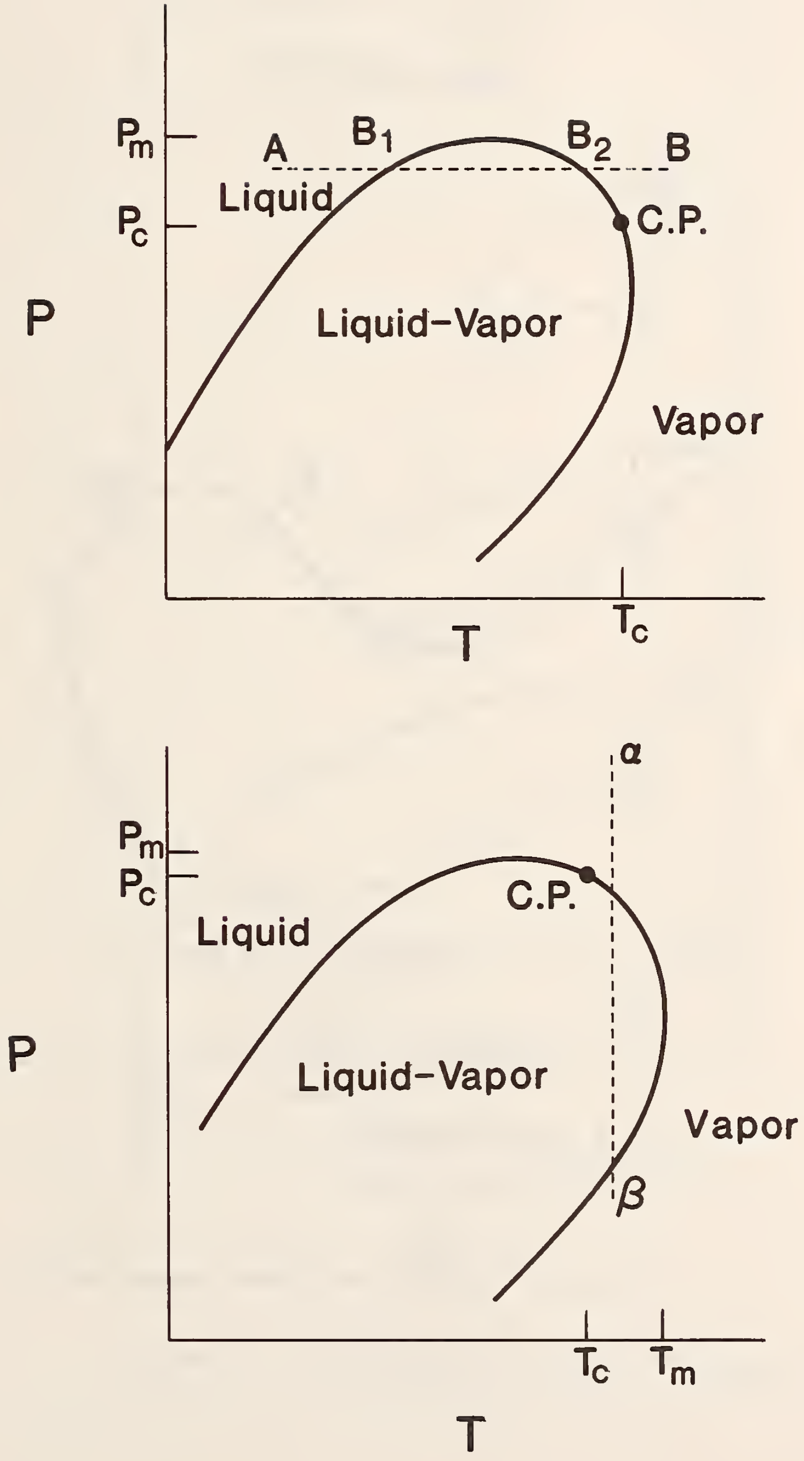


Figure 3. Retrograde vaporization (a) and condensation (b).

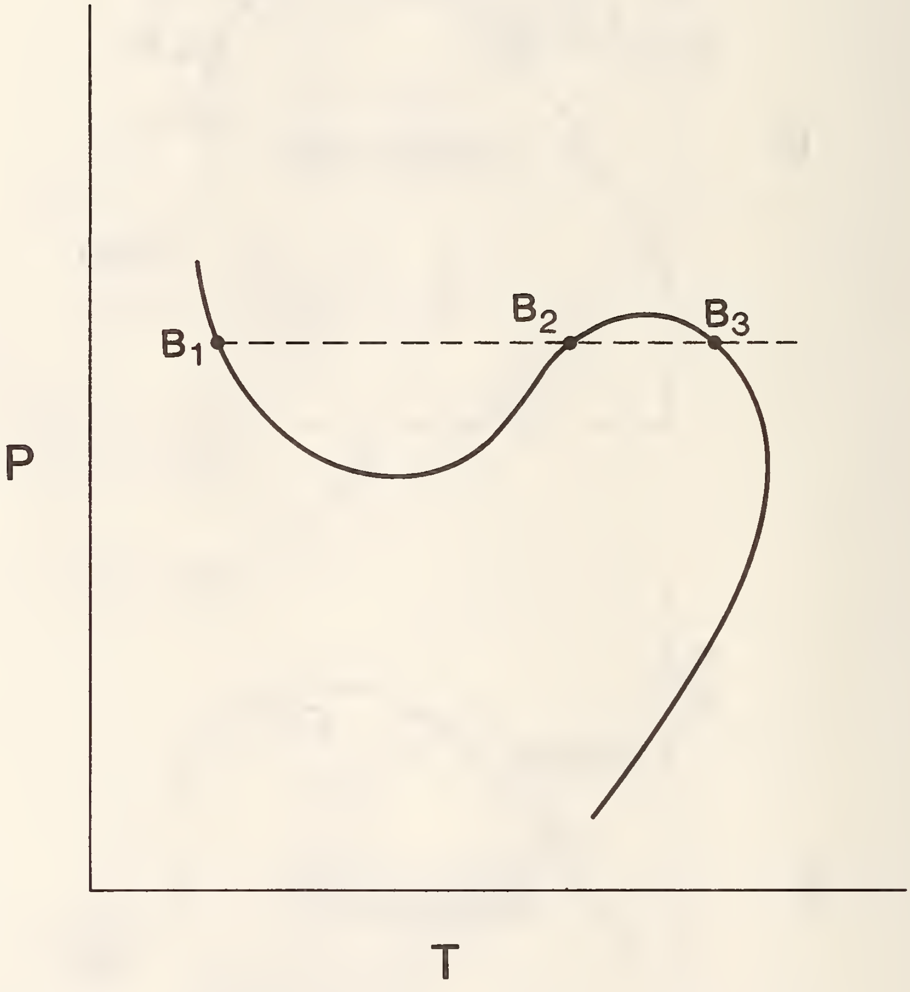


Figure 4. Double retrograde vaporization.

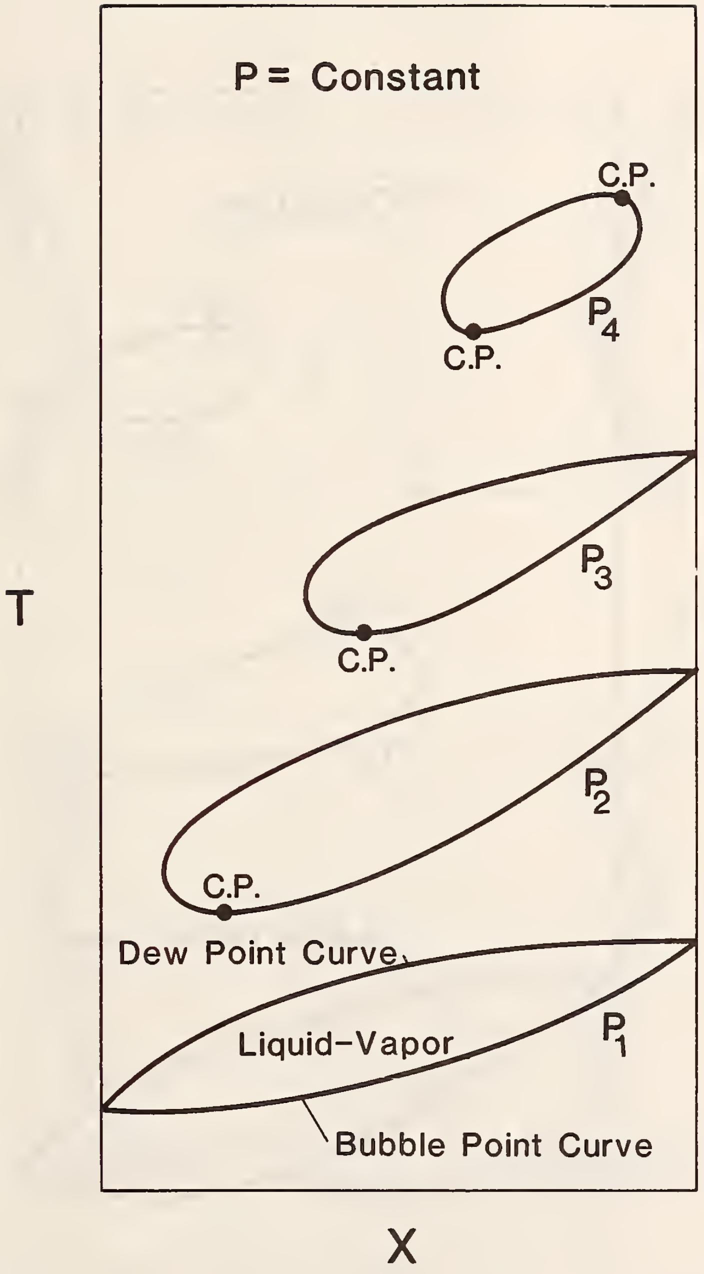


Figure 5. T-x diagram for a type I system.

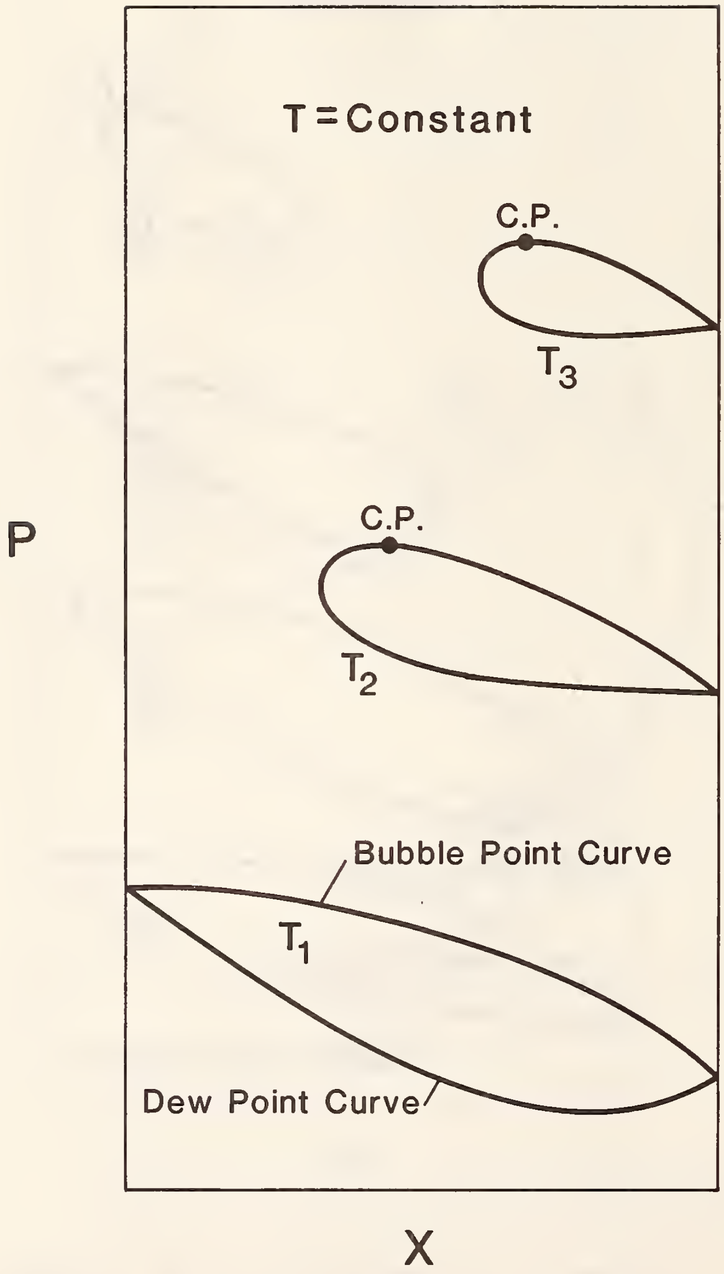


Figure 6. p-x diagram for a type I system.

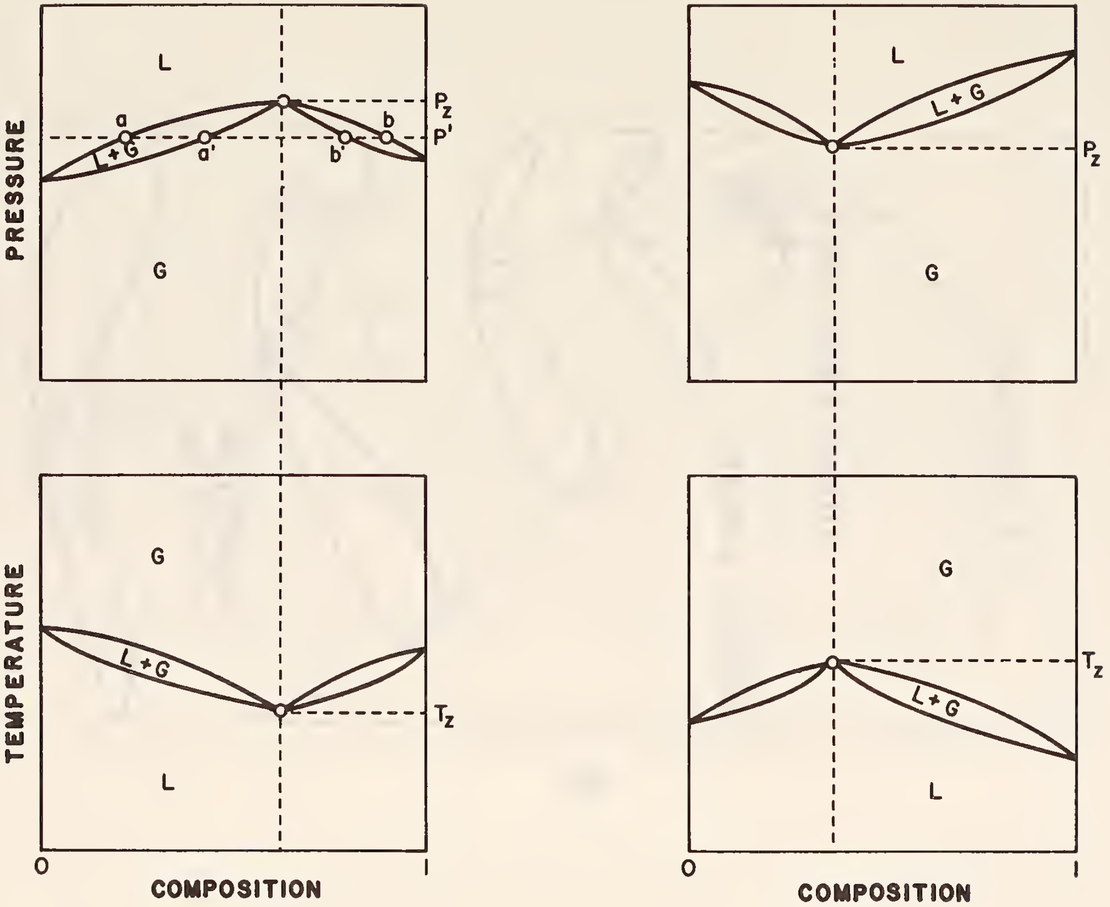


Figure 7. T-x and p-x diagrams for systems exhibiting azeotropes [8].

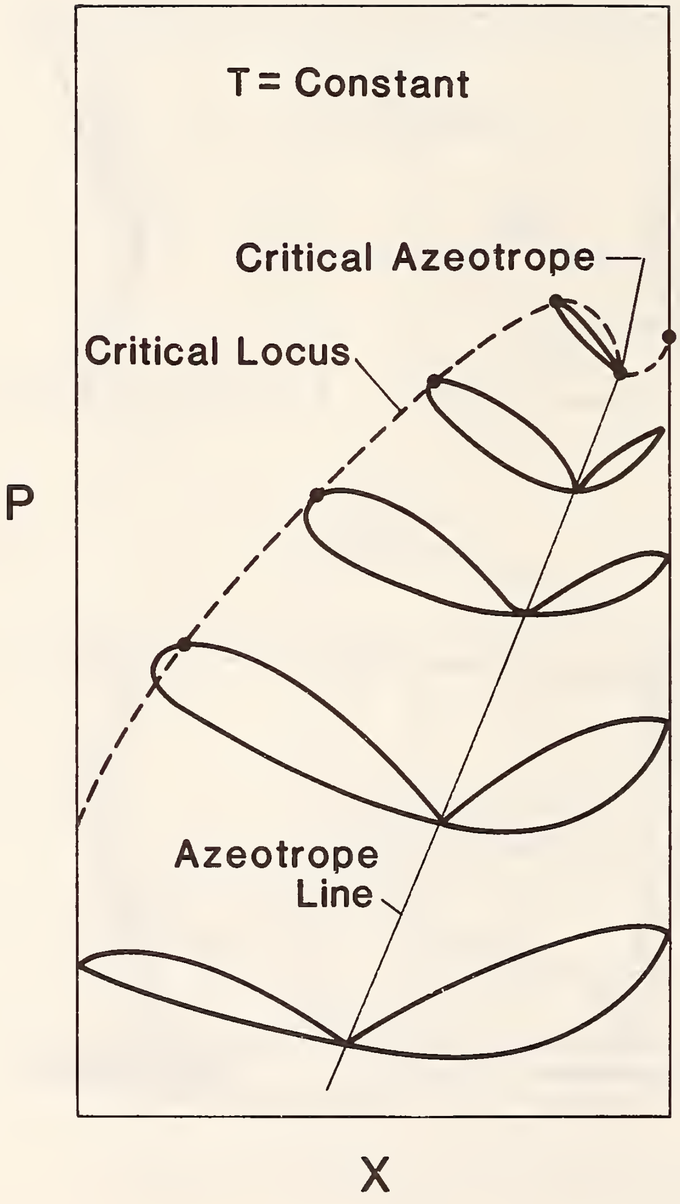


Figure 8. p-x diagram for a system exhibiting a critical azeotrope.

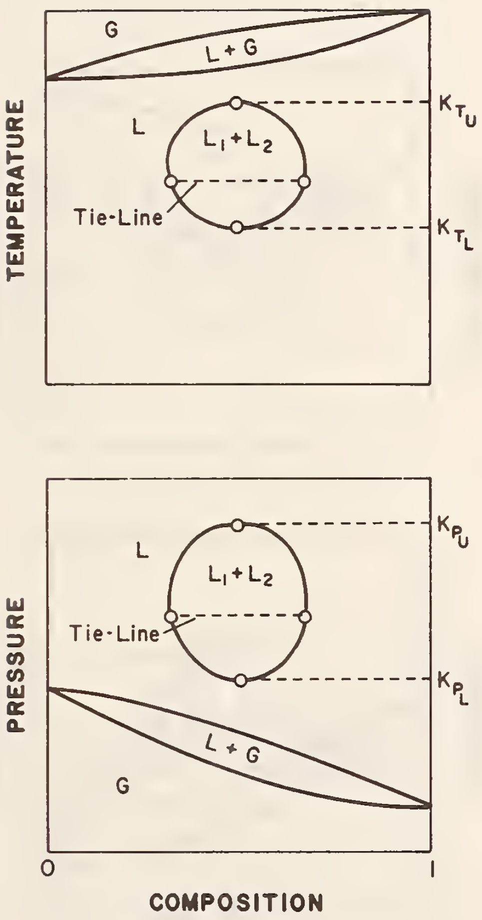


Figure 9. T-x and p-x diagrams for a system which exhibits a miscibility gap [8].

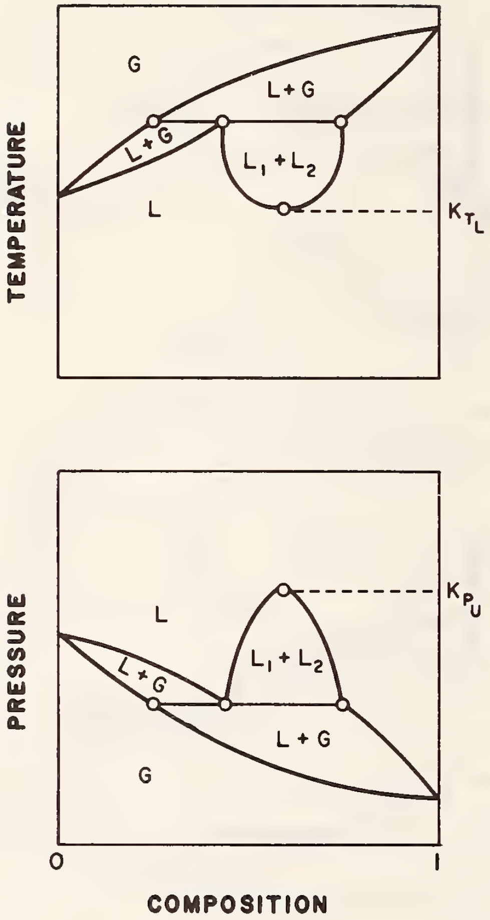


Figure 10. p-x and T-x projections for a system having an upper critical solution pressure, K_{pu} and lower critical solution temperature K_{TL} [8].

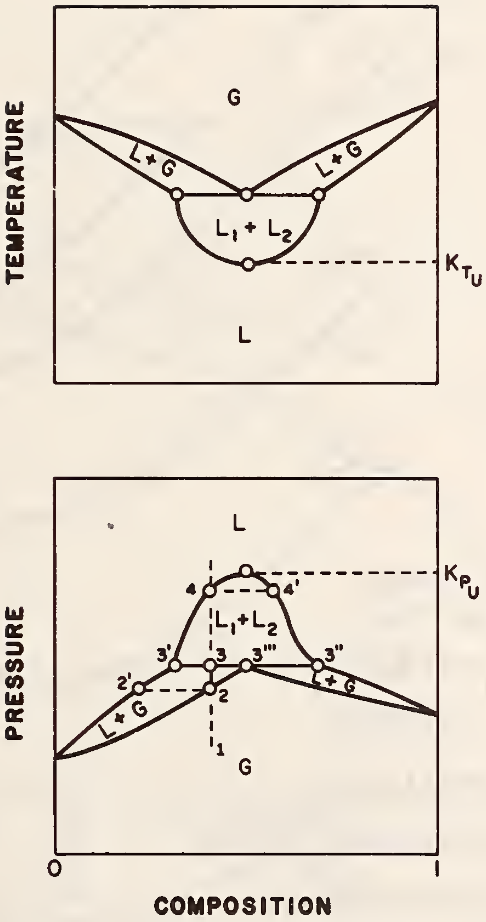


Figure 11. Azeotropic systems which also have a lower critical solution temperature K_{TL} or upper critical solution pressure K_{pu} [8].

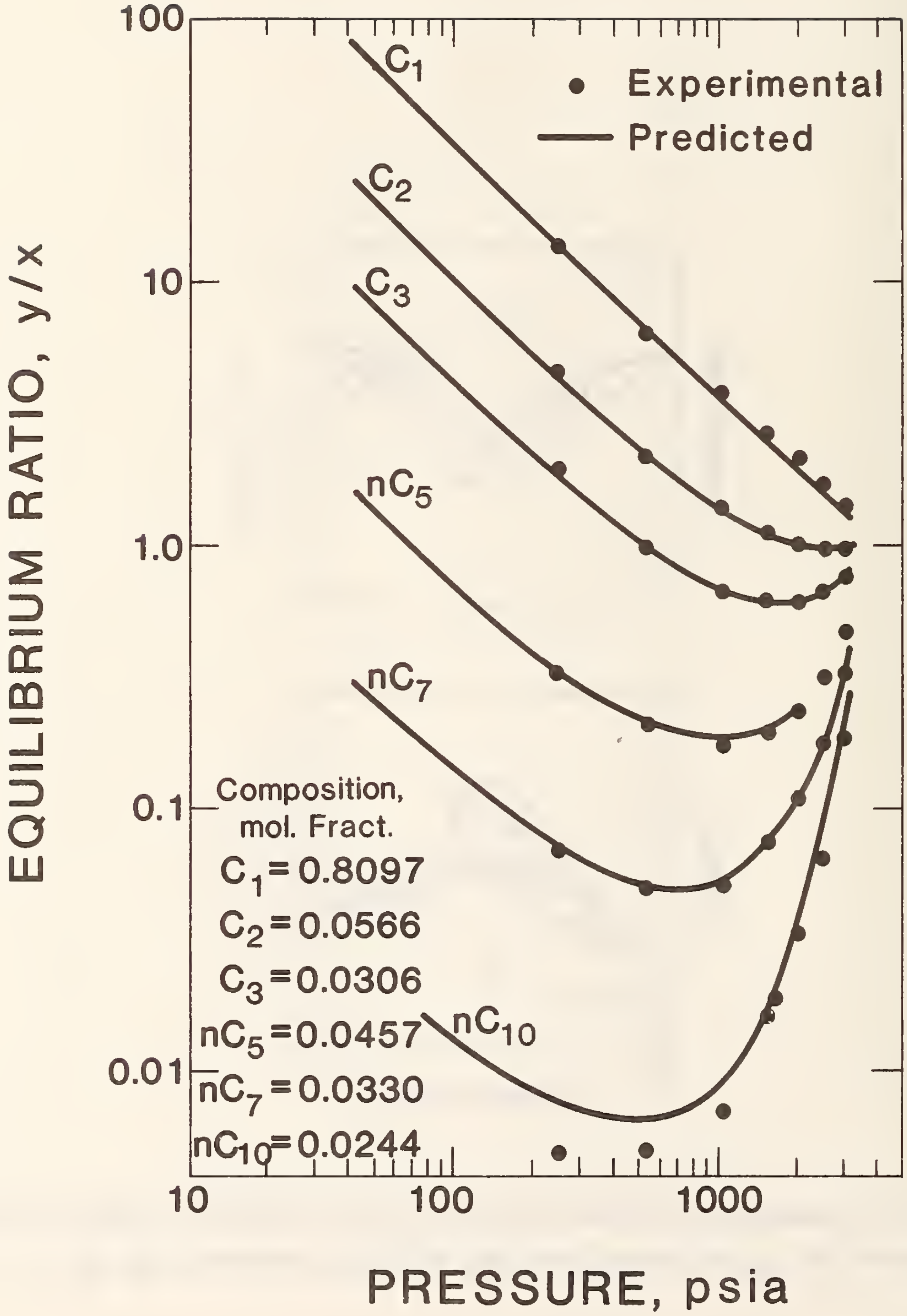


Figure 12. Comparison of Peng-Robinson predicted K values with data for a six-component mixture [32].

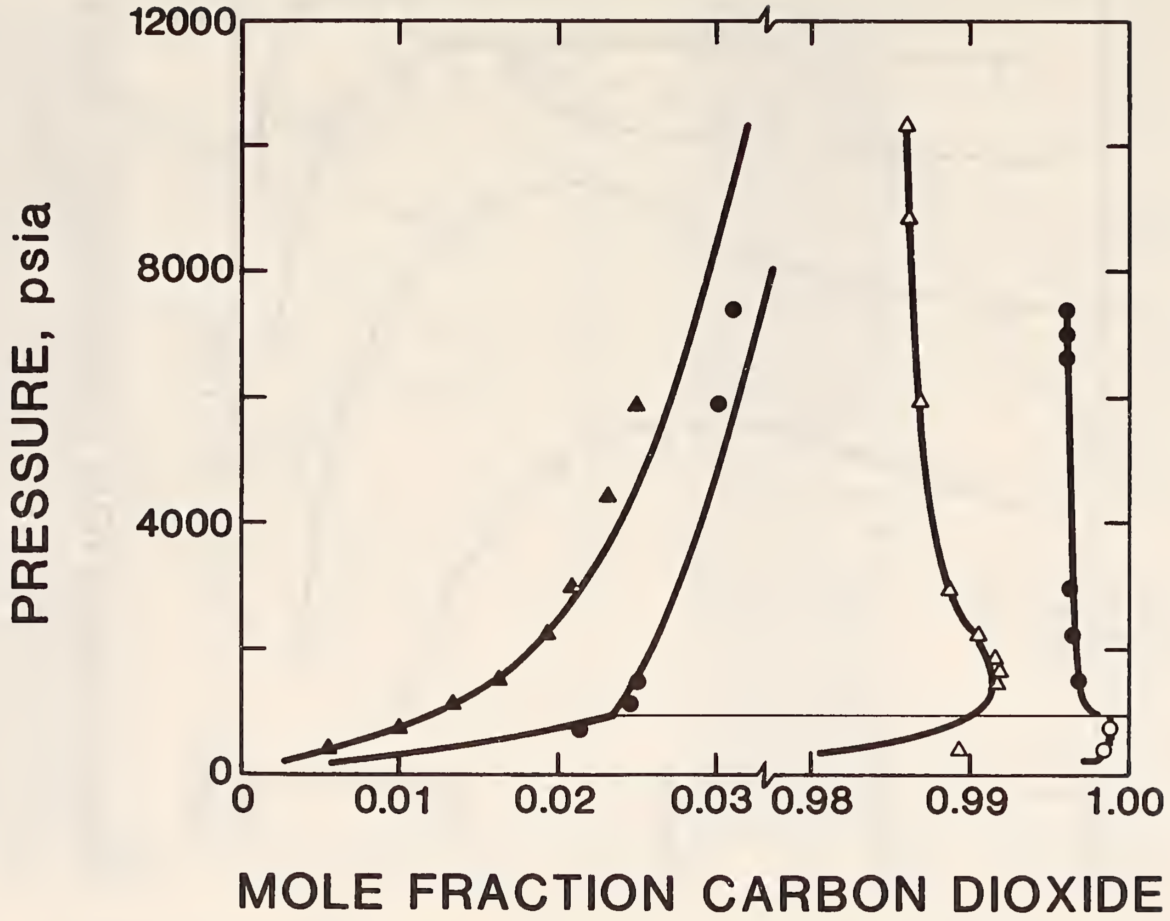


Figure 13. Comparison of calculated and experimental CO_2 solubility in water using the PRS equation of state [41]. Liquid - ▲ 167°F, ● 77°F; vapor - △ 167°F, ○ 77°F.

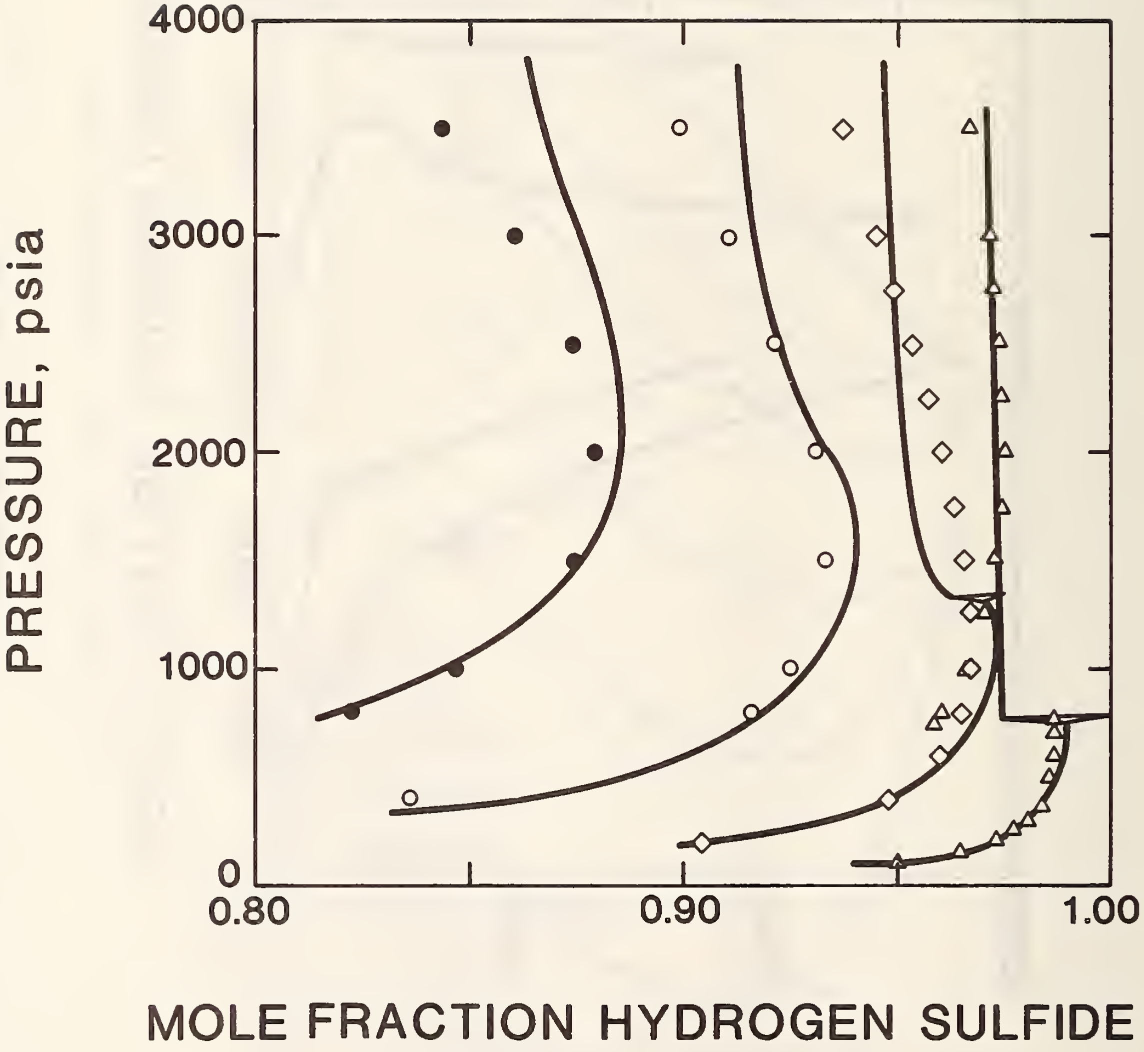


Figure 14. Comparison of the calculated and experimental solubilities of H_2S in water using the PRS equation of state [41]. ● 340°F, ○ 280°F, ◇ 220°F, △ 160°F.

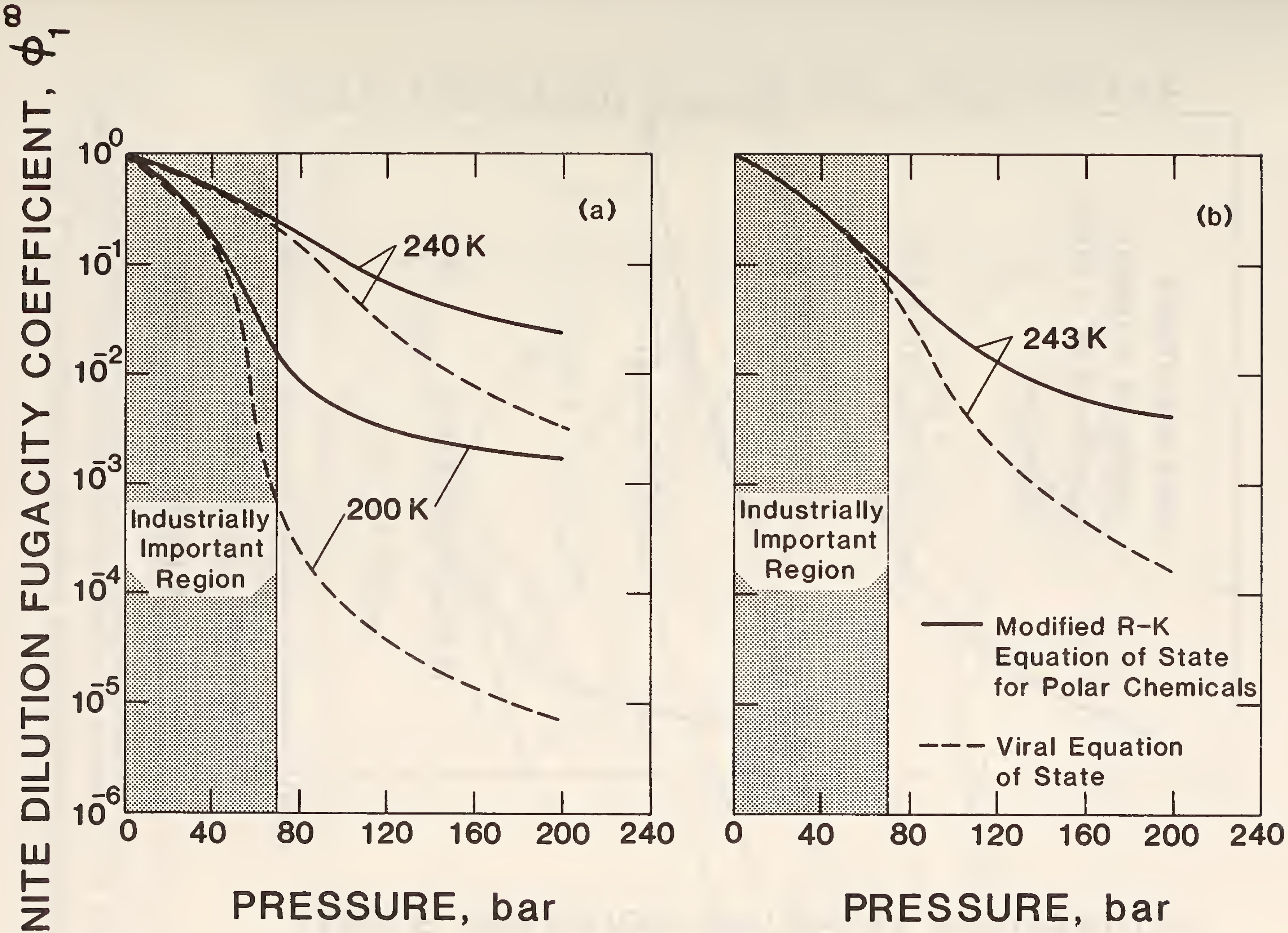


Figure 15. Comparison of infinite dilution fugacity coefficients of methanol in (a) methane and (b) methanol in a 80/20 methane/CO_2 mixture using the virial and modified RK equations of state [45].

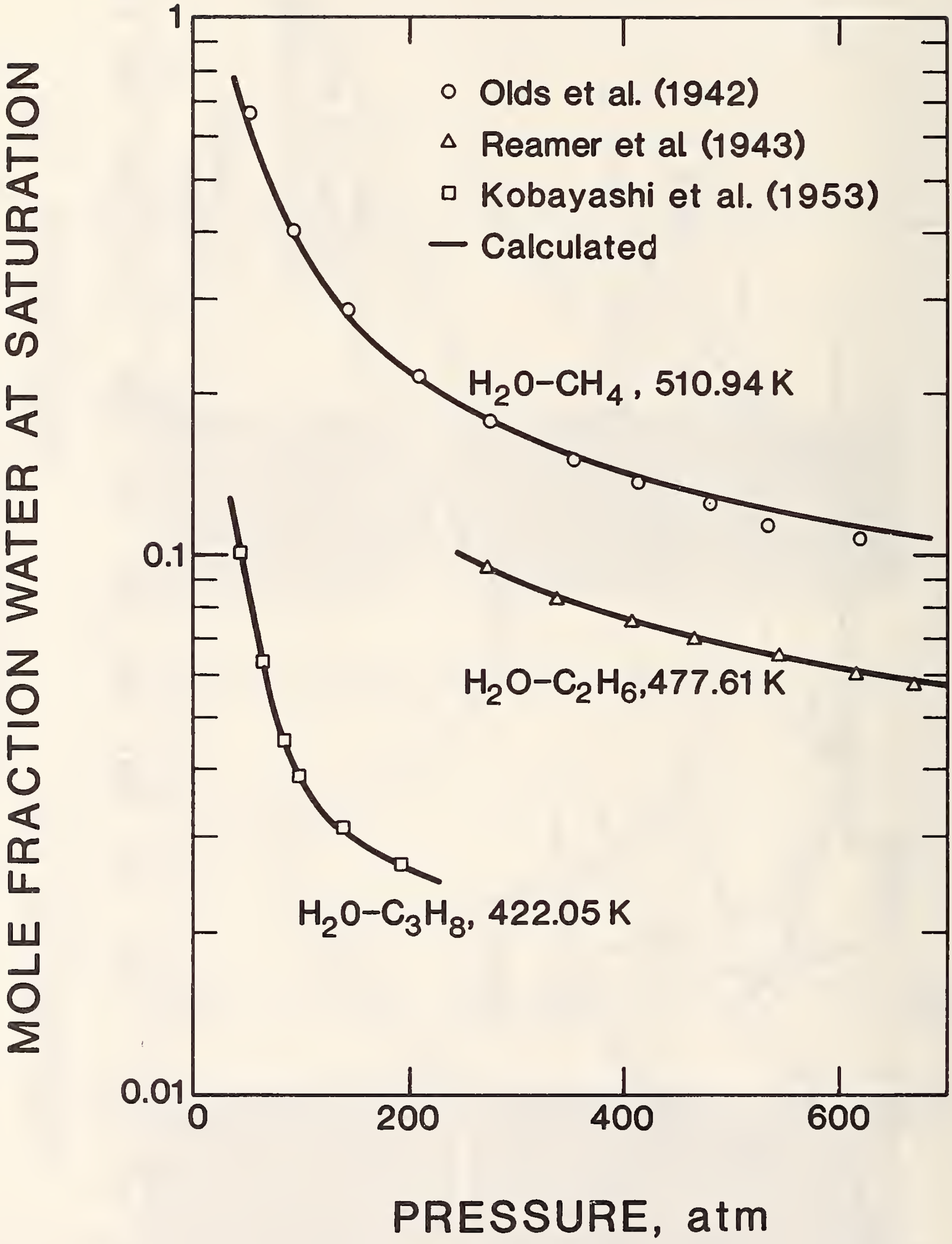


Figure 16. Comparison of calculated and experimental solubility of water in various hydrocarbons using a modified RK equation of state [44].

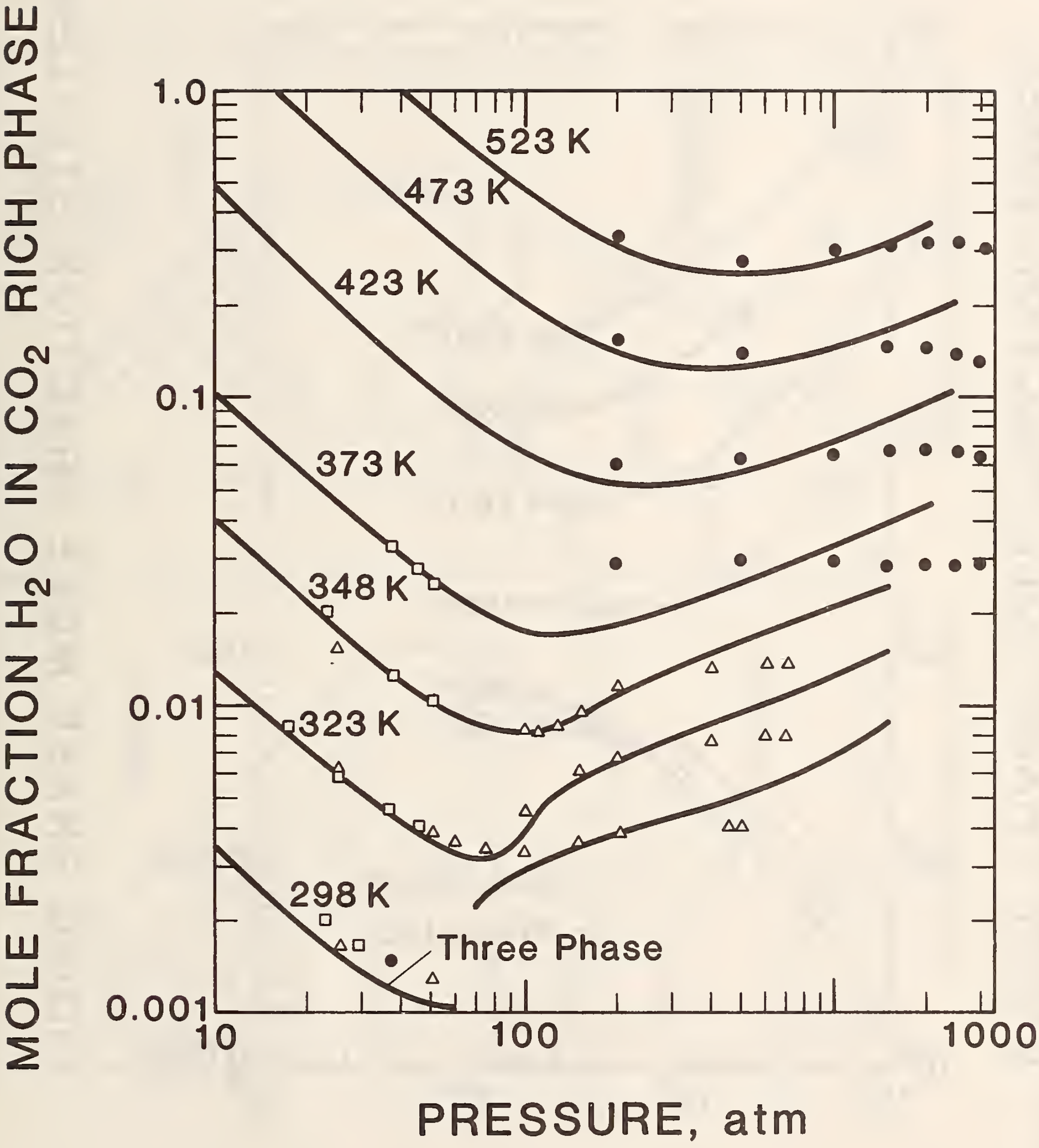


Figure 17. Comparison of calculated and experimental water solubilities in CO_2 using an interaction coefficient in the repulsive parameter of the RK equation of state [46].

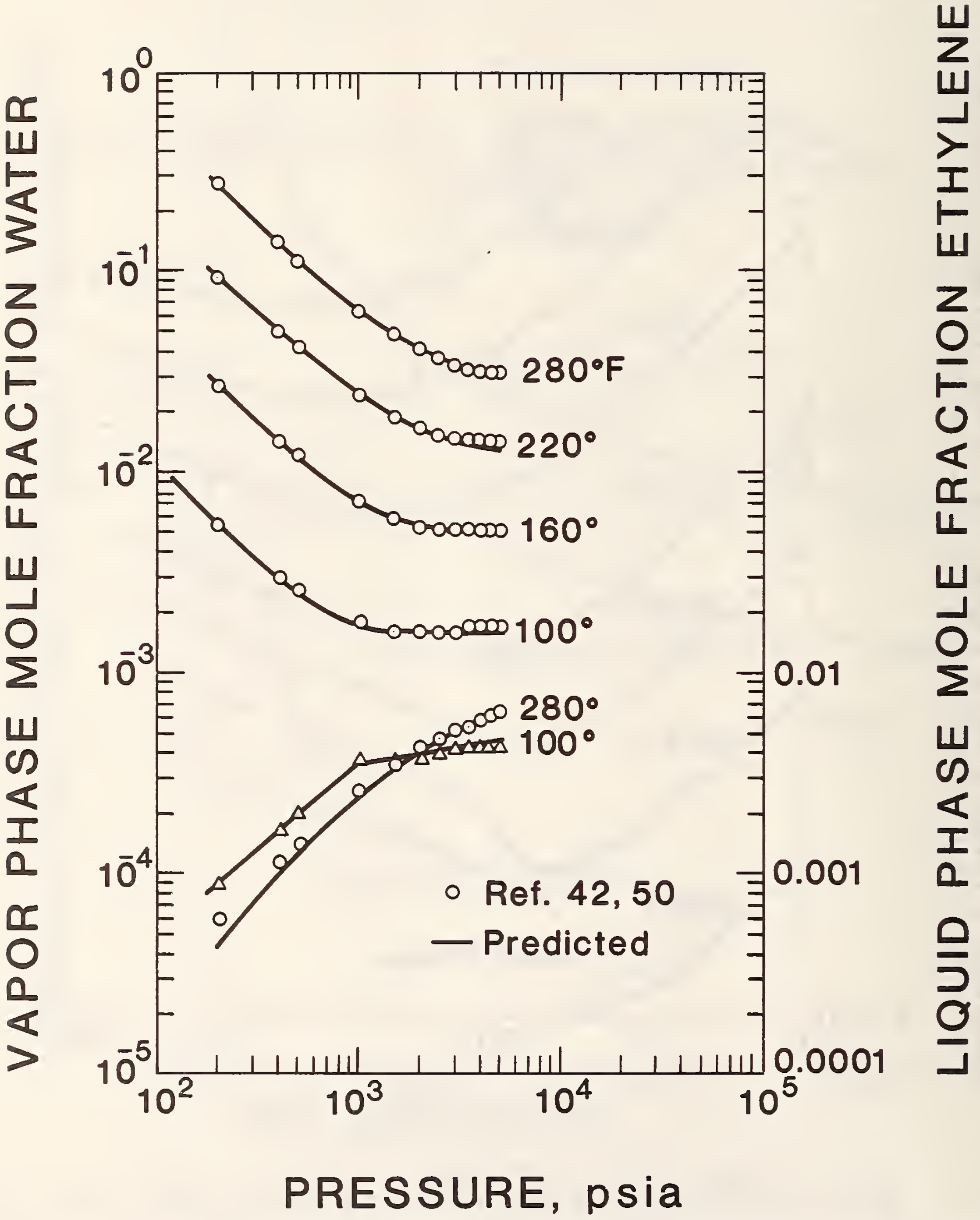


Figure 18. Comparison of calculated and experimental solubilities in the water/ethylene system using a size binary interaction coefficient in the RKS equation [47].

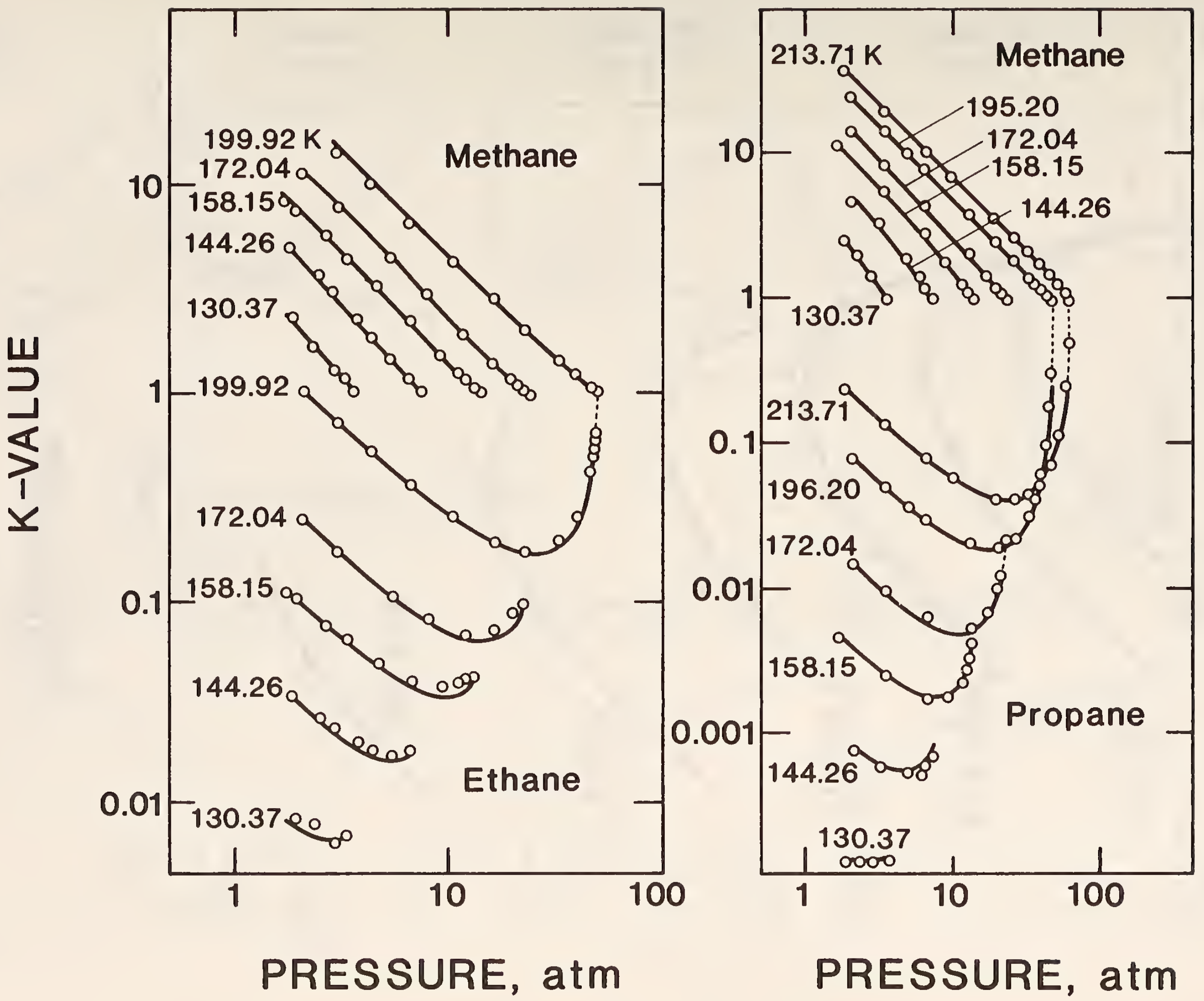


Figure 19. Comparison of calculated and experimental K-values in the methane/ethane and methane/propane systems using the conformal solution model [70].

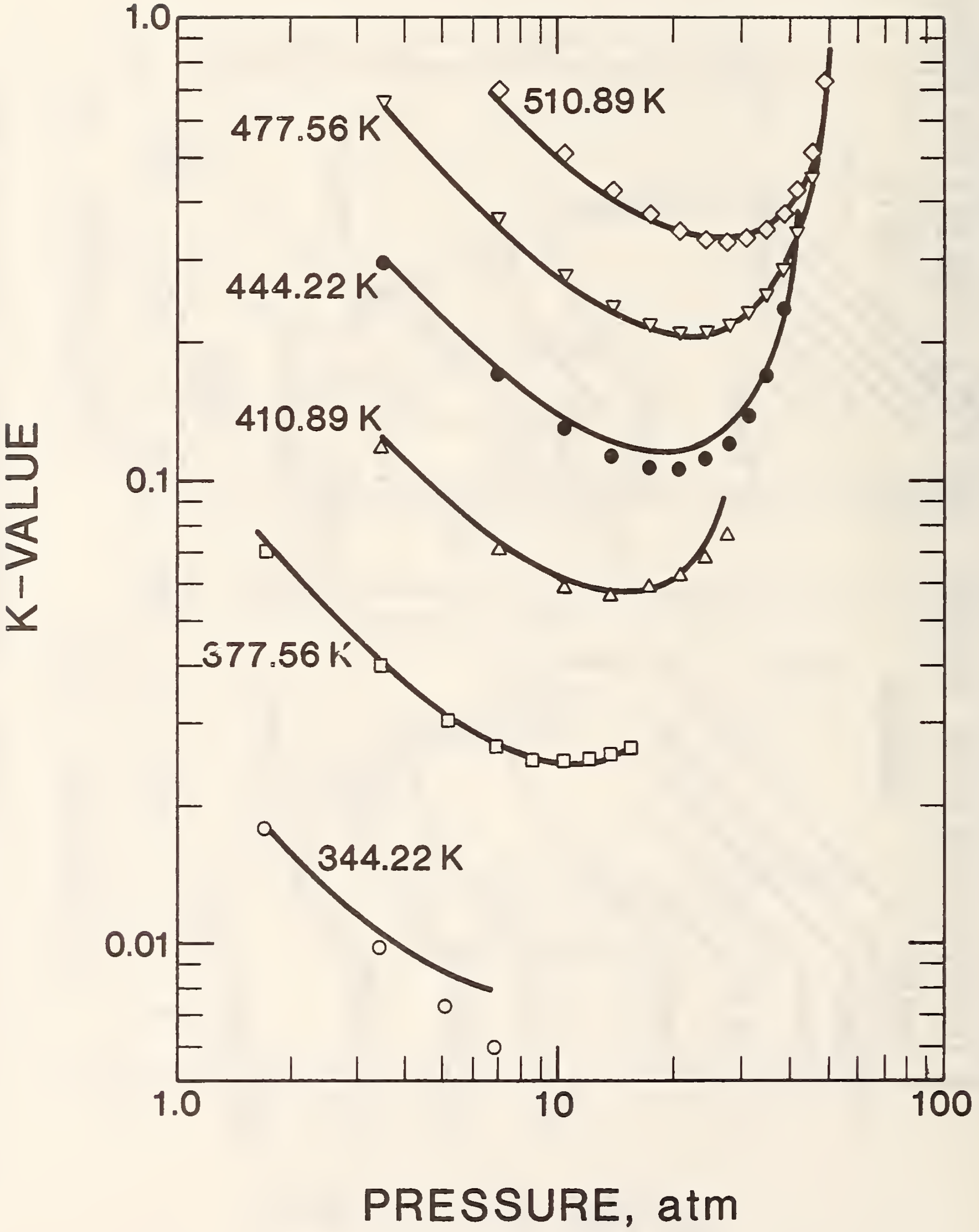


Figure 20. Comparison of calculated and experimental decane K-value in the butane/decane mixture using the conformal solution approach [69].

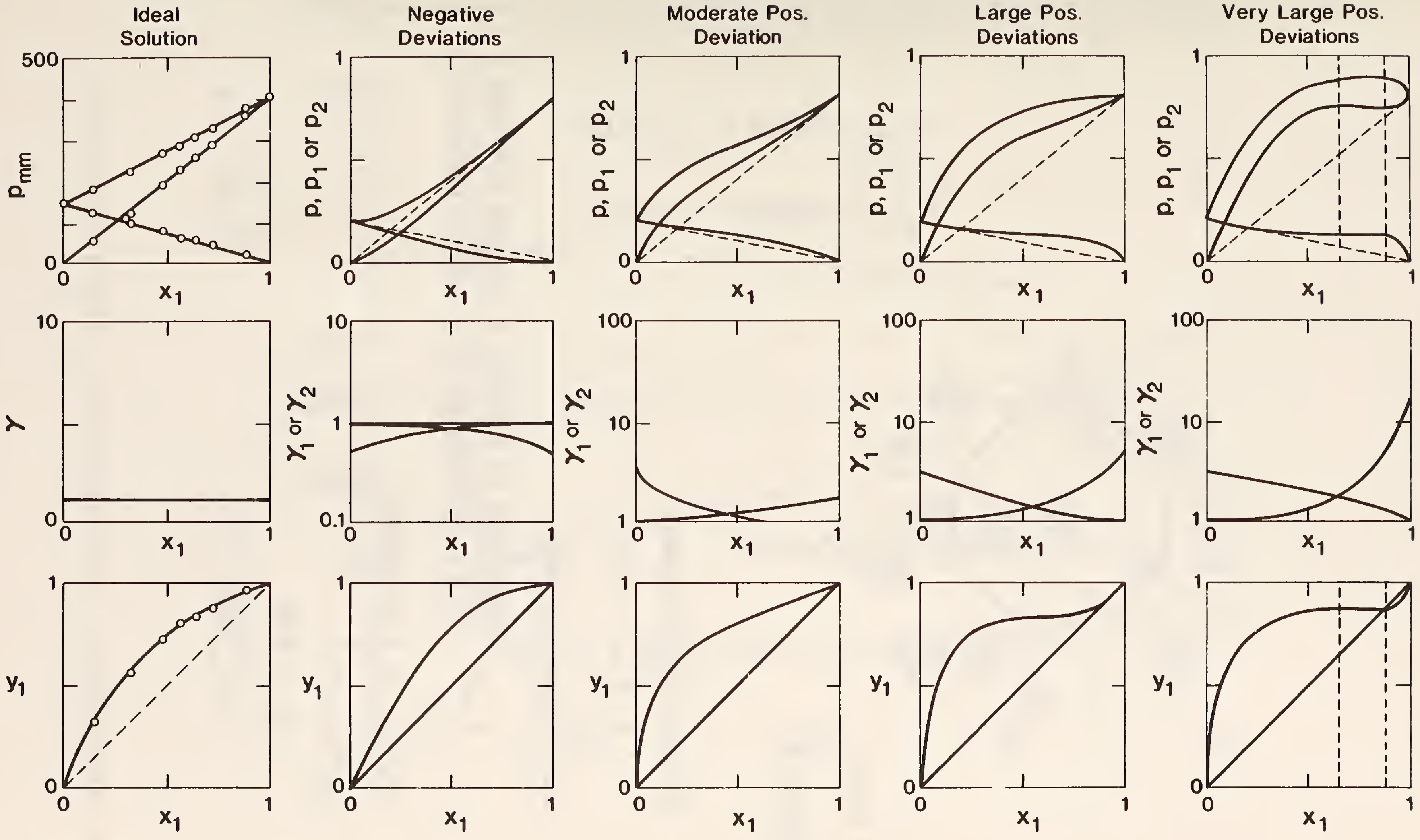
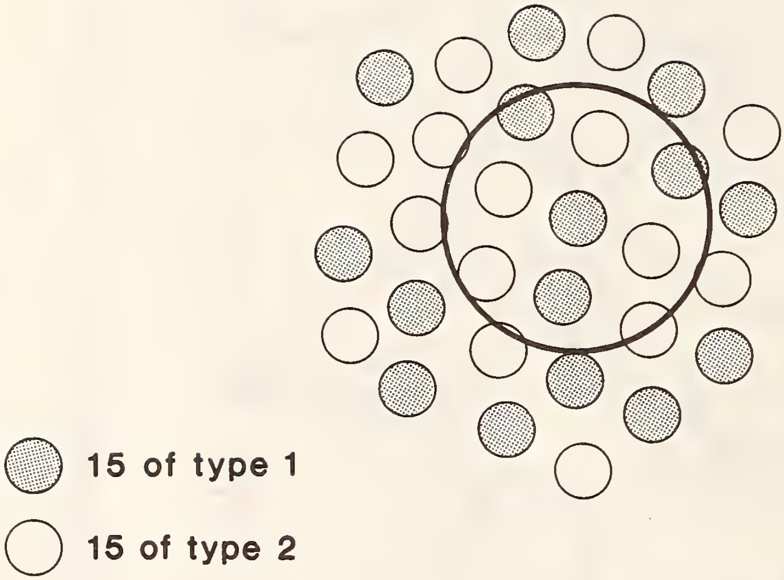


Figure 21. Illustration of different types of deviations from ideal solution behavior.



Overall mole fractions :

$$x_1 = x_2 = 1/2$$

Local mole fractions :

$$x_{21} = \frac{\text{Molecules of 2 about a central molecule 1}}{\text{Total molecules about a central molecule 1}}$$

$$x_{21} + x_{11} = 1, \text{ as shown}$$

$$x_{12} + x_{22} = 1$$

$$x_{11} \sim 3/8$$

$$x_{21} \sim 5/8$$

Figure 22. Illustration of local composition in liquid mixtures [113].

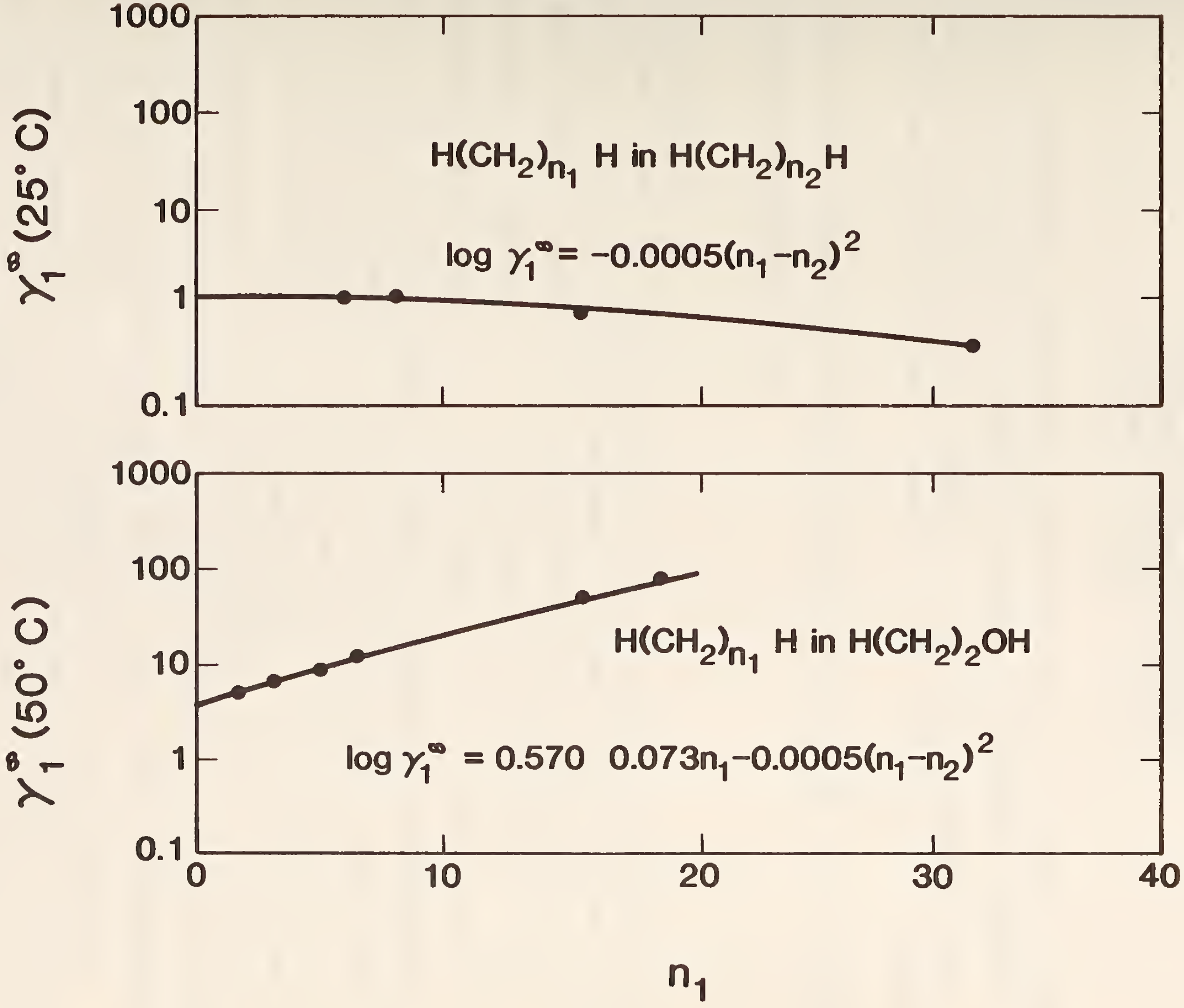


Figure 23. Infinite dilution activity coefficients in paraffin/paraffin and paraffin/n-alcohol mixtures as a function of carbon number [122].

THE EXTENDED CORRESPONDING STATES METHOD APPLIED TO THE NITROGEN-METHANE SYSTEM

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An extended corresponding states method of predicting the equation of state for the N_2-CH_4 system is reviewed. Comparisons between the predictive method and experimental PVTx data have revealed basic problems with the method. A review of this ongoing work is presented.

Key words: equation of state; extended corresponding states; mixtures; predictive methods; PVTx.

1. Introduction

Several years ago the properties of fluids group at NBS-Boulder, undertook a long range project to develop a mathematical model of the equation of state of LNG which would be capable of predicting densities given the pressure, temperature and composition of a LNG mixture. Several different models were investigated during the course of that project, each of which proved to be adequate under the limited scope of pressure, temperature and components of LNG [1]. One of the methods, the "extended corresponding states" method proved to be the most versatile and suggested the possibility of describing the equation of state of a mixture over a much broader range of pressure and temperature in a truly predictive sense. The purpose of the present work is to explore that possibility. The binary system of CH_4-N_2 was chosen as a test case because of the availability of good experimental data for that system and because the CH_4-N_2 system is one of the binary systems studied in the LNG project.

Although the work on this system is by no means complete, this paper reports the progress in that investigation to date. In order to better understand the principle of corresponding states and its evolution to the modifications being used here (there are many other modifications) a short history is given in the next section.

2. Background

Before the method can be applied to mixtures, one must understand the application of the method to pure fluids.

Van der Waals proposed the original law of corresponding states in 1881. Noticing a similarity in the shape of the PVT surfaces of many different fluids, van der Waals proposed the following:

$$f(P_r, V_r, T_v) = 0 \qquad \text{for all gases} \tag{1}$$

where

$$P_r = P/P_c \quad , \quad V_r = V/V_c \quad \text{and} \quad T_r = T/T_c \tag{2}$$

Now introduce fluid 0 and fluid 1 so that

$$\frac{P_1}{P_{c1}} = P_r = \frac{P_o}{P_{co}} \quad \text{or} \quad \frac{P_o}{P_{co}} = \frac{P_1}{P_{c1}} \quad \text{and} \quad P_o = P_1 \frac{P_{co}}{P_{c1}} \tag{3}$$

and it follows that

$$V_o = V_1 \frac{V_{co}}{V_{c1}} \quad \text{and} \quad T_o = T_1 \frac{T_{co}}{T_{c1}} \tag{4}$$

therefore if we have an equation of state for fluid 0, i.e.,

$$P_o = f(V_o, T_o)$$

then to use this equation of state for fluid 1 via the van der Waals corresponding states we may substitute into f for V_o and T_o the equations in 3 and 4

$$P_1 \frac{P_{co}}{P_{c1}} = f\left(V_1 \frac{V_{co}}{V_{c1}} \ , \ T_1 \frac{T_{co}}{T_{c1}}\right) \tag{5}$$

it follows then that

$$Z_o = Z_1 \frac{Z_{co}}{Z_{c1}} \tag{6}$$

but as $\rho \rightarrow 0$, $Z_1 \rightarrow 1$ and $Z_o \rightarrow \frac{Z_{co}}{Z_{c1}}$ which is only 1 if $Z_{co} = Z_{c1}$ therefore to insure correct ideal gas behavior one of the three original reducing parameters is eliminated by equating $Z_{co} = Z_{c1}$, i.e.,

$$Z_{co} = \frac{P_{co}V_{co}}{RT_{co}} = \frac{P_{c1}V_{c1}}{RT_{c1}} \tag{7}$$

which then may be solved for any one of the critical parameter ratios in (3) and (4).

Since critical volumes were typically the most uncertain of the critical parameters the $\frac{P_{c1}}{T_{c1}} \frac{T_{co}}{P_{co}}$ was usually substituted [2] for $\frac{V_{co}}{V_{c1}}$ which achieved the correct ideal gas limit at the expense of the critical point inaccuracy (unless Z_{co} happened to equal Z_{c1}) and reduces the number of reducing parameters required from three to two. Although this modification of the original principle improved the performance of corresponding states, significant deviations between predicted and actual PVT surfaces was observed especially between fluids with dissimilar molecular structure. The extended corresponding states principle proposed by Rowlinson and Watson [3] is an extension of the above two parameter version except that instead of eliminating the V_{co}/V_{c1}, P_{co}/P_{c1} is eliminated, i.e., from (3)

$$P_o = P_1 \frac{V_{c1}}{V_{co}} \frac{T_{co}}{T_{c1}} \tag{8}$$

which corresponds to

$$P_1 = P_o \, (h_{1,o}/f_{1,o}) \tag{9}$$

where

$$f_{1,o} = \frac{T_{c1}}{T_{co}} \, \theta(T_r V_r) \tag{10}$$

and

$$h_{1,o} = \frac{V_{c1}}{V_{co}} \, \phi(T_r, V_r) \tag{11}$$

if θ and $\phi = 1$. Then if the θ and ϕ (shape factors) are defined by the equations

$$Z_1 = Z_o \left(V_1/h_{1,o},\ T_1/f_{1,o}\right) \tag{12}$$

and

$$A_1 = f_{1,o} A_o \left(V_1/h_{1,o},\ T_1/f_{1,o}\right) - RT\ \ell n \left(h_{1,o}\right) \tag{13}$$

where Z is the compressibility factor and A is the helmholtz free energy one has two equations with two unknowns which means that an exact correspondence between two fluids (for those two properties) exists providing one knows the correct f and h.

It is interesting to note that in the early 60's a variation of this idea was used by McCarty, et al. [4] to generate PVT data for neon. In that application only one shape factor was used to modify the density so that

$$P_1 = \frac{P_o P_{c1}}{P_{co}} = P_o \left(V_1/h_{1,o},\ \frac{T_1 T_{co}}{T_{c1}}\right) \tag{14}$$

in that case models of the equation of state for nitrogen and argon were used to determine the $h_{1,o}$ which was then used to transform the nitrogen surface to the neon surface. Figure 1 illustrates that transformation function which in this case is called density ratio. The validity of the assumption that the shape factors are general between similar fluids is the key to whether or not the extended corresponding states method is truly a predictive method or not and is equally crucial to the Rowlinson definition.

The stage is now set to apply the extended corresponding states method to mixtures. If one assumes that the equation of state of a mixture of fixed composition behaves the same as that of a pure fluid then eqs (12) and (13) apply, i.e.,

$$Z_x = Z_o \left(V_x/h_{x,o},\ T_x/f_{x,o}\right) \tag{15}$$

and

$$A_x = f_{x,o} A_o \left(V_x/h_{x,o},\ T_x/f_{x,o}\right) \tag{16}$$

where the subscript x denotes the mixture and the o subscript denotes "base" fluid, and the $f_{x,o}$ and $h_{x,o}$ are defined by

$$h_{x,o} = \sum_i \sum_j x_i x_j h_{ij,o} \tag{17}$$

$$f_{x,o} h_{x,o} = \sum_i \sum_j x_i x_j f_{ij,o} h_{ij,o} \tag{18}$$

$$f_{ii,o} = f_{i,o} \tag{19}$$

$$f_{ij,o} = \xi_{ij} (f_{ii,o}, f_{jj,o})^{1/2} \tag{20}$$

$$h_{ij,o} = \eta_{ij} \left(\frac{1}{2} h_{ii,o}^{1/3} + \frac{1}{2} h_{jj,o}^{1/3} \right)^3 \tag{21}$$

The ξ_{ij} and η_{ij} are binary interaction parameters and functions of a particular binary system and the $f_{i,o}$ and $h_{i,o}$ are functions of the pure fluids only.

3. Nitrogen-Methane

As was stated earlier the main purpose of this work is to explore the possibility of using the extended corresponding states method to describe the properties of mixtures over a much broader range of pressure and temperature than was the case in the LNG project.

The starting point of this study was the extended corresponding states results of the LNG project and the PVTx experimental data by Straty and Diller [5]. Figure 2 shows the most serious deviations between calculated and experimental densities at the starting point. Even though these deviations are much greater than the accuracy of the experimental data, the comparison does produce further encouragement of eventual success of the method. The extended corresponding states equation of state for the nitrogen-methane system resulting from the LNG project, except for the methane equation of state which is a wide range equation of state for the base fluid, is based entirely on low temperature saturated liquid PVTx data. The comparison of the mixture equation of state with the Straty and Diller experimental N_2-CH_4 data then constitutes an extrapolation of the mixture parameter to much higher temperatures and lower densities.

Since there are many more variables involved in an equation of state for mixtures than there are for a pure fluid, a plan was developed to proceed from this point which would systematically investigate the effects of each variable.

Step 1. A 32 term MBWR was fit to the 50-50 composition data of Straty and Diller. This step provided a sort of yard stick for the development of the mixtures equation of state as well as a means of comparison at arbitraty P and and T.

Step 2. The binary interaction parameters ξ and η in eqs (19) and (20) were re-estimated using the Straty/Diller data. The new parameters from a least squares fit improved the performance only slightly, indicating further work.

Step 3. The $\theta(V_r, T_r)$ and $\phi(V_r, T_r)$ (eqs (10) and (11)) from the LNG project was eliminated by a direct solution of eqs (12) and (13) using the equation of state for N_2 and CH_4. This proved to be a difficult task and a completely satisfactory solution is still not in hand. A good deal of time was spent trying to find a fail safe method of solving for θ and ϕ without success. A method was found however which works enough of the time to allow a comparison to a sufficient number of experimental points to determine that very little improvement over the θ and ϕ from the LNG project was achieved.

Step 4. Step 2 was repeated using the results of step 3. The results of this exercise could be predicted to be not much different than the results of the original step 2 but the procedure was carried out anyway out of the interest of being thorough.

At this point one can conclude that the failure of the method must be a consequence of one of two things or perhaps a combination thereof. Either the theory is wrong or one or both of the equations of state used for N_2 and CH_4 are wrong. A third possibility that the experimental PVTx data are wrong is highly unlikely since the fit of the 50-50 data to the MBWR was satisfactory.

Step 5. In an attempt to discover where the method breaks down, step 4 was repeated using data of various combinations of restricted ranges of density, temperature and composition to try to determine if the binary interaction parameters exhibited a dependence of any kind. The results of this procedure are quite interesting. If one leaves all of the data below 11 mol/L at temperatures below 164 K out of the fit, the rest of the data can be represented adequately and the resulting binary interaction parameters are very nearly the same as those determined in the LNG project. This has only been observed for the 50-50 composition and further experimentation using data from the other two compositions is yet to be accomplished.

This is about where the work stands at present except for one other calculation which has been made which is of interest. Using experimental PVTx data from the region of failure as input, the mixture equation of state was solved first for a θ of CH_4 to N_2 holding ϕ constant such that the equation of state predicted the experimental PVTx exactly and then the same calculation was made with the roles of θ and ϕ reversed. The results of this calculation indicated that an error in θ is much more important than an error in ϕ. When the ϕ is held constant, a small change in ϕ (1 or 2 percent) produces an 8 percent change in density but over a 100 percent change in θ is required to achieve the same results when holding θ constant. This would indicate that the reason the method fails is a result of the theory being wrong rather than the N_2 or CH_4 equation of state because while the equations of state may easily be wrong by several percent density in the region of failure, it is highly unlikely that they are wrong in temperature by 1 or 2 percent.

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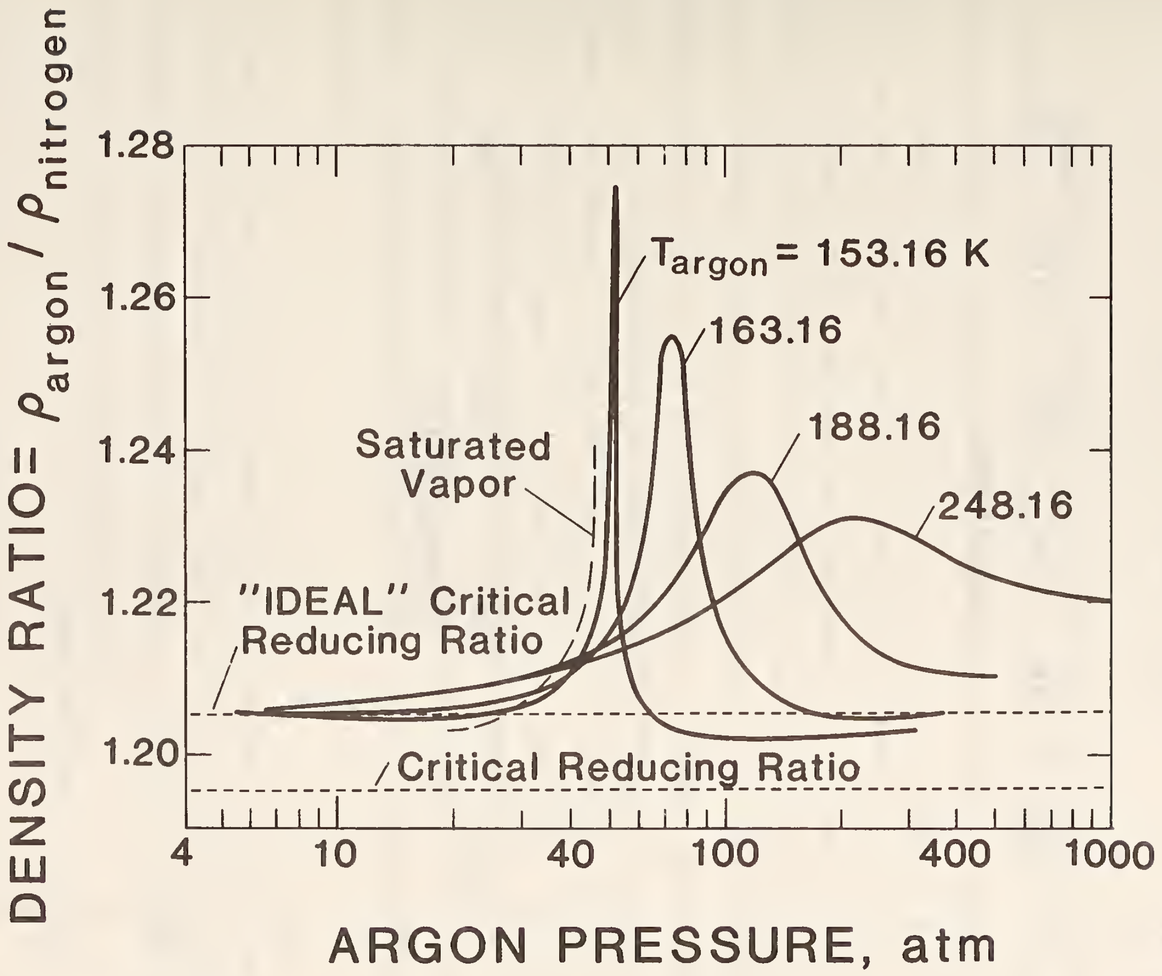

Figure 1. A plot of the transformation function necessary to produce an exact correspondence between nitrogen and argon.

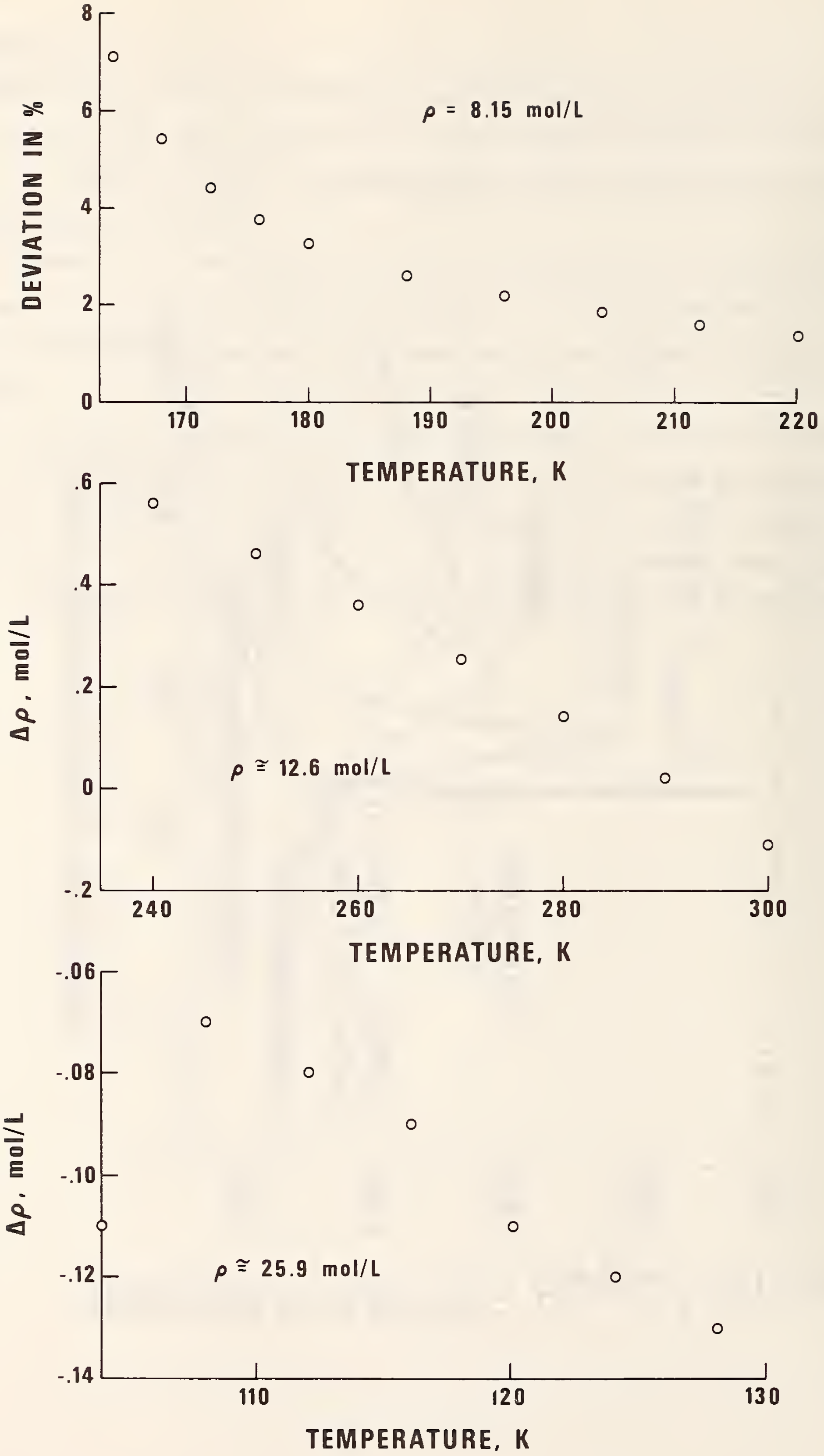

Figure 2. Maximum deviations between the N_2-CH_4 PVTx experimental data of Straty and Diller [5] and the extended corresponding states model from [1].

VAPOR-LIQUID EQUILIBRIUM OF BINARY MIXTURES NEAR THE CRITICAL LOCUS

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A new method is presented for the prediction and correlation of vapor-liquid equilibrium of binary mixtures in the critical region. The basic qualitative features of the problem are first reviewed, as well as the previous theories of Griffiths and Wheeler, Leung and Griffiths, and Moldover and Gallagher, and the concepts of field and density variables, corresponding states, and scaling-law equations of state. The Moldover-Gallagher recipe is modified by making the dependent variable of corresponding states a quadratic combination of density change and composition change across the phase boundary, rather than density change alone. The revised method is applied to the nitrogen-methane data of Bloomer and Parent. Along the locus of points twelve percent below the mixture critical temperature in suitably reduced units, the prediction of composition difference across the phase boundary is greatly improved. The revised procedure is shown not to be significantly different from that of Moldover and Gallagher for mixtures where the latter has been successful.

Key words: binary mixtures; corresponding states; critical exponents; critical line; dew-bubble curves; field variables; Leung-Griffiths procedure; nitrogen-methane VLE; quadratic coupling; scaling-law equation of state; vapor-liquid equilibrium.

1. Introduction

In the previous talk by Jim Ely [1], a wide variety of equations and techniques used in industry to predict vapor-liquid equilibrium (VLE) of mixtures was described. As Jim pointed out, these methods are not as accurate near the critical locus, i.e., within about 10 percent of the critical temperature, as they are farther away. In fact, modern theories of phase transitions predict that the "classical" equations of state commonly used in industry give incorrect critical exponents and thus have fundamental limitations in predicting thermophysical behavior near the critical locus. The talk following mine, by Brian Eaton [2], will describe methods for predicting the critical locus of a binary mixture.

My talk is intermediate in range of temperature as well as order of presentation. In the present lecture, we will not be concerned with VLE at temperatures less than about 85 percent of the critical temperature. Nor will we be concerned with prediction of the critical line itself, which we take as given. Rather, we pose the following question: Given the vapor pressure curves of the pure components and the critical line of a binary mixture, can we quantitatively predict VLE behavior over the region near the critical line, where the industrially oriented methods tend to break down?

This lecture will concentrate on a line of research, more academically oriented and less industrially oriented than the methods described in Jim Ely's lecture, which has made significant progress in answering the above question over the past decade. The research essentially began with the classification by Griffiths and Wheeler [3], in 1970, of thermodynamic variables into two kinds, density and field variables. It continued in 1973 with the prediction by Leung and Griffiths [4] of VLE of a simply behaved binary mixture, namely ^{3}He-^{4}He. Later, Moldover and Gallagher [5] modified the Leung-Griffiths method so that it could be applicable to mixtures with more complicated VLE behavior (e.g., azeotropy). The Moldover-Gallagher recipe was remarkably successful for several binary mixtures, but tended to break down for systems with large composition differences between liquid and vapor.

Most recently, I have proposed a modification of the Moldover-Gallagher method, tentatively named the "quadratic coupling recipe," to account for mixtures with large composition differences. Although the results are admittedly preliminary at present, the modified recipe appears quite promising so far. It yields significantly improved agreement between theory and experiment for the liquid-vapor composition difference of nitrogen-methane, and is rooted in plausible theoretical assumptions.

This line of research, at least since Moldover and Gallagher [5], has been intimately connected with the law of corresponding states. The lectures by Brian Eaton [2] and Bob McCarty [6] will describe the law of corresponding states in more sophistication; here we consider only its most basic form. In essence, the law characterizes an intermolecular potential by two parameters, a length scale and an energy scale. Then, so long as the potentials for different fluids have basically the same shape, the thermophysical properties of those fluids are predicted (in appropriately reduced units) to obey universal behavior. The principle is general in that it is independent of the particular shape of the potential.

Furthermore, the law of corresponding states is an essential tool for the understanding of fluid mixtures [7]. At least sufficiently far from the two-phase region, a mixture may be represented as a hypothetical pure fluid. With the appropriate mixing rules (i.e., weighted averages over the length and energy scales of the pure components), and application of the law of corresponding states, PVT properties of mixtures may be predicted accurately over a wide range of thermodynamic variables [7].

Here we consider the question of whether the law of corresponding states is useful in understanding and predicting the VLE behavior of fluid mixtures. For the sake of simplicity, we restrict the discussion to binary mixtures which are miscible in both the liquid and gaseous phases. Specifically, we ask the questions:

(1) In terms of the most commonly used physical variables, is the VLE behavior of binary mixtures even qualitatively similar to VLE of pure fluids?

(2) If the answer to (1) is negative, can a transformation of variables be made such that the VLE properties of mixtures and pure fluids are qualitatively similar?

(3) Can such a transformation be found with no appreciable difficulty in performing both the direct and inverse transformations?

(4) Can we predict which variables, both dependent and independent, "obey corresponding states" in the transformed spaces?

Our answers will be negative to (1) and positive, in a qualified and tentative way, to (2), (3) and (4).

2. VLE of Pure Fluids: Scaling Laws

We first review the basic VLE properties of pure fluids. These may be characterized by coexistence curves in the T (temperature) - ρ (density) plane as shown in figure 1, and the P (pressure) - T plane as shown in figure 2. The first figure shows the "coexistence dome" with the critical point at the point of highest temperature. The curve may be represented by [5]

$$\rho/\rho_c = 1 \pm C_1 |t|^{\beta} + C_2 t \qquad (1)$$

where

$$t = (T - T_c)/T_c \ , \qquad (2)$$

the subscript c denotes critical point value, and β is a fractional exponent. The plus refers to the more dense liquid, the minus to the less dense vapor. For any $T < T_c$, a liquid phase and a vapor phase coexist at the same temperature and pressure. C_2 is the inverse slope of the rectilinear diameter.

Figure 2 shows the VLE curve in the P-T plane, a single curve terminating at the critical point and separating the liquid phase (above) and gas phase (below). There are several possible ways to represent this curve. One method, according to the so-called scaling law equation of state, is [5,8]

$$(P/P_c)/(T/T_c) = 1 + C_3 |t|^{2-\alpha} + C_4 t + C_5 t^2 + C_6 t^3 \ . \qquad (3)$$

Here α is the exponent for the divergence of the specific heat at constant volume, C_v, along the critical isochore,

$$C_v \sim (T - T_c)^{-\alpha} \qquad (4)$$

where, typically, $\alpha \gtrsim 0.1$. In the so-called classical equations of state (van der Waals, Redlich-Kwong [9], Peng-Robinson [10], etc.), C_v does not diverge and $\alpha = 0$. However, for <u>all</u> equations of state the specific heat at constant pressure C_p diverges according to

$$C_p \sim (T - T_c)^{-\gamma} \qquad (5)$$

where, for scaling-law equations of state, $\gamma \gtrsim 1.2$, and for classical equations of state $\gamma = 1$.

The critical exponents α, β and γ have been the subject of extensive theoretical investigation [11]. They are not independent; the Rushbrooke inequality [12] becomes the following equality according to Widom's homogeneity hypothesis [13].

$$\alpha + \gamma + 2\beta = 2 \ . \qquad (6)$$

Furthermore, according to powerful renormalization group approaches [14] the three-dimensional liquid-vapor transition has been shown to be in the same universality class as the three-dimensional Ising model and should therefore have the same critical exponents. A puzzling aspect of this analysis is that fluid exponents obtained experimentally have appeared to differ from Ising exponents [11]. For example, fits to VLE data give $\beta \gtrsim 0.35$ whereas the Ising exponent is $\beta = 0.325$. However, there is recent experimental evidence that Ising exponents are obtained when one examines behavior extremely close to the critical point [11].

There are considerable differences of opinion within the physics and engineering communities on the utility and importance of scaling-law equations of state. The extreme views are, on the one hand, that PVT data in the critical region, for practical purposes, are adequately represented by classical equations of state, and, on the other hand, that the critical exponents are required to equal Ising values on theoretical grounds. We adopt the intermediate point of view that scaling-law equations of state are the most efficient means of representing thermophysical data within the critical region, but that the exponents which best fit the data need not exactly equal Ising exponents. Following Moldover and Gallagher [5], we set $\beta = 0.355$ and $\alpha = 0.1$.

Equations (1) and (3) are written in terms of reduced units. Therefore, the law of corresponding states predicts that the coefficients C_i, $i = 1,...6$, should have the same values for all fluids. Moldover and Gallagher [5] have tabulated these coefficients for a variety of pure fluid systems and find that they are indeed roughly constant from fluid to fluid, except for C_2, the inverse slope of the rectilinear diameter, and C_6. Variations in C_6 are of no fundamental significance, since that coefficient multiplies the highest order term in a truncated polynomial series.

3. V-L-E of Binary Mixtures

3.1 Qualitative Features

We now return to question (1) posed in the introduction, and acknowledge that the answer is negative. Within the most common usage, one considers a binary mixture with a fixed mole fraction x. This is clearly the most convenient point of view for experiment and is (at first) conceptually simplest although we will later maintain that, to understand fluid mixtures properly, it is better to abandon the notion that x is a fixed and given number.

If x is fixed, the VLE behavior of a mixture is qualitatively different from that of a pure fluid. Instead of the single vapor-pressure curve of figure 2 we have a dew-bubble curve of finite width, as shown in figure 3 in the P-T plane [15].

The region above the dew-bubble curve is the single-phase liquid; that below is the single-phase vapor. If, starting from the liquid, the pressure is lowered along an isotherm (vertical line), bubbles of vapor will form when point A, the bubble point, is reached. Similarly, if the pressure is raised after starting from the vapor, dew or liquid will begin to form at point B, the dew point. The locus of dew and bubble points, for all temperatures, is the dew-bubble curve (for fixed x).

Unlike a pure fluid, the dew and bubble points do not have the same pressure. Furthermore, and most significantly different from a pure fluid, in the two-phase region the compositions of the liquid and vapor are not identical. The vapor is rich in the more volatile component, the liquid rich in the less volatile component. Thus at point C in figure 3, where the bubble curve of $x_1 < x$ intersects the dew curve of $x_2 > x$, liquid of composition x_1 coexists with vapor of composition x_2.

For a "normal" (i.e., nonazeotropic) mixture [15], a family of dew-bubble curves exists as shown in figure 4. This family terminates in the vapor-pressure curves of the two pure fluids.

An alternate representation of mixture VLE is the P-x diagram as shown in figure 5 for nitrogen-methane. The solid curve is an isotherm for T less than the critical temperatures of both pure fluids. As the pressure is lowered from the bubble point to the dew point, the system passes through a series of coexisting liquids and vapors of different composition, as shown by the intersections of the horizontal lines with the solid curves. The dashed line is an isotherm for T between the two pure critical temperatures. It terminates, in a rounded manner, at some value of x less than one.

So far we have not discussed the critical point of a mixture. A mixture of fixed composition does indeed have a critical point, but its meaning and nature are somewhat different from that of a pure fluid.

In figure 4, the critical line is the envelope of the family of dew-bubble curves, and the critical point of a mixture of fixed x is the intersection of that particular dew-bubble curve with the envelope. In general, a critical point is defined as the point where the physical properties of two different, coexisting phases approach equality. The locus of critical points cannot lie inside the envelope of dew-bubble curves since at such points two phases of <u>different</u> properties coexist, in contradiction to the definition. This should not be confused with the envelope of isotherms in the P-x plot (figure 5), for T between the two pure critical temperatures. In the latter case the critical line is inside, and not identical to, the envelope. Rather, the critical line is the locus of points of highest pressure along the isotherms. The previous argument that the critical line is the envelope does not apply to the P-x plot since states with the same P and x, but different T, are not coexisting.

Note that, in contrast to pure fluids, the critical point is not necessarily the point of highest temperature of the dew-bubble curve, nor the point of highest pressure, nor even necessarily a point between those two. One may also construct a T-ρ plot for a mixture, but it does not have the symmetry of figure 1, and the point of highest temperature is again not in general the critical point.

Figure 4 shows that the two-phase region is an area of the P-T plane bounded by the critical line and the two vapor-pressure curves of the pures. At each point in this region a bubble curve of one composition intersects a dew curve of a different composition, and liquid of the former coexists with vapor of the latter. Thus each point in this region denotes a pair of coexisting states. The "liquid" is usually defined, perhaps arbitrarily, as the state of greater density.

The critical line may be represented parametrically by the critical temperature $T_c(x)$, critical pressure $P_c(x)$, and critical density $\rho_c(x)$. For T greater than $T_c(x)$ but less than the maximum temperature of the dew-bubble curve for x, the interesting phenomenon of <u>retrograde condensation</u> can occur [17]. As the pressure is lowered along an isotherm from the liquid side, the new phase which appears is of greater density than the phase continuous with the original liquid. Thus lowering the pressure causes "condensation," in contrast to the usual situation where lowering the pressure causes boiling. Retrograde condensation is a general feature of binary fluid mixtures.

In contrast to the "normal" fluid mixtures described so far, there also exist <u>azeotropic</u> fluid mixtures [15] where, along a particular locus, called the azeotrope, the compositions of liquid and vapor are identical. An example is carbon dioxide-ethane [18], where the azeotrope is approximately the line $x = 0.32$ ($x = 1$ for pure ethane).

The P-x plot for this azeotropic mixture is shown in figure 6 for $T < \min(T_c(x))$, cf. figure 5. Note that for $x < 0.32$ ethane is more volatile, whereas for $x > 0.32$ carbon dioxide is more volatile.

The P-T plot is shown in figure 7. Note that CO_2 and ethane have almost identical critical temperatures, but the critical temperature of the mixture can be significantly lower. There is no single "standard" manner by which the critical line travels from one pure critical point to the other. Its path depends on the intermolecular forces in a complicated way, and figure 8 suggests that the forces between unlike molecules are weaker than those between like molecules. However, in this lecture we make no attempt to predict the critical line; rather, that problem is considered in the following lecture [2].

The azeotrope is tangent to the critical line [15]. Figure 7 shows a case of "positive" azeotropy; "negative" azeotropy is also possible [15]. Here the P-T plane contains two separate "sheets" of the coexistence region, bounded by the azeotrope, the critical line, and the two pure vapor-pressure curves respectively. These regions overlap; in the non-overlapping areas each $\{P,T\}$ point corresponds to a pair of coexisting phases, while in the overlapping area (cf. figure 6) each point corresponds to two distinct pairs of coexisting phases. The dew-bubble curves, not shown, approach zero width at the pure curves and at the azeotrope.

More complicated phase diagrams are possible. For example, the azeotrope may terminate, or the critical line may intersect a line of liquid-liquid or even gas-gas immiscibility. We do not consider such cases here.

3.2 Field Variable and Scaling-Law Theories

It can be seen at this point that a naive application of the law of corresponding states will not work for VLE of a binary mixture. Specifically, we might represent a mixture as a hypothetical pure fluid with critical parameters $P_c(x)$, $\rho_c(x)$ and $T_c(x)$ and then determine its VLE properties from corresponding states and some chosen reference fluid. But this process would yield a pure-fluid-like vapor-pressure curve rather than a dew-bubble curve of finite width.

However, in recent years it has been shown that corresponding states can indeed be applied to VLE of mixtures if the proper <u>transformed</u> variables are used, instead of the "usual" variables P, T, ρ and x. The first step in this direction was the distinction between field variables and density variables made by Griffiths and Wheeler [3] in 1970.

According to Griffiths and Wheeler, a thermodynamic system is characterized by N intensive variables such that, if N-1 of them are given, the remaining one is determined. N = 3 for a pure fluid and N = 4 for a binary mixture. Along a phase change boundary, there exist N field variables which are continuous across the boundary, but derivatives of the field variables with respect to each other, called density variables, are discontinuous across the boundary.

For a pure fluid, one possible choice of the field variables is [3]

$$f_1 = \mu \;;\; f_2 = -P \;;\; f_3 = T \tag{7}$$

where μ is the chemical potential; the minus sign on f_2 is chosen for reasons of thermodynamic stability [3]. The first field, arbitrarily chosen, is called the "potential" in this formalism. The density variables are the partial derivatives of the potential with respect to the other fields,

$$\rho_i = \partial f_1/\partial f_{i+1},\; i = 1, \ldots N-1 \;. \tag{8}$$

In the present case

$$\rho_1 = v \;;\; \rho_2 = s \tag{9}$$

where v is the molar volume (inverse molar density) and s is the entropy per mole.

For a binary mixture one possible choice of field variables is [3]

$$f_1 = \mu_2 \;;\; f_2 = \mu_1 - \mu_2 \;;\; f_3 = -P \;;\; f_4 = T \;, \tag{10}$$

where μ_1 and μ_2 are the chemical potentials of the two components, in which case the densities are

$$\rho_1 = x \;;\; \rho_2 = v \;;\; \rho_3 = s \;. \tag{11}$$

In addition, one may transform from one set of field variables to another (linearly independent) set, i.e.,

$$f_1, \ldots f_N \rightarrow f'_1, \ldots f'_N \tag{12}$$

and the same principles apply, as long as certain stability conditions are satisfied [3].

The most important point to note here for VLE of binary mixtures is that x, the composition, is a density variable rather than a field variable. The physics of a phase change is described most simply in terms of field variables. Thus the use of x as an independent variable is not an optimal procedure.

The next step in the development of a theory of mixture VLE near the critical region was to discover an efficient choice of field variables. This was first accomplished by Leung and Griffiths [4], and later was refined by Moldover and Gallagher [5]. The original motivation of the Leung and Griffiths paper was to analyze an apparent discrepancy between the predictions of Griffiths and Wheeler [3] for divergences of specific heats near the critical point [cf. eqs (4-5)] and data in the critical region of the ^{3}He-^{4}He mixture due to Wallace and Meyer [19]. Their end result, however, was the first thermodynamic description of VLE of a binary mixture using field variables and a scaling-law equation of state, and it forms the basis for all subsequent work to date.

Leung and Griffiths [4] choose for the potential

$$\omega = P/RT \tag{13}$$

and use the transformed field variables ζ, τ and h, defined below. The potential is assumed to consist of a regular part ω_r, analytic in the field variables, and a singular part ω_s. The latter is defined according to the Schofield linear model [20], a scaling-law formalism which incorporates adjustable critical exponents.

Some aspects of the Leung-Griffiths formalism, while adequate for the ^{3}He-^{4}He mixture, are inadequate for binary mixtures in general. In particular, Leung and Griffiths do not allow for a finite slope in the rectilinear diameter. Whereas C_2, eq (1), is negligible for the heliums, it is not negligible in general. They truncate the polynomial for ω_r in a somewhat arbitrary manner and treat the coefficients as adjustable parameters rather than, as Moldover and Gallagher [5] do, quantities determined from a definite corresponding states recipe. Using a degree of freedom in the definition of ζ (see below), Leung and Griffiths impose a constraint which cannot possibly hold in general. These deficiencies were overcome in large measure by Moldover and Gallagher, and it is the latter formalism on which we focus attention.

Although x is not a field variable, it is convenient to work with a field variable which, so far as possible, corresponds to x. This variable is ζ, defined by Leung and Griffiths [4] as

$$\zeta = \frac{e^{\mu_1/RT}}{K e^{\mu_2/RT} + e^{\mu_1/RT}} \quad . \qquad (14)$$

As the mole fraction of fluid i vanishes, $\mu_i \rightarrow -\infty$. Therefore, $\zeta = 1$ for pure fluid 1($x = 0$) and $\zeta = 0$ for pure fluid 2($x = 1$). Furthermore, the constant K is arbitrary, and may be varied by changing the zero level of the chemical potentials for the separate fluids [4], a change which (classically) should not alter the final physical results.

Moldover and Gallagher presume a choice of K such that, along the critical line,

$$x = 1 - \zeta \quad . \qquad (15)$$

Equation (15) cannot hold exactly. It is, rather, the first in a series of essentially empirical assumptions. It is assumed that a K may be chosen such that eq (15) is approximately true along the entire critical line. For example, the critical line maps into a family of curves in the ζ-x plane, for different K, which all pass through [1,0] and [0,1]; we could choose the value of K such that the critical line is closest, in some least-squares sense, to eq (15). The value of K is not explicitly calculated; instead it is assumed that a K exists which has such a behavior.

This method, in effect, bypasses the explicit evaluation of the chemical potentials, which are not subject to direct experiment but must be found by integration of the equation of state, not a priori known. Leung and Griffiths [4] use this degree of freedom to make the inverse critical temperature, instead of x, linear in ζ. Such a constraint, altered in some later modifications of the method [21], is clearly inappropriate for a system like CO_2 - ethane where T_c is not a monotonic function of x.

The next field variable is t, a measure of the distance, in temperature, from the critical line (cf. eq (2)),

$$t = (T - T_c(\zeta))/T_c(\zeta) \quad . \qquad (16)$$

Here the transformation P, T, μ_1, μ_2 $\rightarrow \omega, \zeta, t, h$ is such that each new variable is defined in terms of both the old and previously defined new variables. $T_c(\zeta)$ is the critical temperature for the chosen value of ζ. Leung and Griffiths choose, instead of t,

$$\tau = (RT_c(\zeta))^{-1} - (RT)^{-1} \tag{17}$$

which has the disadvantage of not being dimensionless.

The last field variable is h, which measures the distance away from the coexistence surface,

$$h = \ell n \left(K e^{\mu_2/RT} + e^{\mu_1/RT} \right) - \ell n \left(K e^{\mu_2^\sigma(\zeta,\tau)/RT} + e^{\mu_1^\sigma(\zeta,\tau)/RT} \right) \tag{18}$$

where $\mu_i^\sigma(\zeta,\tau)$ is the value of μ_i on the coexistence surface, or its extension above the critical line [4], for the given (ζ,τ).

In the transformed space, the phase transition region has a particularly simple geometry. The critical line is the line segment $t = 0$, $h = 0$, $0 \leq \zeta \leq 1$, and the coexistence surface is the plane region $t < 0$, $h = 0$, $0 \leq \zeta \leq 1$.

The essential feature of the Moldover-Gallagher formalism [5] is to make a correspondence, for each value of ζ between 0 and 1, with a hypothetical pure fluid, and to assume the VLE properties of this hypothetical pure fluid are given by the law of corresponding states and a dual system of reference fluids (the two pure fluids) with a linear interpolation "mixing rule." In particular, the "vapor pressure" curve for a locus of fixed ζ on the coexistence surface is [cf. eq (3)],

$$PT_c(\zeta)/TP_c(\zeta) = 1 + C_3(\zeta)|t|^{1.9} + C_4(\zeta)t + C_5(\zeta)t^2 + C_6(\zeta)t^3 \tag{19}$$

and this hypothetical fluid has a coexistence dome in the T-ρ plane given by [cf. eq (1)]

$$\rho/\rho_c(\zeta) = 1 \pm C_1(\zeta)|t|^{.355} + C_2(\zeta)t \tag{20}$$

where, i = 1,...6,

$$C_i(\zeta) = C_i^{(2)} + (C_i^{(1)} - C_i^{(2)})\zeta = C_i^{(2)} + C_i'\zeta \ , \tag{21}$$

and the superscripts refer to the respective pure fluids. Note that the superscripts were incorrectly reversed in reference [5], eq (8). This error did not affect the final results of reference [5].

Figure 8 shows lines of constant ζ in the P-T plane for the nitrogen-methane system. Equations (19) and (21) predict that these lines form a nearly parallel curvilinear grid, which is an additional empirical assumption. Note that, if the two fluids obey corresponding states exactly, $C_i^{(1)} = C_i^{(2)} = C_i(\zeta)$ for all ζ. In general, $C_i(\zeta)$ is never expected to be very far from either pure fluid value.

As explained previously, each (P,T) point within the coexistence region corresponds to two coexisting phases of different densities and compositions. Thus, given ζ and t, our goal is to predict ρ_{liq}, ρ_{vap}, x_{liq} and x_{vap}. The densities are given by eq (20). Leung and Griffiths, in a lengthy analysis, have worked out the inverse transformation from the field variables to the composition. In the Moldover-Gallagher formalism [5], this transformation is

$$x = (1 - \zeta)\left\{1 - \zeta\left[\frac{\bar{Q}(\zeta,T)}{\rho} - \frac{\bar{Q}(\zeta,0)}{\rho_c} - \bar{H}(\zeta,t)\right]\right\} \tag{22}$$

where

$$\begin{aligned}\bar{Q}(\zeta,t) = {} & \frac{PT_c}{RTP_c}\,\frac{d}{d\zeta}\left(\frac{P_c}{T_c}\right) \\ & + \frac{P_c}{RT_c}\left[C_3'|t|^{1.9} + C_4't + C_5't^2 + C_6't^3\right] \\ & + \frac{P_c}{R}\,\frac{d}{d\zeta}\left(\frac{1}{T_c}\right)(1 + t)[-1.9\,C_3|t|^{0.9} + C_4 + 2C_5t + 3C_6t^3]\end{aligned} \tag{23}$$

and T_c, P_c and C_i are functions of ζ. Substitution of $\rho = \rho_{liq}$ and $\rho = \rho_{vap}$ in eq (22) yields, respectively, x_{liq} and x_{vap}.

The function $\overline{H}(\zeta,t)$ has an explicit and rather complicated definition (eqs (A3) and (A7) of reference [5]) in terms of thermodynamic derivatives. For our applications, it is assumed to be a smooth function with adjustable fitting parameters. Note that, for eq (15) to hold on the critical line,

$$\overline{H}(\zeta,0) = 0 \ . \tag{24}$$

In their first recipe, Moldover and Gallagher make the additional empirical assumption that $\overline{H} = 0$ over the entire coexistence surface, thus completing the construction of a closed recipe to predict x.

In practice, given the vapor pressure curves of the pure fluids and the mixture critical line, we seek to construct isotherms in the P-x plane, figure 5, and dew-bubble curves for fixed x, figure 3. For the former, we merely choose successive values of ζ from 0 to 1. Then, for a fixed T, the variables t, P, x_{liq} and x_{vap} are determined algebraically, yielding a series of points which describes the isotherm. Construction of dew-bubble curves is more complicated. The bubble curves are loci of constant x_{liq}, the dew curves of constant x_{vap}. To find points on these curves, we must perform a numerical root-finding search on eq (22), since direct algebraic inversion is not possible. Alternately, we could calculate x_{liq} and x_{vap} on a sufficiently fine grid of (ζ,t) points as in figure 8, and construct a complete family of dew-bubble curves by interpolation.

There are at present only a limited number of binary mixtures with accurate experimental data for the critical line; particularly scarce are those with accurate measurements of $\rho_c(x)$. Moldover and Gallagher [5,22] tested their method on four binary mixtures: ^{3}He-^{4}He (with results [22] essentially equivalent to those of Leung and Griffiths), carbon dioxide-ethane, sulfur hexafluoride-methane, and propane-octane. The method yields excellent agreement between theory and experiment for all but the last mixture. Of particular interest is the excellent VLE predictions for the azeotropic mixtures CO_2-C_2H_6 and SF_6-CH_4. As functions of commonly used thermodynamic variables the VLE surfaces of these mixtures appear to have a very complicated topological structure. However, upon transformation to field variables, application of the Moldover-Gallagher formalism, and performance of the inverse transformation, the apparently complex VLE surfaces are predicted to high accuracy (see, for example, figures 3, 4 and 6 of reference [5]).

For the normal mixture C_3H_8-C_8H_{18}, Moldover and Gallagher found significant discrepancies between theory and experiment, particularly for propane-rich mixtures. In an attempt to correct this, they proposed a second recipe where, instead of setting H = 0 for all $\{\zeta,t\}$, they assumed that

$$\overline{H}(\zeta,T) = C_H \, T_c^{-1} \, \frac{\partial T_c}{\partial x} \, t \quad , \qquad (25)$$

with T_c evaluated at $\zeta = 1 - x$.

Note that eq (24), and hence eq (15), are still valid. Moldover and Gallagher give some theoretical justification for this form in their Appendix B. The constant C_H is, in effect, an adjustable parameter and the choice $C_H = -25$

provides a best fit to the propane-octane VLE data. However, for propane-rich mixtures such a fit is still not entirely satisfactory.

3.3 The Quadratic Coupling Recipe

At this point, we seek a revised version of the Moldover-Gallagher [5] technique that incorporates the appropriate modifications for mixtures on which their methods break down, but which reduces to their methods for those mixtures where it does currently work. To do this, we first must try to decide, with the available clues, what features are held in common by mixtures on which the Moldover-Gallagher recipe does or does not work. We mention here that their methods appear also not to predict properly VLE behavior of the normal system nitrogen-methane [figure 4].

The feature most immediately evident is that systems with small composition difference between liquids and vapor phases are described accurately by the Moldover-Gallagher formalism, whereas systems with large composition differences are not. Comparing figures 5 and 6, we see that the presence of an azeotrope tends to "pinch" the VLE curves in the P-x plane, and hence makes the vapor-liquid composition difference in general smaller than that of a normal mixture. In addition, the composition difference generally becomes larger with wider dew-bubble curves. Propane-octane and nitrogen-methane both have wide dew-bubble curves, whereas those of the normal mixture ^3He-^4He happen to be very narrow.

It is illuminating to rewrite eqs (20) and (22) in terms of averages and differences of properties in the vapor and liquid phases,

$$\rho_{avg} = \rho_c(1 + C_2(\zeta)t) \tag{26}$$

$$\Delta\rho = 2\rho_c C_1(\zeta)|t|^{.355} \tag{27}$$

$$x_{avg} = (1 - \zeta)\left\{1 - \zeta\left[\frac{\bar{Q}(\zeta,t)}{2\rho_{liq}} + \frac{\bar{Q}(\zeta,t)}{2\rho_{vap}} - \frac{\bar{Q}(\zeta,0)}{\rho_c} - \bar{H}(\zeta,t)\right]\right\} \tag{28}$$

$$\Delta x = \zeta(1 - \zeta)\left[\frac{\bar{Q}(\zeta,t)}{\rho_{vap}} - \frac{\bar{Q}(\zeta,t)}{\rho_{liq}}\right] . \tag{29}$$

As stated above, the success of the Moldover-Gallagher formalism appears to depend on Δx being small. The formalism is, necessarily, a mixture of rigorous theory and empiricism, and the assumptions above $\overline{H}(\zeta,t)$ in eq (25) provide a degree of freedom in fitting experiment. Note, however, that Δx is <u>independent</u> of $\overline{H}$. Thus, if Δx is incorrectly predicted by the present Moldover-Gallagher recipe, such predictions cannot be rectified merely by variation of $\overline{H}$.

At this point we consider whether it is reasonable to assign a quantitative "size" to a phase change. In essence, a phase change means a difference in the magnitude of certain physical properties between two coexisting phases as a function of a parameter (in our case t) which measures the distance from a critical point at which such a difference disappears. With the variables used here, a pure fluid phase change is characterized by $\Delta\rho$ only, whereas for a mixture the phase change is characterized by both $\Delta\rho$ and Δx. In the limit of small t, eqs (27) and (29) give

$$\begin{aligned} \Delta x &= \zeta(1-\zeta)\Delta\rho\,\bar{Q}(\zeta,0)/\rho_c^2(\zeta) \\ &= 2C_1(\zeta)|t|^{.355}\,\zeta(1-\zeta)\,\bar{Q}(\zeta,0)/\rho_c^2(\zeta) \quad . \end{aligned} \tag{30}$$

Let us first consider two fluids which obey exactly corresponding states, so that, within the Moldover-Gallagher recipe, $C_1^{(1)} = C_1^{(2)} = C_1(\zeta)$. In reduced units, as a function of t, $\Delta\rho$ is an invariant for all mixtures but not Δx. We now conjecture that it is not $\Delta\rho$ which should be an invariant, but rather some "amount of phase change" A(t) which is restricted to be a monotonically increasing function of both $\Delta\rho$ and Δx. If this rather broad assumption is true, it follows that the Moldover-Gallagher formalism gives too large an A(t) for mixtures and hence overestimates $C_1(\zeta)$, $\Delta\rho$, and Δx. Indeed, it appears from an examination of their figures for propane-octane that Moldover and Gallagher predict dew-bubble curves and density coexistence domes which are too wide, and thereby overestimate both Δx and $\Delta\rho$.

As we have as yet no fundamental theory to determine A(t), we proceed semi-empirically and seek a simple form, with the constraint that A reduce to $\Delta\rho/\rho_c$ for the pure fluid. One possible choice would be a linear combination of $\Delta\rho$ and Δx, but since the Moldover-Gallagher recipe works very well as it stands for mixtures with small Δx, we believe a quadratic combination is more probably correct to leading order, i.e.,

$$A^2 = [(\Delta\rho)^2 + [f(\zeta)\ \Delta x]^2]/\rho_c^2 \tag{31}$$

where the small-t asymptotic behavior is implied. To leading order this is equivalent to

$$A(t) = \frac{\Delta\rho}{\rho_c}\left[1 + \frac{1}{2}\left[f(\zeta)\right]^2\left(\frac{\Delta x}{\Delta\rho}\right)^2\right] , \tag{32}$$

where $f(\zeta)$ must have dimensions of density. The simplest choice is

$$\frac{1}{2}\,[f(\zeta)]^2 = [\rho_c(\zeta)]^2 \tag{33}$$

or

$$A(t) = \frac{\Delta\rho}{\rho_c}\left[1 + [\rho_c(\zeta)]^2\left(\frac{\Delta x}{\Delta\rho}\right)^2\right] . \tag{34}$$

We assume, for mixtures whose pure components exactly obey corresponding states, that $A(t)$ is invariant for the mixture, which requires a redefinition of $C_1(\zeta)$.

$$2C_1^{(\mathrm{pure})}|\,t\,|^{.355} = 2C_1(\zeta)|\,t\,|^{.355}\left\{1 + \zeta^2(1-\zeta)^2\left[\frac{\bar{Q}(\zeta,0)}{\rho_c(\zeta)}\right]^2\right\} \tag{35}$$

or

$$C_1(\zeta) = \frac{C_1^{(\mathrm{pure})}}{1 + \zeta^2(1-\zeta)^2\left[\dfrac{\bar{Q}(\zeta,0)}{\rho_c(\zeta)}\right]^2} . \tag{36}$$

For fluids which do not exactly obey corresponding states, the natural generalization of eq (36) is

$$C_1(\zeta) = \frac{C_1^{(2)} + \zeta(C_1^{(1)} - C_1^{(2)})}{1 + \zeta^2(1-\zeta)^2\left[\dfrac{\bar{Q}(\zeta,0)}{\rho_c(\zeta)}\right]^2} . \tag{37}$$

Equation (37), together with eq (21) for $i > 1$, embodies our extension of the Moldover-Gallagher recipe which we shall call the "quadratic coupling recipe."

It is emphasized that the new formalism remains thermodynamically consistent. An examination of Appendix A of Moldover and Gallagher [5], in which thermodynamic functions are derived from an explicit potential, shows that the final results, eqs (19)-(23), retain the same form for any C_1 and C_2 which are functions of ζ alone. However, changing C_i, $i = 3,...6$, from a linear function of ζ would alter the end result, in particular eq (23).

An interesting pictorial representation of the quadratic coupling recipe is given in figure 9. We imagine, in this description, a croquet wicket which moves from left to right with increasing ζ. For the pure fluids, the plane of the wicket is perpendicular to the line of sight of a first observer, but for mixtures (of constant ζ) it is tilted at an angle θ, which we call the "angle of volatility." The first observer sees a projection of the wicket which represents $\Delta\rho$; that is, if t is the vertical distance from the apex and the wicket has an intrinsic width $w_0(t)$, then the first observer sees an apparent width of $w_0(t) \cos \theta$.

A second observer is placed on a line of sight perpendicular to that of the first observer, and sees a projection of the wicket which represents Δx, with an apparent width $w_0(t) \sin \theta$. The angle of volatility goes to zero for a pure fluid, and also for an azeotrope. Then the Pythagorean theorem leads to eq (31). The main point is that the Moldover-Gallagher recipe makes the <u>projection</u> of the wicket as seen by the first observer an invariant of the mixture, whereas the quadratic coupling recipe makes the <u>inherent</u> width of the wicket an invariant of the mixture. Our tentative answer, therefore, to question (4) posed in the introduction is that t is the independent variable, and A(t), the "amount" of phase change, is the dependent variable which, together, "obey corresponding states."

This picture might also be useful for representing the liquid-liquid immiscibility problem [23]. For vapor-liquid equilibrium of binary mixtures, $\Delta\rho$ is large and Δx is small. The inverse situation applies for liquid-liquid immiscibility; there Δx is large and, for liquids with nearly equal pure molar densities, $\Delta\rho$ is small. We could represent the latter similarly with an angle θ close to 90 degrees.

The present hypotheses go somewhat against the spirit of the description of field variable spaces by Griffiths and Wheeler [3]. Those authors note that the space of field variables in some respects resembles a conventional vector space. However, since the field variables in general have different dimensions, it is contended that no natural way exists to define orthogonality. For example, the vapor pressure curve of a pure fluid, at the critical point, picks out a definite direction in the P-T plane, but Griffiths and Wheeler [3] contend this is the only direction with physical meaning since pressure and temperature are incommensurate. By contrast, the quadratic coupling recipe is based on the assumption that a particular functional combination of change of density and change of composition behaves like the invariant length of a vector. In the following section we describe an application of the quadratic coupling recipe to nitrogen-methane. Although our results are highly preliminary, if the "amount of phase change" described above should prove to be an invariant for a wide variety of components and compositions, we would feel justified in attributing some fundamental physical significance to it.

4. Application to Nitrogen-Methane

4.1 Vapor Pressure Curves and Critical Line

We now describe the limited progress to date in testing the quadratic coupling recipe with the binary system nitrogen-methane. It is emphasized that the results at this point are highly preliminary.

Data used for VLE of nitrogen-methane was that of Bloomer and Parent [16]. In order to avoid problems matching different sets of experiments, we used data for the vapor-pressure curves of the pure components given by Bloomer and Parent, together with some additional nitrogen points generated from the fit of Dodge and Dunbar [24], which Bloomer and Parent quote below their table 3 and with which their data agree quite well.

Since Bloomer and Parent do not provide an adequate tabulation of coexisting densities of the pure components, we used for nitrogen the densities given in NBS Tech. Note 648 by Jacobsen, et al. [25], and for methane those given in NBS Tech. Note 653 by Goodwin [26]. As this work is an initial feasibility study, we did not analyze systematically the accuracy of the mixture data.

With the pure fluid density data of references [25] and [26] and standard least-squares fitting techniques, we fitted $\rho_{avg}(t)$ and $\Delta\rho(t)$ to the pure-fluid versions of eqs (26-27), and thereby determined values of C_1, C_2 and ρ_c.

Taking data such that $|t| < .25$, we found for nitrogen

$$\begin{aligned} C_1 &= 1.8365 \\ C_2 &= -.7146 \qquad (38) \\ \rho_c &= 11.20 \text{ kg-mol/m}^3 \end{aligned}$$

and for methane

$$\begin{aligned} C_1 &= 1.8330 \\ C_2 &= -.7088 \qquad (39) \\ \rho_c &= 10.14 \text{ kg-mol/m}^3 \end{aligned}$$

The critical density of nitrogen is given as 11.21 kg-mol/m^3 in reference [25], and that of methane is given as 10.000 kg-mol/m^3 in reference [26].

As pointed out by Moldover and Gallagher [5], it is not practical to determine C_3 from vapor pressure data. Rather, they infer C_3 from the equation of state correlations of Levelt Sengers, et al. [8], and find that it is close to 30 for all fluids studied. For simplicity we <u>assume</u> $C_3 = 30$ for nitrogen and methane, i.e.,

$$\frac{PT_c}{P_cT} - 30|t|^{1.9} = 1 + C_4t + C_5t^2 + C_6t^3 \qquad (40)$$

and fit the left side of eq (40), determined from the data, to a cubic polynomial in t. Our results for nitrogen are

$$\begin{aligned} C_4 &= 4.935 \\ C_5 &= -30.16 \qquad (41) \\ C_6 &= -11.22 \end{aligned}$$

and for methane are

$$\begin{aligned} C_4 &= 5.084 \\ C_5 &= -28.11 \qquad (42) \\ C_6 &= -5.85 \ . \end{aligned}$$

These results for C_i conform to the range of values listed in table 1 of Moldover and Gallagher [5].

Determination of the critical line presents some further difficulties. Bloomer and Parent [16] measure dew-bubble curves for five different compositions and tabulate a critical point for each curve. We have attempted an independent calculation of the critical line from the Bloomer-Parent data as follows. For each dew-bubble curve, we estimate visually the data point closest to the critical point. We fit a critical line (P versus T) with these data points and, at the same time, fit the chosen data point and the two closest neighboring data points to a parabola. The critical point finally chosen is that point on the parabola which has the same slope as that of the first fit to the critical line at the initially chosen data point.

We then reexamine graphically our choice of the critical point and that of Bloomer and Parent. When in doubt as to which is preferable, we elect to use the latter; however, our method appears to give a more reasonable value for the critical point at x = .5088. The values chosen are listed in table 1.

We fit $P_c(x)/T_c(x)$ and $1/T_c(x)$ to fourth order polynomials in x. Our results are

$$P_c(x)/T_c(x) \;=\; 10^{-2}\,[2.418 + 2.183x - 1.384x^2 - 0.975x^3 + 0.446x^4] \qquad (43)$$

$$1/T_c(x) \;=\; 10^{-3}\,[5.248 + 1.337x + 1.557x^2 - 0.689x^3 + 0.470x^4] \qquad (44)$$

with P_c in MPa and T_c in K.

The critical density presents additional difficulties. In fact, for application of the Moldover-Gallagher recipe it is the critical density which is least frequently known and is the greatest barrier to general use of the formalism. Bloomer and Parent [16] do not tabulate critical densities; however, in their figure 16, they show the mass (not molar) critical density to be approximately a linear function of critical temperature.

In the absence of better information, we assume that such a linear relation between critical temperature and mass density holds exactly. Mass densities for the pure components are taken from the respective NBS Tech. Notes [25,26]. The fit of mass density $\rho_{mc}(x)$ [kg/m^3] to composition then is

$$\rho_{mc}(x) \;=\; 10^2\,[1.627 + 1.159x + 0.882x^2 - 0.803x^3 + 0.273x^4] \qquad (45)$$

and the molar density is subsequently calculated as

$$\rho_c(x) = \rho_{mc}(x)/[28.0134x + 16.043 (1 - x)] \tag{46}$$

in kg-mole/m^3.

This completes the collection of input information needed for both the Moldover-Gallagher and quadratic coupling recipes. As shown in figure 8, we construct a grid of $\{\zeta,t\}$ points with steps in ζ of 0.1 and steps in t of 0.02. At each point, we calculate ρ_{liq}, ρ_{vap}, x_{liq}, and x_{vap} according to eqs (20) and (22), and the two respective recipes for $C_i(\zeta)$. We choose $\bar{H}$ to be zero throughout. These results are to be compared with the experimental VLE properties as represented by the dew-bubble curves of Bloomer and Parent [16].

4.2 Interpolation of Data

In previous studies, Leung and Griffiths [4], as well as Moldover and Gallagher [5], have employed computer graphics methods [27] in which the experimental dew-bubble curves have been a fixed part of the graphics output. Theoretical calculations of the dew-bubble curves are graphically superimposed, and the adjustable parameters are varied until a best fit (determined visually, not mathematically) is obtained.

One of our pending projects is the development of such graphics methods for the quadratic coupling recipe. For our initial study, however, we have chosen an alternate and perhaps less biased method. The grid of (ζ,t) points constructed do not coincide with the experimental dew-bubble curves. However, if we interpolate between the dew-bubble curves, we can find "experimental" values of x_{liq} and x_{vap} at any point within the coexistence region of the P-T plane. Recall that the bubble curves are loci of constant x_{liq} and the dew curves loci of constant x_{vap}.

It is difficult in general to interpolate two-dimensional curves as shown. But we can make a transformation such that, approximately, the curves become straight lines. A well-known approximate representation of the vapor pressure curve of a pure fluid is [28]

$$\log P = a T^{-1} + b \tag{47}$$

where a and b are constants. Hence, on an appropriate semilog plot, the pure-component vapor pressure curves become straight lines. Equation (46) is an approximation derived from the Clapeyron equation [28], in contrast to eq (3) which, apart from higher-order nonanalytic terms, is the form predicted by scaling-law theories [8].

Bloomer and Parent [16] demonstrate that the dew-bubble curves, plotted on a semilog graph, also appear to be linear in a region sufficiently far from the critical line. In figure 10, the dew-bubble curves for nitrogen-methane are shown on a semilog plot. So represented, they appear to be two straight lines joined by a curved segment at the top.

We first determine the equation and maximum pressure of each linear segment. Then, for each (ζ,t) or (P,T) point, the points of intersection of the constant-pressure line with the sloping dew and bubble lines are located. Finally, x_{liq} and x_{vap} are determined by an Aitken interpolation routine [29] from the four closest points of intersection (provided they all fall within the regions of linear behavior). By this approach, interpolated "experimental" values of x_{liq} on the grid points of figure 8 are generated.

4.3 Results

The differences between Δx_{INT}, the value of Δx from interpolation of the experimental data, and, respectively, Δx_{MG}, the prediction of the Moldover-Gallagher recipe [5], and Δx_{QCR}, the prediction of the quadratic coupling recipe, are tabulated in table 2.

The interpolation methods are not valid close to the critical line, as explained above, so values for all ζ are only available for $|t| \geq 0.12$. As expected from the discussion of section 3.3, the Moldover-Gallagher recipe significantly <u>overestimates</u> Δx, especially in the central part ($\zeta \overset{\sim}{>} 0.5$) of the coexistence region where the dew-bubble curves are widest.

On the other hand, the quadratic coupling recipe is in much better agreement with "experiment," particularly for the lower $|t|$ values. Significantly, there appears to be no systematic trend in the <u>sign</u> of the difference, as there is with Moldover and Gallagher. At larger $|t|$ values the agreement with experiment is not as good, but this is the region where the scaling law equations of state are expected to break down anyway [5].

The results for $|t| = 0.12$ are displayed in table 3. We emphasize that there are many sources of uncertainty in these numbers. There are uncertainties in the data itself and the critical line, as well as in the interpolation procedures. Theoretically, there are uncertainties due to the empirical assumptions made by Moldover and Gallagher [5], in particular that a value of K exists [eq (14)] such that eq (15) holds accurately, and that, with this value, lines of constant ζ are given by eq (19) or the curvilinear grid of figure 8. Therefore, an overall uncertainty of at least 0.01 in Δx is to be expected, and the agreement at this level is most satisfactory.

A similar interpolation scheme could be tried on the densities, to test the predictions of $\Delta\rho$. However, this would require a double interpolation of the experimental data, and density predictions depend very sensitively on the critical density [27] which is not accurately known here. Hence such a density analysis has not been attempted at this time.

5. Summary and Future Projects

We have described in this lecture a line of theoretical research into the VLE behavior of binary mixtures near the critical locus which is based on scaling-law equations of states and field (rather than density) variables as defined by Griffiths and Wheeler [3].

The first explicit recipe created for such prediction of VLE behavior, given the critical line and the vapor pressure equation of the pures, was that of Leung and Griffiths [4]. Their method, the foundation of subsequent work, was limited in many respects to very simply behaving binary mixtures like ^{3}He-^{4}He. It was significantly extended in range (although some empirical assumptions were incorporated) by Moldover and Gallagher [5], who were successful particularly in predicting VLE of azeotropic mixtures. Finally, we have proposed an extension of the Moldover-Gallagher recipe which shows promise of working for mixtures with large composition difference between coexisting phases, yet which alters only minutely the Moldover-Gallagher predictions for those cases where their recipe is successful.

We conclude the lecture by listing some unanswered questions and some projects for the future.

1) Although we have found very good agreement using the quadratic coupling recipe for Δx of nitrogen-methane at $|t| = 0.12$, roughly the limit of the range where scaling laws are expected to hold, we have not demonstrated comparable agreement for values of $|t|$ between 0.12 and the critical line. This is probably best verified by a computer graphics method as described in section 4.2, and may require minor adjustments in the critical line, particularly $\rho_c(x)$. Checks of coexisting <u>density</u> predictions should be made by the same method.

2) The formalism incorporates certain empirical assumptions about ζ, which is a function of the chemical potentials, and bypasses explicit calculation of those chemical potentials. Certain classical equations of state described in Jim Ely's lecture [1], while yielding incorrect critical exponents, show a certain limited degree of quantitative success in predicting VLE near the critical line, and one of these, the Peng-Robinson equation [10], provides an explicit algebraic form for the chemical potential. Thus it would be instructive to use the Peng-Robinson equation in conjunction with the present methods. Explicit variation of the parameter K in the definition of ζ can be used to test the self-consistency of our empirical assumptions.

3) While our method predicts Δx well, it fails rather poorly in the prediction of x_{avg} (for $\bar{H} = 0$). As explained in section 3.3, this can be remedied by changing $\bar{H}$; however, the second Moldover-Gallagher recipe [eq (25)] might not, at this stage, remain optimal. As recommended in Appendix B of Moldover and Gallagher, classical equations of state can also be studied to help select an appropriate general model for $\bar{H}(\zeta,t)$.

4) To demonstrate the general validity of our recipe we must, of course, test it on a variety of different mixtures, not only nitrogen-methane. The logical choice of a second system is propane-octane. Good data is available and that mixture is an example which is of particular present interest to our group, as it contains molecules of widely disparate sizes.

The most frequent limitation to use of the method is the absence of accurate data for $\rho_c(x)$. In this context, we expect that the techniques described by Brian Eaton [2] in the following lecture should prove helpful. If $T_c(x)$ and $P_c(x)$, but not $\rho_c(x)$, are known accurately, it may be possible to determine $\rho_c(x)$ theoretically from the equation of state with parameters which best fit T_c and P_c, and use the theoretically calculated $\rho_c(x)$ as input.

5) Although we have restricted our discussion to prediction of the coexistence surface, the Leung-Griffiths formalism, in principle, predicts an equation of state for the entire region (one-phase and two-phase) around the critical line. In fact, such predictions have been used and compared with experiment for ^{3}He-^{4}He by Doiron, Behringer and Meyer [30].

It is of interest to predict similarly an equation of state for the entire critical region according to the Moldover-Gallagher and quadratic coupling recipes. A note of caution must be made, however [27]. For $C_2 \neq 0$ in eq (1), the Moldover-Gallagher formalism singles out the supercritical extension of the rectilinear diameter as a special direction. It appears more appropriate to single out the critical isochore as a special direction, so the formalism should by some means be revised accordlingly. Some ideas for doing this are suggested in the recent review by Moldover [31].

6) An important unresolved problem in the theory of fluids is the proper matching of equations of state valid inside the critical region with those outside it. For pure fluids, Goodwin's equation of state [32] is designed to predict PVT properties both within and outside the critical region. However, Goodwin's method has thus far never been applied to mixtures. It would be interesting to reformulate the Goodwin equation of state in terms of field variables and perhaps thereby obtain an equation of state for mixtures valid over the entire range of fluid thermodynamic variables.

7) Finally, fundamental theories of phase changes should be examined with the hope of shedding light on the "amount of phase change" A(t) defined in section 3.3. As stated earlier, use of this function appears to violate the "orthodox" view of field variable vector spaces, namely that field on density variables of differing dimensions cannot be added in a meaningful way. But if A(t) is seen empirically to be an invariant for a wide variety of mixtures, this will be sufficient motivation to search for its fundamental significance, and hopefully thereby add to our basic understanding of phase transitions.

Note added March 1982: Since the original presentation of this lecture in October 1980, the author and Mike Moldover have made significant progress in achieving some of the goals listed above. This progress [33] is briefly summarized:

We have developed an efficient minicomputer program and graphics routine which calculates and plots several dew-bubble curves or constant-composition temperature-density curves per minute, over the range $-0.1 \leq t \leq 0$. When our method is applied to the nitrogen-methane data of Bloomer and Parent [16], excellent agreement is obtained between experiment and theory with $C_H = -8$ [eq (25)] for the dew-bubble curves. The temperature-density curves do not fit well if we retain the previous assumption that the mass density is linear in temperature along the critical line. However, variation of the T-ρ critical line, in the direction of higher critical densities, leads to excellent agreement with experiment in the T-ρ plane without degrading the fit in the P-T plane. We believe that, by analogy with pure fluids, such a fitting procedure may prove to be a superior means of determining $\rho_C(x)$ than direct experimental measurement (cf. eq (39) and ρ_C from reference [26]).

We find also that a linear coupling recipe works as well as, and perhaps better than, the present quadratic coupling recipe. The linear coupling method replaces eq (34) is by

$$A = |\Delta\rho|/\rho_C + C_X|\Delta x| \tag{48}$$

and modifies eqs (36)-(37) accordingly, where C_X is an adjustable parameter. The best fit to nitrogen-methane VLE data in the linear coupling model occurs for $C_H = -6$, $C_X = 0.3$.

We also have constructed a very good fit to the n-butane-octane data of Kay, et al. [34] with the additional feature that C_H can depend linearly on ζ. The optimal fitting parameters for n-butane-octane are $C_X = 0.3$ and $C_H = -12 (1 - 1.3\,\zeta)$. At present it is not clear whether the linear or quadratic coupling model is superior in general.

The present (quadratic) theory has also been applied by Al-Sahhaf [35] to a variety of binary mixtures and with a mixed record of success. Al-Sahhaf has analyzed the same systems with the Peng-Robinson equation [10] and has compared our method with that of Peng and Robinson. The author thanks Dendy Sloan and Taher Al-Sahhaf for many helpful discussions concerning their work.

6. Acknowledgments

This work would not have been possible without the research and guidance of Mike Moldover, with whom the author acknowledges an ongoing collaboration. The author thanks Mike for his encouragement and patient elucidation of the principles of phase transitions. He thanks Hal Raveché and the staff of the Thermophysics Division, National Bureau of Standards, Washington, DC for their hospitality during the author's visit in 1979, when this work was commenced. Finally, he thanks Howard Hanley and the staff of the Thermophysical Properties Division for numerous valuable suggestions.

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Table 1. Critical Line for Nitrogen-Methane

x	T_c (K)	P_c (MPa)
0.0000	190.555	4.608
0.1002	185.09	4.861
0.2879	174.21	5.068
0.5088	159.21	4.888
0.6970	146.93	4.482
0.8422	136.87	3.985
1.0000	126.22	3.394

Table 2. Predicted Deviations in Δx

Upper Entry: $\Delta x_{MG} - \Delta x_{INT}$

Lower Entry: $\Delta x_{QCR} - \Delta x_{INT}$

ζ	t =	.12	.14	.16	.18
.1		.0124	.0108	.0084	.0058
		.0105	.0083	.0051	.0013
.2		.0314	.0124	.0108	.0095
		.0013	-.0037	-.0105	-.0186
.3		.0233	.0247	.0269	.0310
		-.0069	-.0151	-.0250	-.0369
.4		.0387	.0448	.0524	.0631
		-.0099	-.0184	-.0293	-.0426
.5		.0482	.0593	.0731	.0901
		-.0099	-.0159	-.0236	-.0342
.6		.0484	.0634	.0807	.1015
		-.0049	-.0055	-.0081	-.0128
.7		.0439	.0587	.0756	.0957
		.0079	.0119	.0150	.0172
.8		.0344	.0469	.0599	.0758
		.0192	.0265	.0339	.0417
.9		.0056	.0109	.0168	.0236
		.0032	.0079	.0127	.0182

Table 3. Comparison of Δx Predictions for $|t| = 0.12$

Percent = $[(\Delta x)_i - (\Delta x)_{INT}]/(\Delta x)_{INT}$

ζ	Δx_{INT}	Δx_{MG}	Δx_{QCR}	$(\text{Percent})_{MG}$	$(\text{Percent})_{QCR}$
.1	.1200	.1324	.1306	10.3	8.8
.2	.2344	.2478	.2357	5.7	0.6
.3	.3155	.3388	.3086	7.4	-2.2
.4	.3604	.3990	.3505	10.7	-2.7
.5	.3751	.4233	.3652	12.8	-2.6
.6	.3594	.4078	.3545	13.5	-1.4
.7	.3076	.3515	.3155	14.3	2.6
.8	.2233	.2577	.2425	15.4	8.6
.9	.1297	.1353	.1329	4.3	2.5

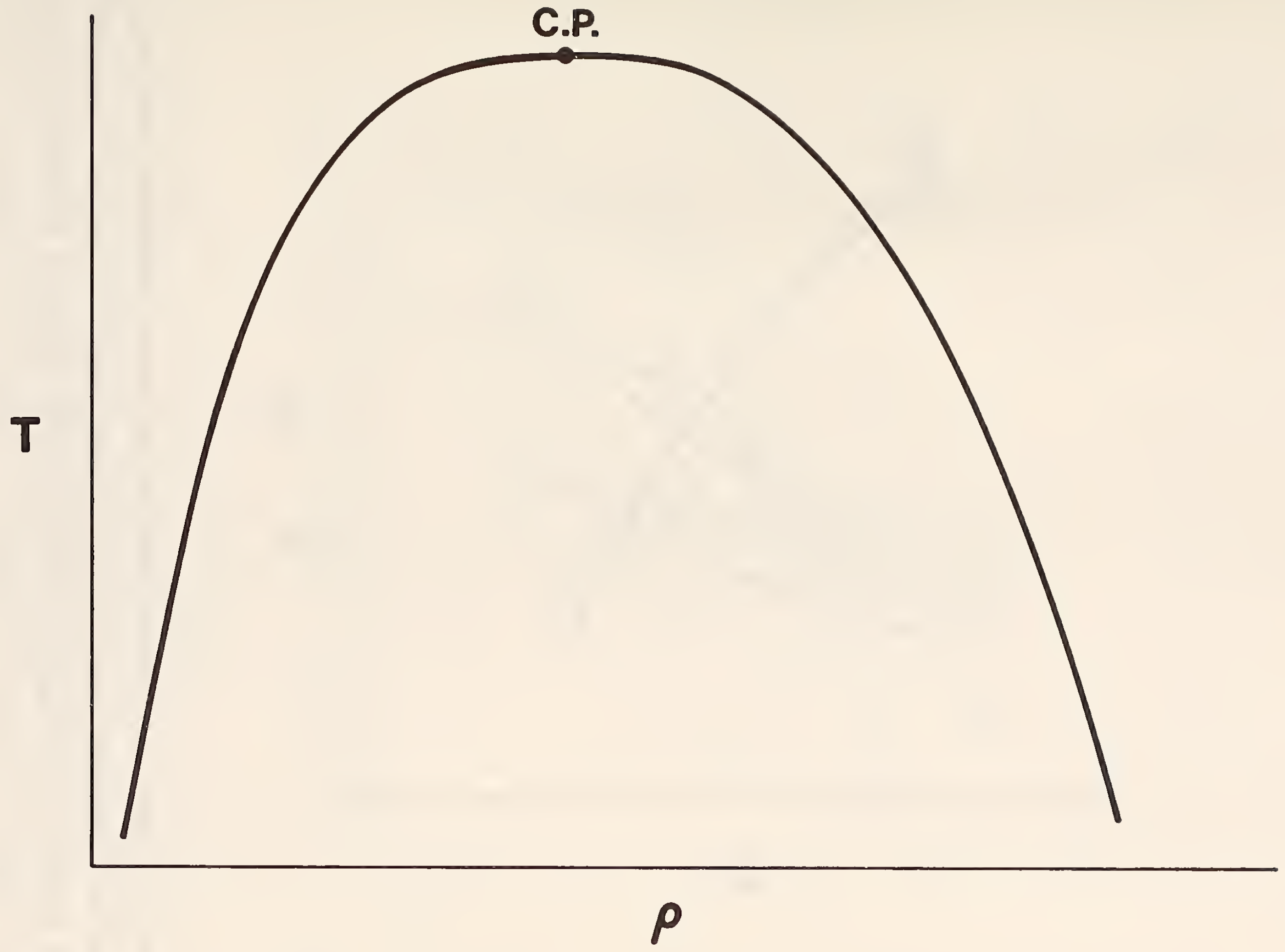

Figure 1. Temperature-density plot of the coexistence "dome" for a pure fluid (schematic). The critical point (C.P.) is the point of highest temperature.

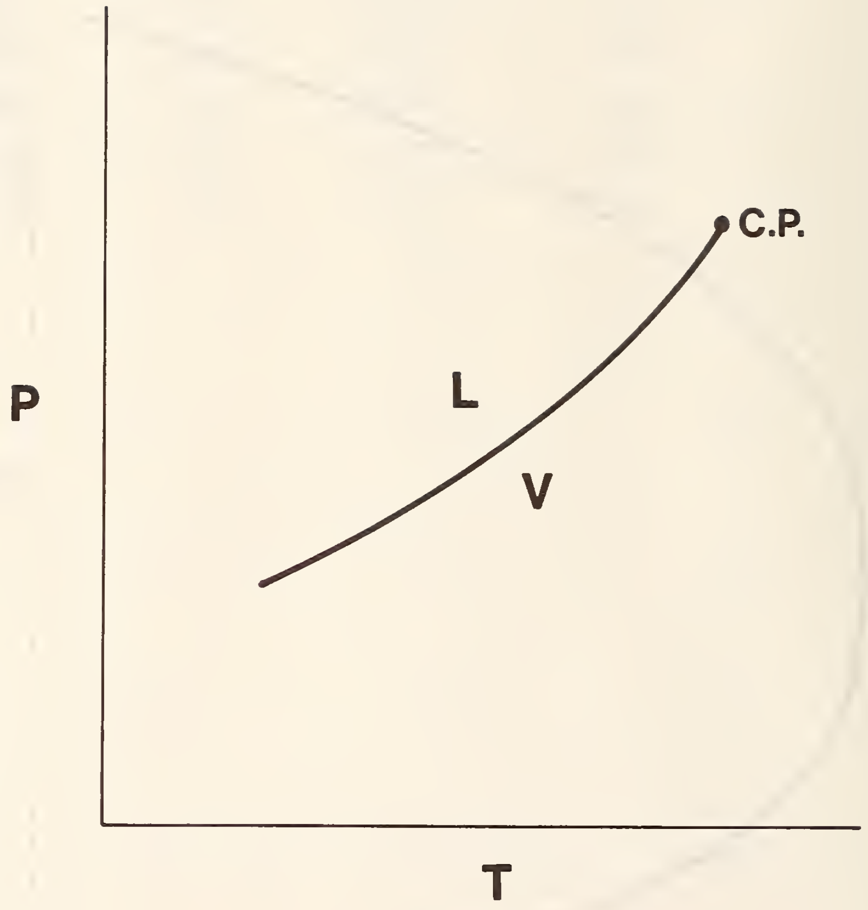

Figure 2. Pressure-temperature plot of the vapor pressure curve for a pure fluid which separates the liquid (L) and vapor (V) phases (schematic). At its highest pressure and temperature the vapor pressure curve terminates in a critical point (C.P.).

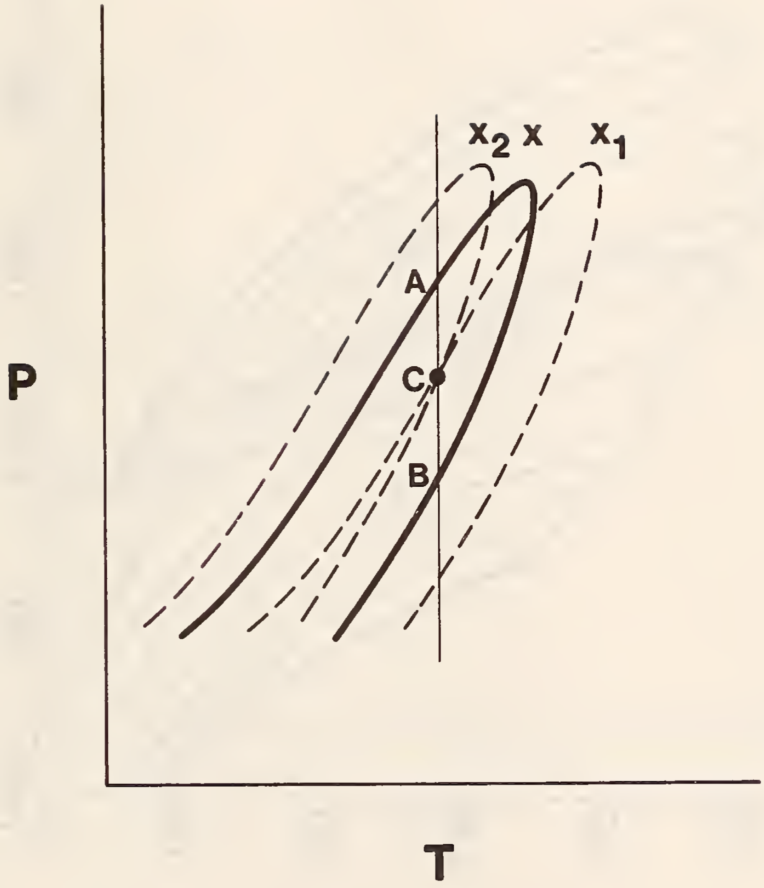

Figure 3. Pressure-temperature plot of dew-bubble curves for a binary mixture (schematic). For a mixture of composition x along the indicated isotherm, A is the bubble point, and B is the dew point. At point C, liquid of composition x_1 coexists with vapor of composition x_2.

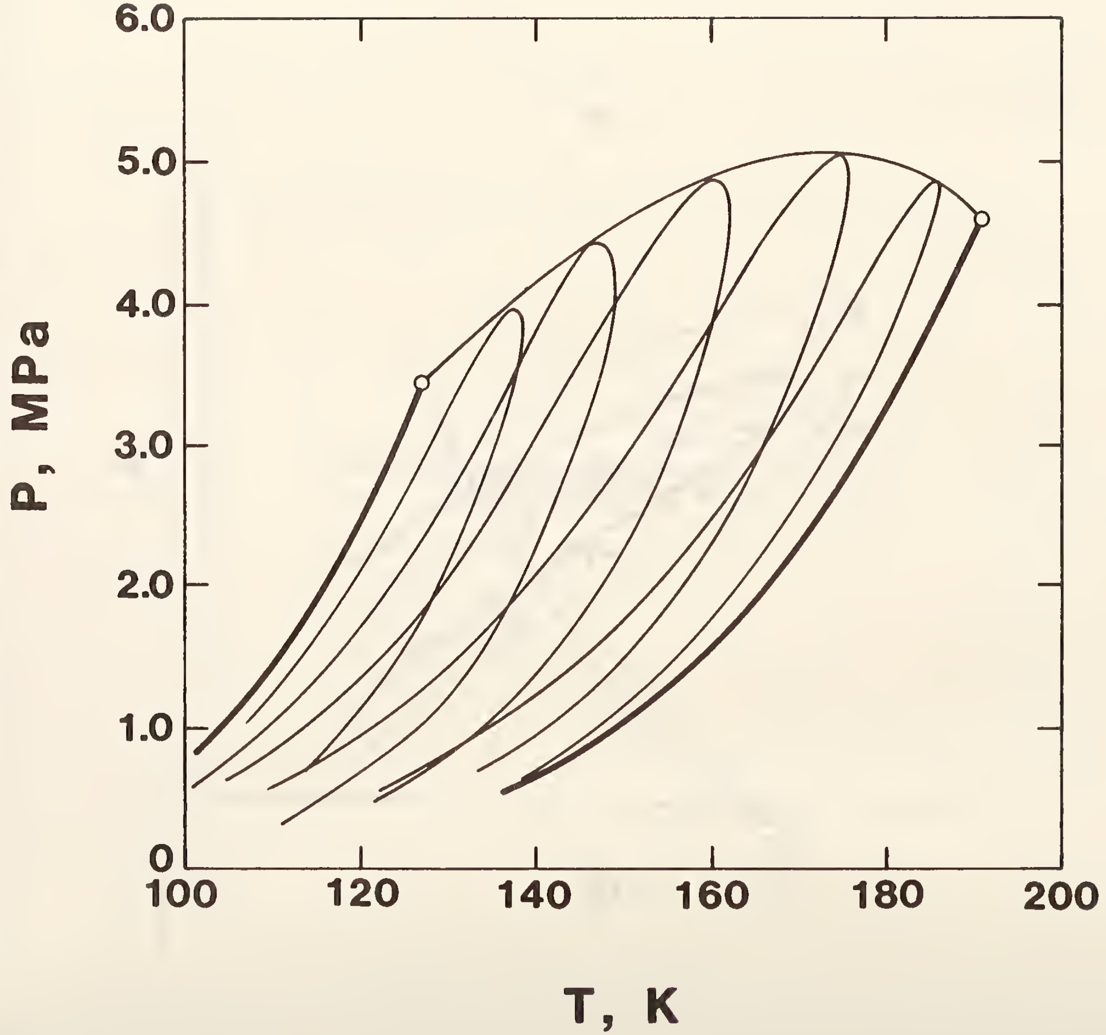

Figure 4. Pressure-temperature plot of pure vapor pressure curves, dew-bubble curves and the critical line for the normal binary mixture nitrogen-methane. Adapted from reference [16], figure 7.

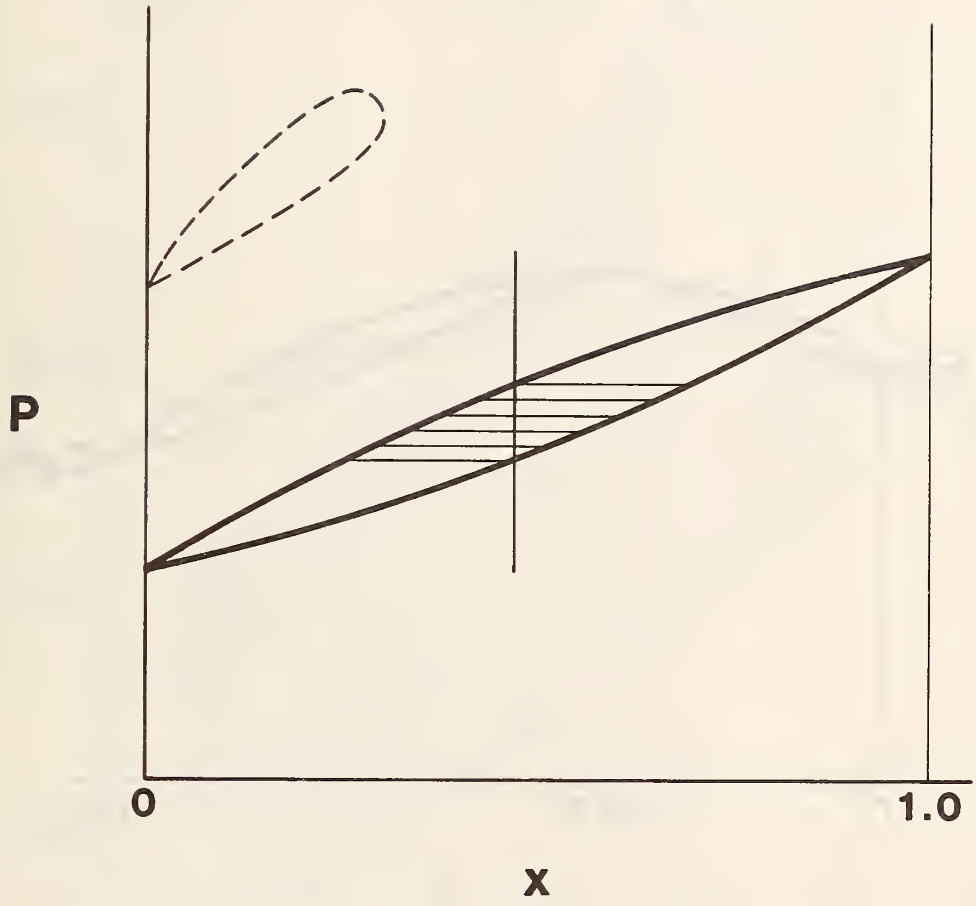

Figure 5. Pressure-composition plot of coexistence isotherms for a normal binary mixture (schematic). The horizontal tie lines indicate coexistence between liquid of the composition to the left and vapor of composition to the right. For a pure sample of the more volatile component, x = 1. The dotted line is an isotherm at a temperature between the critical temperatures of the two pure components.

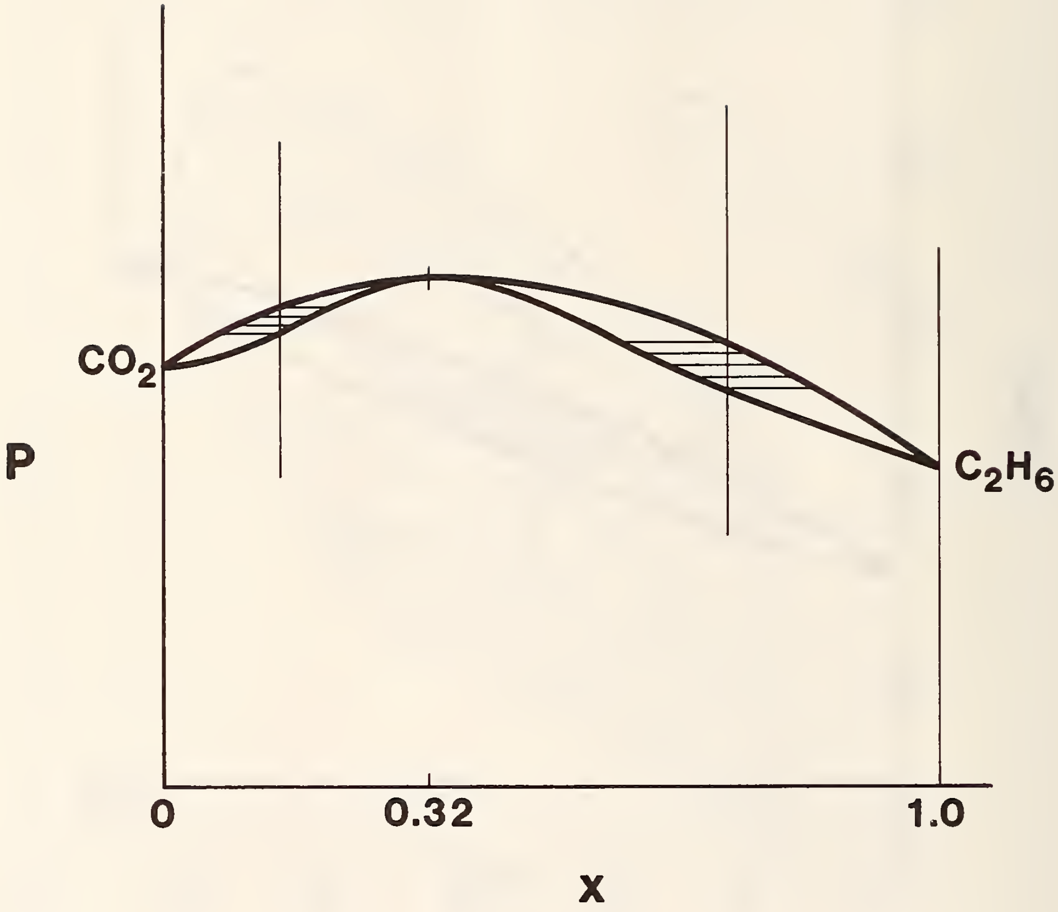

Figure 6. Pressure-composition plot of a coexistence isotherm for the azeotropic binary system carbon dioxide-ethane. At the azeotrope ($x \gtrsim 0.32$) the liquid and vapor have the same composition. For $x < 0.32$, ethane is more volatile; for $x > 0.32$ carbon dioxide is more volatile.

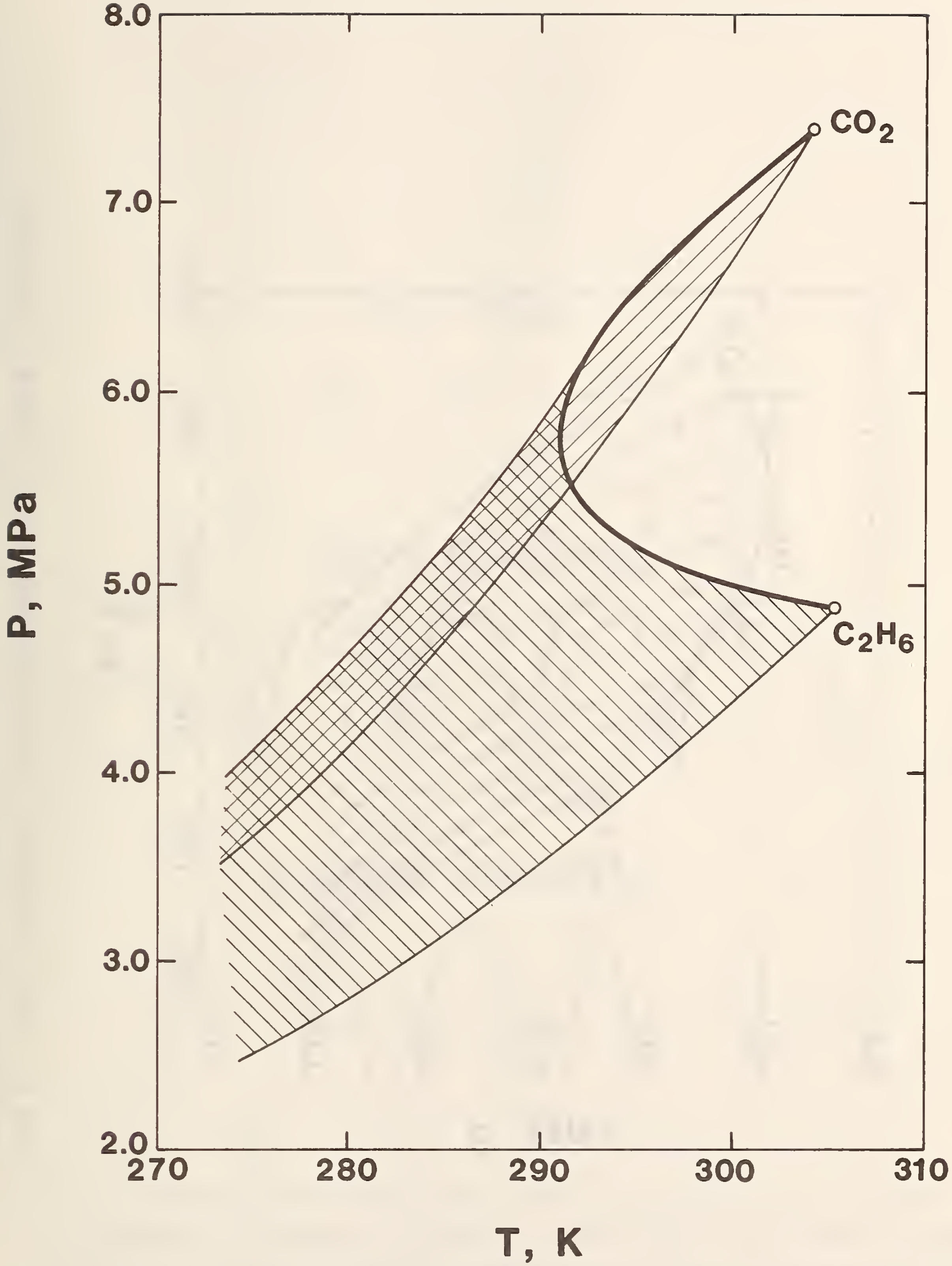

Figure 7. Pressure-temperature plot of the coexistence region for the azeotropic binary system carbon dioxide-ethane. Adapted from reference [16], figure 5. The azeotrope, upper left, is tangent to the critical line. The coexistence region consists of two separate "sheets," hatched horizontally and vertically respectively, with some overlap.

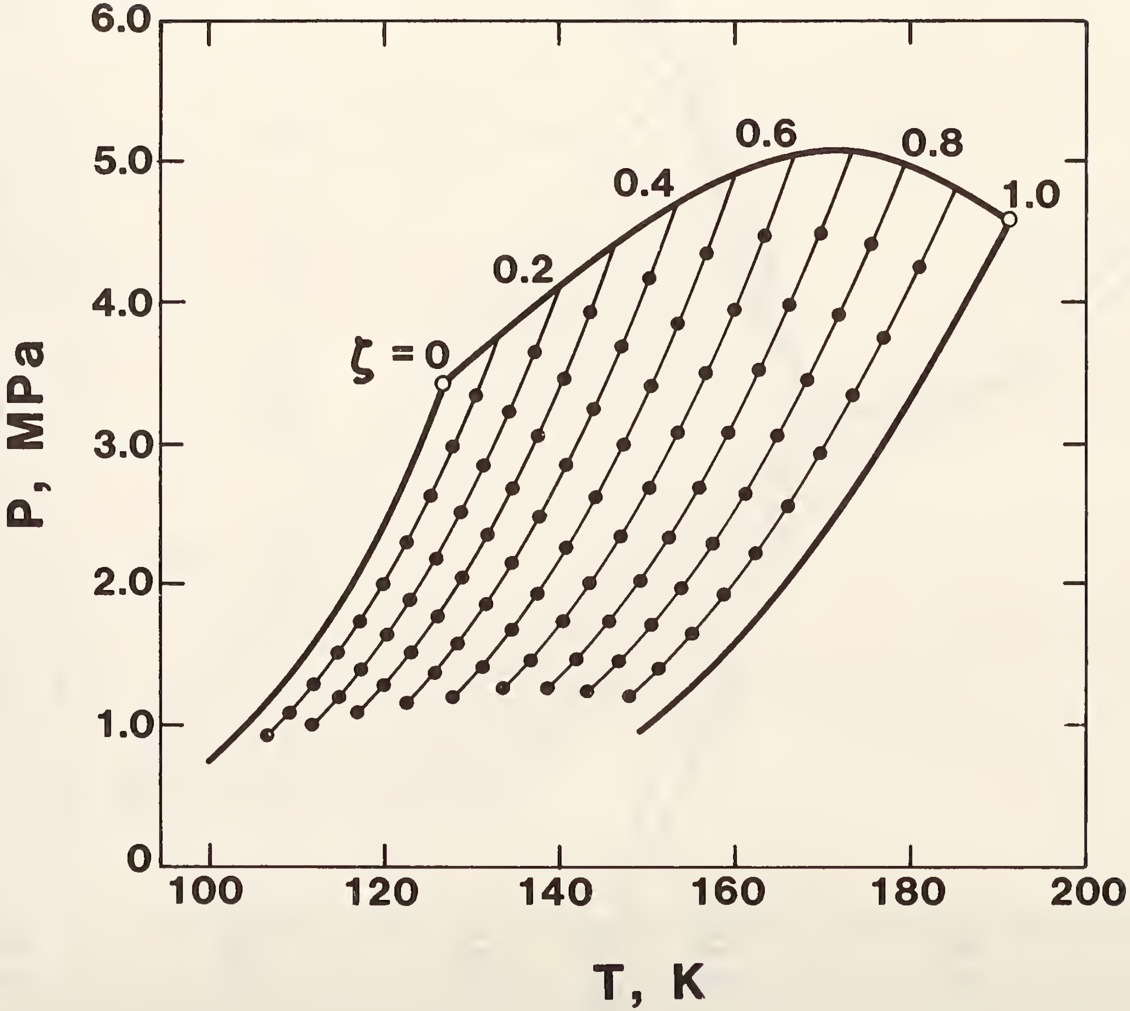

Figure 8. Lines of constant ζ for nitrogen-methane, cf. figure 4. The dots denote steps in t of 0.02.

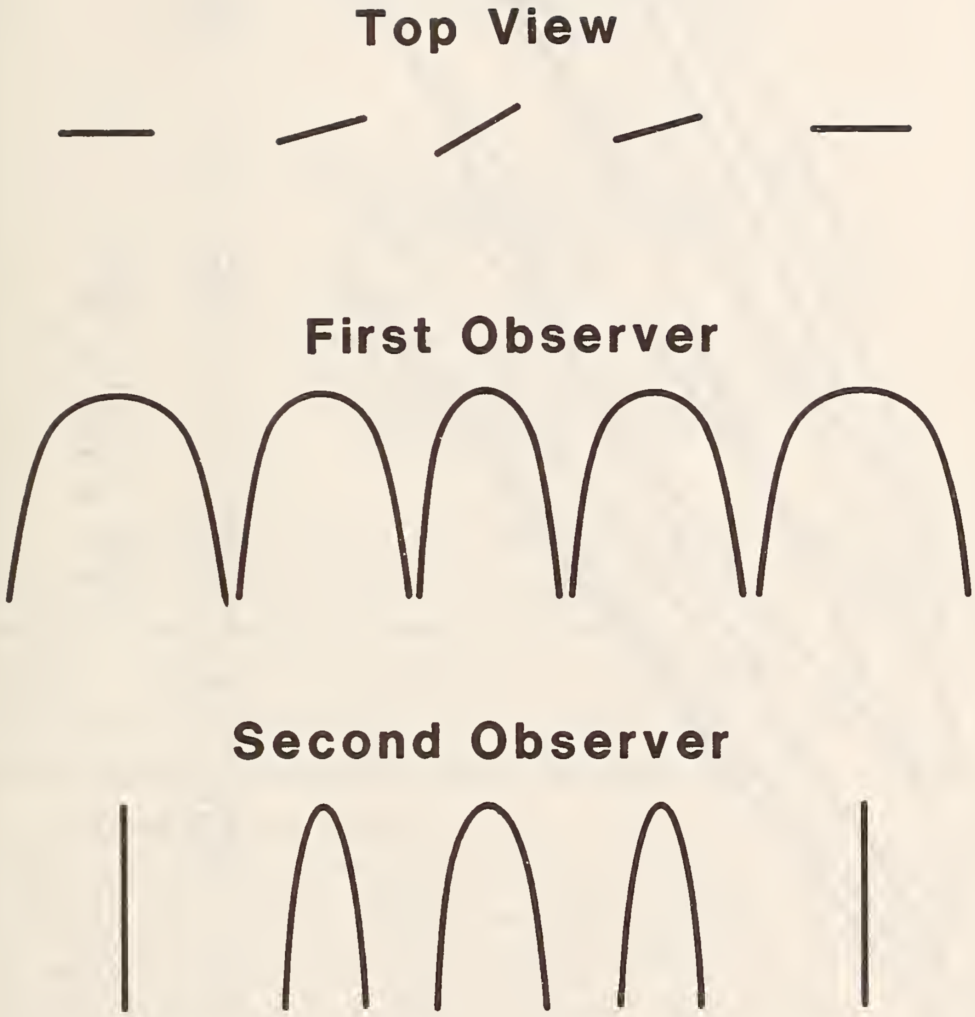

Figure 9. "Tilted croquet wicket model" for the quadratic coupling recipe. As θ is increased, the apparent, projected width of the wicket becomes narrower for the first observer [a symbolic representation of $\rho(t)$] and wider for the second observer [a symbolic representation of $x(t)$].

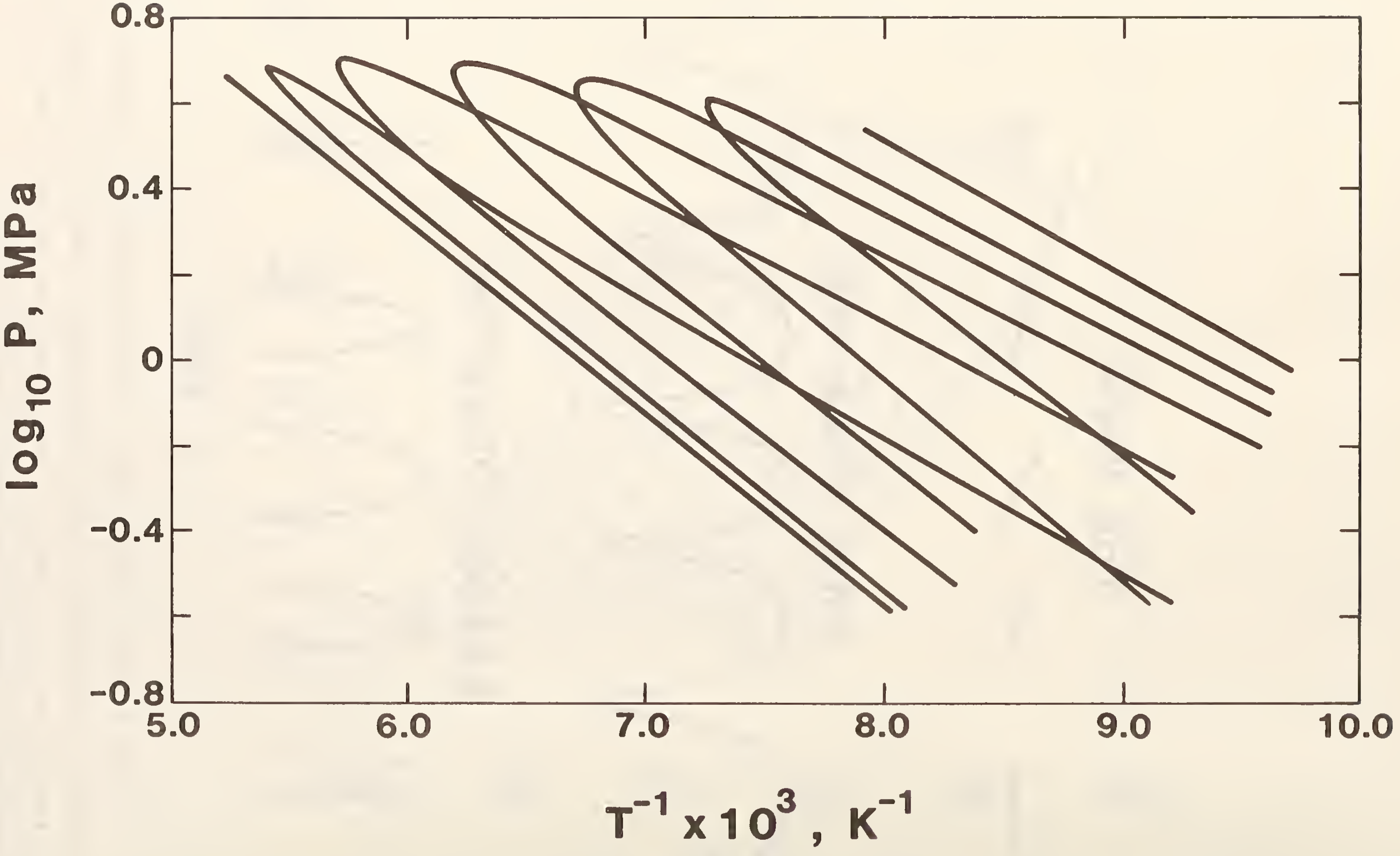

Figure 10. Semilog plot of the dew-bubble curves for nitrogen-methane. Except near the critical region, the curves in this representation are linear to a good approximation.

PREDICTION OF THE CRITICAL LINE OF A BINARY MIXTURE: EVALUATION OF THE INTERACTION PARAMETERS

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The critical line of the binary mixture methane-ethane is calculated via the extended corresponding states Van der Waals one fluid theory. The Gibbs free energy criticality criteria are solved numerically. The numerical derivatives are compared with the exact analytical results derived previously for the special case of the shape factors of the extended corresponding states set equal to unity. Binary interaction parameters are adjusted to give a best fit of the critical line to experimental data. These interaction parameters are then used to evaluate vapor liquid equilibrium data away from the critical region. It appears that a fit of the critical line is not sufficient to obtain binary interaction parameters of general applicability. Optimization of the critical point predictions for the pure components is also discussed.

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Key words: binary interaction parameters; criticality criteria; extended corresponding states; gas-liquid critical line; one fluid theory; van der Waals theory; VLE prediction.

1. Introduction

The prediction of phase equilibria is both a classical problem of the theory of liquids and a problem of engineering concern. Today the chemical and fuel industries have to increase productivity and conservation and have to transfer to new feedstocks; phase equilibria is a major factor. But it is well-known that the prediction, even the correlation, of the properties of the appropriate systems can be exceptionally difficult if the results are required to any reasonable accuracy. Prediction techniques are needed especially because the number of possible systems makes measurement an overwhelming task. Prediction requires an understanding of theory but, unfortunately, theory cannot yet always handle adequately the complex systems encountered: the gap between a systematic practical theory and reality is large. One technique, however, has been applied successfully to simple systems and does show promise in that the assumptions can be identified clearly. This method is extended corresponding states. Here we apply it to a system of methane and ethane. A specific objective is to calculate the gas/liquid critical line and to observe the effect of the binary interaction parameters on the calculation. It is then interesting to see how these parameters, optimized for the critical line, represent vapor liquid equilibrium (VLE) data.

The critical line in a binary mixture may be calculated by solving the equations

$$\left(\frac{\partial^2 \tilde{G}}{\partial x^2}\right)_{T,p} = 0 \quad ; \quad \left(\frac{\partial^3 \tilde{G}}{\partial x^3}\right)_{T,p} = 0$$

for a temperature (T) and pressure (p) with the mole fraction (x) specified. $\tilde{G}$ is the molar configurational Gibbs free energy of the mixture. In this work these second and third order derivatives were evaluated numerically, but have been compared with the analytical results of Wielopolski [1] in the special case when the extended corresponding states shape factors are unity. The accuracy of the approach has thus been evaluated.

The system methane/ethane was selected for comparison with experiment since the VLE data have been evaluated for thermodynamic consistency by Hiza, et al. [2]. The procedure is quite general, however, and we have applied it to several mixtures. Variations have been reported extensively by Watson and Rowlinson [3], Gunning and Rowlinson [4], Teja and Rowlinson [5], Mollerup and Rowlinson [6], and Mollerup [7,8]. The overall objective is to develop a general technique for calculating the critical line of a binary mixture and to see if the binary interaction parameters can be reliably evaluated by adjusting them to give the best least squares fit of the critical line data.

2. Corresponding States and Equations

The basic postulate of the theory used here -- the van der Waals one fluid theory -- is that if the components α ($\alpha = 1,n$ where n is the total number of species) of a mixture separately obey classical corresponding states, then their mixture will also obey corresponding states as if it were a single substance. The components can be represented by selected parameters, e.g., critical temperature (T^c_α) and critical molar volume (V^c_α), and the hypothetical equivalent substance, designed by subscript $\underline{x}$, can be characterized by some suitable composition dependent averaged parameters T^c_x and V^c_x. The method then assumes that the properties of a pure substance at p and T, or V and T, can be evaluated with respect to those of a reference fluid, designated by subscript $\underline{o}$, via

$$T_o = T/f_{\alpha\alpha,o} \quad \text{and} \quad V_o = V/h_{\alpha\alpha,o} \tag{1}$$

where the scaling ratios h and f are defined respectively by

$$h_{\alpha\alpha,o} = V^c_\alpha/V^c_o \quad \text{and} \quad f_{\alpha\alpha,o} = T^c_\alpha/T^c_o \tag{2}$$

For a mixture the most natural definition of h_x and f_x follows from the work of Henderson and Leonard [9] to give the van der Waals one fluid mixing rules:

$$h_{x,o}\, f_{x,o} = \sum_\alpha \sum_\beta x_\alpha x_\beta\, f_{\alpha\beta,o}\, h_{\alpha\beta,o} \tag{3}$$

$$h_{x,o} = \sum_\alpha \sum_\beta x_\alpha x_\beta\, h_{\alpha\beta,o} \tag{4}$$

The cross coefficients $f_{\alpha\beta,o}$ and $h_{\alpha\beta,o}$ are left unspecified until further combination rules are defined, e.g.,

$$f_{\alpha\beta,o} = \xi_{\alpha\beta,o} \left(f_{\alpha\alpha,o} f_{\beta\beta,o}\right)^{1/2} \tag{5}$$

$$h_{\alpha\beta,o} = \eta_{\alpha\beta,o} \left[\frac{1}{2} \left(h_{\alpha\alpha,o}\right)^{1/3} + \frac{1}{2} \left(h_{\beta\beta,o}\right)^{1/3}\right]^3 \tag{6}$$

where $\xi_{\alpha\beta,o}$ and $\eta_{\alpha\beta,o}$ are the binary interaction coefficients which, although formally close to unity, can play a major role in the calculation of phase equilibria.

2.1 One Fluid Mixture Equations

The properties of a mixture can be evaluated in terms of the reference substance and the ratios of eq (2). The basic equations are:

Compressibility factor, Z

$$Z\ (T,V,x) \equiv Z_x(T,V,x) \tag{7}$$

$$= Z_o(T/f_{x,o},\ V/h_{x,o}) \tag{8}$$

Molar configurational Helmholtz free energy, $\tilde{A}$

$$\tilde{A}\ (V,T,x) \equiv \tilde{A}_x(V,T,x) + RT \sum_\alpha x_\alpha \ell n\ x_\alpha \tag{9}$$

where

$$\tilde{A}_x(V,T,x) = f_{x,o}\ \tilde{A}_o(V/h_{x,o},\ T/f_{x,o}) - RT\ \ell n\ h_{x,o} \tag{10}$$

or the molar configurational Gibbs free energy, $\tilde{G}$

$$\tilde{G}\ (p,T,x) \equiv \tilde{G}_x(p,T,x) + RT \sum_\alpha x_\alpha \ell n\ x_\alpha \tag{11}$$

where

$$\tilde{G}_x(p,T,x) = f_{x,o}\ \tilde{G}_o(ph_{x,o}/f_{x,o},\ T/f_{x,o}) - RT\ \ell n\ h_{x,o} \tag{12}$$

The symbol $\sim$ refers to the molar quantity. Equations (7)-(12) which define the properties of an n-component mixture, can also be used for pure component properties if all subscript x's are replaced with α's.

2.2 VLE Equations

For pure component VLE, equating the molar Gibbs free energy of each phase results in the following expression:

$$[\tilde{A}_o^{Res}/RT_o - \ln Z_o - 1 + Z_o]_{vap} = [\tilde{A}_o^{Res}/RT_o - \ln Z_o - 1 + Z_o]_{liq} \qquad (13)$$

where

$$\tilde{A}_o^{Res} \equiv \tilde{A}\,(T/f_{\alpha\alpha,o}, V/h_{\alpha\alpha,o}) - \tilde{A}_{pg}(T/f_{\alpha\alpha,o}, V/h_{\alpha\alpha,o}) \qquad (14)$$

In eq (13) superscript Res refers to the residual value defined by eq (14) with $\tilde{A}_{pg}$ the value of the equivalent perfect gas. Equation (13) is expressed in terms of the residual Helmholtz free energy rather than Gibbs since the reference equation of state has T and V (not T and p) as the independent variables.

For mixture VLE one can calculate the K-value for, say, species α at T and p:

$$K_\alpha = y_\alpha/x_\alpha \qquad (15)$$

where one can derive

$$RT \ln K_\alpha = \left(\mu_\alpha^{Res}\right)_{Liq} - \left(\mu_\alpha^{Res}\right)_{Vap} \qquad (16)$$

with μ^{Res} the residual chemical potential. Further manipulations give μ^{Res} in terms of $\tilde{G}$ and, for a binary mixture,

$$\mu_\alpha^{Res} = \tilde{G}_x - RT\, x_\beta \left(\frac{\partial(\tilde{G}_x/RT)}{\partial x_\beta}\right)_{T,p} - RT \ln \frac{p}{kT} \qquad (17)$$

where

$$\frac{\tilde{G}_x}{RT} = \frac{\tilde{A}_o^{Res}}{RT_o} - \ln Z_o - 1 + Z_o + \ln \frac{p}{kT} \qquad (18)$$

2.3 Critical Criteria

The conditions for a critical point at T,p for a mixture are

$$(\partial^2\tilde{G}/\partial x^2)_{T,p} = (\partial^3\tilde{G}/\partial x^3)_{T,p} = 0 \tag{19}$$

Substitution of the one fluid equations gives

$$(\partial^2 (\tilde{G}_x/RT)/\partial x_\alpha^2)_{T,p} + \frac{1}{x_\alpha x_\beta} = 0 \tag{20}$$

and

$$(\partial^3 (\tilde{G}_x/RT)/\partial x_\alpha^3)_{T,p} + \frac{x_\alpha - x_\beta}{(x_\alpha x_\beta)^2} = 0 \tag{21}$$

which can thus be evaluated using eq (18).

The above equations and others have been discussed in full and derived by Rowlinson and Watson [3], by Eaton [10] and by other authors so it has been sufficient to be very brief. The equations form the basics of the evaluation of phase equilibria for a pure fluid or mixture, given the reference equation of state and the reference G_0 or A_0.

2.4 Extended Corresponding States

In general, since classical corresponding states is not obeyed, eqs (8) and (10) or (8) and (12) are not satisfied with the scaling ratios of eq (2). It is possible, however, to <u>define</u> a corresponding states so that eqs (8) and (10) are satisfied <u>exactly</u>. To do this we define shape factors θ and ϕ so that (for a pure, for example)

$$T_o = T\left(\frac{T_o^c}{T_\alpha^c}\right)\frac{1}{\theta_{\alpha\alpha,o}} \quad ; \quad V_o = V\left(\frac{V_o^c}{V_\alpha^c}\right)\frac{1}{\phi_{\alpha\alpha,o}} \tag{22}$$

hence the ratios f and h become

$$f_{\alpha\alpha,o} = \left(\frac{T_\alpha^c}{T_o^c}\right)\theta_{\alpha\alpha,o} \quad ; \quad h_{\alpha\alpha,o} = \left(\frac{V_\alpha^c}{V_o^c}\right)\phi_{\alpha\alpha,o} \tag{23}$$

The point about this redefinition, i.e., the basis of <u>extended</u> corresponding states theory, is that the corresponding states equations can be used formally with the provision that the scaling ratios are given by eq (23). It should be stressed that the ratios could be solved for either a pure or a mixture via eqs (8) and (10) but to do this would require a complete description of the fluids in question: essentially an impossibility. It is convenient to have some generalized analytical relation for θ and ϕ. Leach and Leland proposed the following [11]:

$$\theta_{\alpha\alpha,o} (T_\alpha^*, V_\alpha^*, \omega_\alpha) = 1 + (\omega_\alpha - \omega_o) F(T_\alpha^*, V_\alpha^*) \tag{24}$$

$$\phi_{\alpha\alpha,o} (T_\alpha^*, V_\alpha^*, \omega_\alpha) = \left\{1 + (\omega_\alpha - \omega_o) G(T_\alpha^*, V_\alpha^*)\right\} \frac{Z_o^c}{Z_\alpha^c} \tag{25}$$

where

$$F(T_\alpha^*, V_\alpha^*) = a_1 + b_1 \ell n\, T_\alpha^* + (c_1 + d_1/T_\alpha^*) (V_\alpha^* - 0.5) \tag{26}$$

and

$$G(T_\alpha^*, V_\alpha^*) = a_2 (V_\alpha^* + b_2) + c_2 (V_\alpha^* + d_2) \ell n\, T_\alpha^* \tag{27}$$

Here ω is the pitzer acentric factor or some chosen parameter and a, b, c, d are constants:

a_1 =	0.0892,	a_2 =	0.3903
b_1 =	-0.8493,	b_2 =	-1.0177
c_1 =	0.3063,	c_2 =	-0.9462
d_1 =	-0.4506,	d_2 =	-0.7663

The asterisk denotes the value reduced by the critical value. The equations are constrained in that V_α^* is set equal to 2.0 for all $V_\alpha^* > 2.0$ and to 0.5 for $V_\alpha^* < 0.5$: T_α^* is set to 2.0 if $T_\alpha^* > 2.0$.

We [12] have recently tested the Leach-Leland equations for the hydrocarbons $C_1 - C_{20}$ over an extensive range of experimental conditions and revised coefficients are reported in the reference. We also verified that the original equations were satisfactory for reduced temperatures greater than 0.5.

3. Calculation and Numerical Methods

The objective is to solve the critical criteria eqs (20) and (21) for the methane/ethane system and in so doing, observe the effects of the interaction parameters and η of eqs (5) and (6) on the results. Having these values, we then evaluate some K-values for selected temperatures using eqs (15)-(18). We chose methane as the reference fluid, the equation of state for which is the 32 term BWR of McCarty [13]. Critical parameters and Leach-Leland acentric factors for methane and ethane are given in table 1.

Table 1. Parameters for Methane and Ethane

	T^c (K)	$\tilde{V}^c$ (cm^3/mole)	P^c (Bar)	ω
CH_4	190.555	97.75	44.793	.005
C_2H_6	305.33	147.06	47.448	.105

3.1 Analytical and Numerical Evaluation of the Derivatives

The numerical techniques used in this work are standard. We use the central difference formulas [14] for which the first two terms in the infinite power series expansions are given here. For the derivatives of a function f evaluated at a point x, one has

$$\left.\frac{df}{dx}\right)_x \approx \frac{f_1 - f_{-1}}{2h} - \frac{f_2 - 2f_1 + 2f_{-1} - f_{-2}}{12h} \tag{28}$$

$$\left.\frac{d^2f}{dx^2}\right)_x \approx \frac{f_1 - 2f_0 + f_{-1}}{h^2} - \frac{f_2 - 4f_1 + 6f_0 - 4f_{-1} + f_{-2}}{12h^2} \tag{29}$$

$$\left.\frac{\partial^3 f}{\partial x^3}\right)_x \approx \frac{f_2 - 2f_1 + 2f_{-1} - f_{-2}}{2h^3} - \frac{f_3 - 4f_2 + 5f_1 - 5f_{-1} + 4f_{-2} - f_{-3}}{8h^3} \tag{30}$$

where

$$f_o = f(x) \quad ; \quad f_n = f(x + nh) \tag{31}$$

The difficulty is to choose a value of h which is not too small (otherwise significant figures will be lost in evaluating the numerators of eqs (28)-(30) but not too large (otherwise the truncation error, which can be estimated by the second term of eqs (28)-(30), will be large). One also has to consider the word length of the computer and the convenience of using single versus double precision. In this work we calculated on a CDC 6400 and a CDC 6600 machine with a 60 bit word length (13 significant figures).

We were able to observe definitely the effect of varying h for the special case $\theta = \phi = 1$, i.e., for classical corresponding states. Equations (19) and (20) have been solved analytically by Wielopolski (1980) and the lengthy expressions are reported in an NBS publication [1] and will not be repeated here. For example, table 2 lists the number of figures in the numerical results which were in agreement with the analytical results for the first, second, and third derivatives of $\tilde{G}_x/RT$ for a particular test case. The number of figures in agreement for the function value of $\tilde{G}_x/RT$ itself was 10-12.

Table 2. Comparison of Numerical and Analytical Results for Derivative Calculations Using Single Precision Arithmetic.

h	$(\tilde{G}_x/RT)_x$	$(\tilde{G}_x/RT)_{2x}$	$(\tilde{G}_x/RT)_{3x}$
10^{-3}	6	5	4
10^{-4}	7	5	3
10^{-5}	7	3	0

Table 2 indicates that the first order derivative is truncation error controlled, since its value becomes more accurate as h is decreased. The second and third derivatives are, on the other hand, controlled by the loss of significant figures since as h is decreased, they lose accuracy. Since the third order derivative is the least accurate, we chose the value of h for which it is calculated most accurately.

We now consider what the smallest values of the second and third order derivatives are which can be calculated with $h = 10^{-3}$, since our eventual goal is to solve the equations for the critical point by driving the values of those derivatives to zero. The derivatives go to zero by a cancellation of the two terms in eqs (20) and (21), that is, the contribution from the hypothetical substance is cancelled by the ideal mixture contribution. For this reason, the values of the derivatives cannot be made arbitrarily small. The ideal mixture contribution (which can be computed with negligible error) can only cancel as many significant figures as appear in the hypothetical substance contribution. Consider the case in table 2 with $h = 10^{-3}$. For the second order derivative, the hypothetical substance contribution has five significant figures, and its value is order unity (abbreviated $O(1)$). If the ideal mixture contribution were to cancel all five of these figures, the result would be a number of $O(10^{-5})$ with no significant figures remaining. For the third order derivative, the hypothetical substance contribution contains four significant figures, and is $O(10)$. Cancelling all significant figures would leave a number of $O(10^{-3})$.

In our first attempt at calculating critical lines based on the numerical evaluation of the derivatives in eqs (20) and (21) using single precision arithmetic, we were unable to obtain convergence of the temperature and pressure to five significant figures. The problem appeared to be that there were not enough significant figures in the derivative calculations. While the truncation error is inherent to the formulas being used, the loss of significant figures can be compensated by adding more figures to the function values. This was done by the use of double precision arithmetic which gives us 26 significant figures on the CDC 6400. In table 3 below, the results for the numerical derivatives calculated using double precision arithmetic are compared with the results arrived at analytically. Again, reported in the table are the number of figures of agreement between the two results.

Table 3. Comparison of Numerical and Analytical Results for Derivative Calculations Using <u>Double Precision</u> Arithmetic.

h	$(\tilde{G}_x/RT)_x$	$(\tilde{G}_x/RT)_{2x}$	$(\tilde{G}_x/RT)_{3x}$
10^{-3}	6	5	4
10^{-4}	7	9	6
10^{-5}	7	8	7
10^{-6}	7	8	7
10^{-7}	7	8	7
10^{-8}	7	8	4
10^{-9}	7	8	1

For $h = 10^{-3}$, the single and double precision results are the same, which indicates that truncation error is controlling. Looking at the double precision results, the third derivative shows an increase in accuracy as h is decreased to 10^{-5}; clearly indicating that the truncation error is decreasing to this point. As h is decreased past 10^{-7}, accuracy is lost due to loss of significant figures.

Based on these results, a value of $h = 10^{-6}$ is chosen to compute the derivatives in double precision. Given this value for h, the smallest value of the second derivative which may be calculated (containing no significant figures) is $O(10^{-8})$, and that for the third derivative is $O(10^{-6})$. The calculations of the binary critical line were subsequently made to converge to five significant figures for both temperature and pressure.

4. Results

It must again be stressed that the general procedure for calculating the critical line or VLE is predictive and requires only the critical constants and an acentric factor for the fluid of interest, or of the components in a mixture. For a relatively simple system the results will be reasonable without optimization of any parameters. Since, however, we are concerned only with VLE and the critical point we considered two straightforward optimization procedures involving the factor ω. The first was to adjust ω to give the best representation of the pure component vapor pressure curve, the second was to force the critical temperature and pressure of the pure fluids to correspond exactly with those of the reference substance. This second variation is simply to set $\omega_\alpha = \omega_0$: hence by eqs (24) and (25) $\theta = 1$ and $\phi = Z_0^c/Z_\alpha^c$ -- a form of classical corresponding states. One should note that the two procedures are not the same because the Leach-Leland equations are not constrained at the critical point.

4.1 Ethane: Pure Component Results

We first considered the ethane vapor pressure curve which was obtained using Leach's expression for the shape factors. The value of the acentric factor for the Leach equations was determined by optimizing agreement with the vapor pressure data by a trial and error procedure in which the sum of the average absolute deviations, for the vapor pressure, and saturated vapor and liquid densities, were minimized; temperature being chosen as the independent variable. The temperature range over which the results were optimized was 180 K to 300 K; 180 K being the lower limit for which Leach's equations were designed; 300 K corresponded to the maximum temperature for which the vapor pressure program would converge. Calculated and data values were compared at 10 K increments. The average deviations obtained for several values of acentric factor are given in table 4. The value chosen for acentric factor in this work ($\omega = .094$) is seen to give a substantial improvement over the Pitzer value ($\omega = .105$) which was used by Leach.

The curves for vapor pressure and orthobaric densities ($\rho = 1/V$), obtained using Leach's shape factors with the optimized acentric factor are compared with the correlations of Goodwin, et al. [15] to obtain the deviations plotted in figure 1.

Table 4. Variation of Ethane Vapor Pressure Curve With Acentric Factor (Leach θ, ϕ).

Acentric Factor ω	Ave % $\frac{\lvert\Delta p\rvert}{p}$	Ave % $\frac{\lvert\Delta\rho_{vap}\rvert}{\rho_{vap}}$	Ave % $\frac{\lvert\Delta\rho_{liq}\rvert}{\rho_{liq}}$	Ave %
.105	2.080	3.148	.6158	5.844
.100	1.259	2.215	.3706	3.845
.096	.595	1.460	.3791	2.434
.095	.467	1.270	.3894	2.126
.094	.444	1.164	.4067	2.015
.093	.479	1.127	.4245	2.031
.092	.543	1.137	.4424	2.122
.090	.736	1.241	.4904	2.467
.005	60.579	61.633	4.746	126.958

Also in figure 1, deviations for the vapor pressure and orthobaric density curves predicted using classical corresponding states are presented. This figure emphasizes that the Leach shape factors make a significant difference. The vapor pressure deviations are positive, and become larger as the triple point is approached, since classical corresponding states predicts a slope of the vapor pressure curve (dP/dT) which is too small. The deviation of pressure goes to zero at the critical point because the two parameters are choosen to make the critical temperature and pressure correspond exactly.

The critical point results for ethane are in Table 5. Notice that the results are better using classical corresponding states than with the Leach shape factors. This is because classical corresponding states forces either the critical temperature and density to correspond ($\theta = \phi = 1$), or it forces the critical temperature and pressure to correspond ($\theta = 1$, $\phi = Z_0^c/Z_\alpha^c$).

Table 5. Ethane Critical Point Predictions.

	Data	Leach θ, $\phi(\omega = .094)$	$\theta = \phi = 1$	$\theta = 1$, $\phi = Z_0^c/Z_1^c$
T_c (K)	305.33	307.01 (.55)*	305.33	305.33
P_c (bar)	47.448	48.790 (2.83)	47.750 (.55)	47.448
ρ_c (mol/L)	6.80	6.98 (2.65)	6.80	6.76 (-.59)

* Percent deviation is in parentheses.

4.2 The Critical Line

We first calculate the critical line using the Leach shape factor equations with acentric factors of .005 and .094 for methane and ethane respectively. The results are plotted against the critical line data found in the review article of Hicks and Young [16], and identified in the caption to figure 2 (the symbols used in figure 2 are identical with those used in figures 3 through 7).

The results are presented in the form of T-x and p-x plots in figures 2-5 and show the general trends obtained by varying the binary interaction parameters, ξ and η. Holding ξ constant, figures 2 and 3 show that η has a small effect on the T-x curve, and a large effect on the p-x curve. In both cases, increasing η gives a better representation of the data. Holding η constant, figures 4 and 5 show that ξ has a much larger effect on the T-x curve than did η, and an equally large effect on the p-x curve. The important point to notice is that the maximum value in the p-x curve is shifted towards small mole fraction values (of CH_4) by decreasing ξ. The best representation of the P-x curve in figure 3 (i.e., $\xi = 1.00$, $\eta = 1.08$) indicates that the peak of the curve needs to be shifted towards the smaller mole fractions to improve the agreement, thus, ξ should be decreased.

To achieve the goal of obtaining the interaction parameters by fitting the critical line data, a manual search technique was initiated. The "best fit" was defined in the least squares sense. The results of this search were that $\xi = .97$, and $\eta = 1.13$ were chosen as the "best" values for the interaction parameters. The "best fit" T-x and p-x curves are presented in figures 6 and 7 respectively.

The fit of the T-x curve is good, with only one data point which seems astray. The p-x curve, however, does not have the right shape to fit the data well. Part of the fitting problem is due to the bad prediction which is made for the critical point of pure ethane. This led us to try the second approach of setting $\omega_\alpha = \omega_0$. Hence, the critical endpoints in the T-x, and p-x curves are exact. A new optimization led to the parameter values $\xi = .97$, $\eta = 1.07$. While the fit of the T-x curve was not significantly improved that for the p-x curve was. These results are shown in figures 6 and 7.

4.3 Vapor-Liquid Equilibria Results

Of the VLE data judged to be thermodynamically consistent by Hiza, et al. [2], three representative isotherms were chosen to test the predictions made using the binary interaction parameters determined in the previous section. Two of the isotherms are supercritical (250 K and 199.92 K), and one is subcritical (144.26 K). The sources of the data are: 250 K isotherm, Davalos, et al. [17]; 199.92 K and 144.26 K isotherms, Wichterle and Kobayashi [18].

The VLE calculations used the Leach shape factors with the acentric factors .005 and .094 for methane and ethane respectively. The results are presented as K-value deviation plots for both the methane and the ethane K-value predictions. Figures 8, 9, and 10 contain these curves with the interaction parameters obtained from the critical line fit (i.e., $\xi = .97$, $\eta = 1.07$). These figures also show that setting the interaction parameters to unity gives much better VLE predictions than do the parameters obtained from the best fit of the critical line data.

5. Summary and Conclusions

The proposed technique of calculating binary critical lines by numerically evaluating the second and third order derivatives of the Gibbs free energy has been checked with an analytical solution for the special case of classical corresponding states, and has proven successful. The best least squares fit of the critical line data of the system methane-ethane was then shown to be poor (particularly the p-x curve) if the Leach shape factors are used with an acentric factor optimized for pure component vapor pressure predictions. This is due to a bad prediction of the critical endpoint for ethane. To improve this fit, we use classical corresponding states to force correspondence of the temperature and pressure at the critical line endpoints. However we also show that the pure component vapor pressure predictions are not satisfactory if this is done. Finally, VLE predictions are made using Leach shape factors with the acentric factor optimized for vapor pressure predictions, and the binary interaction parameters obtained from the best fit of the critical line data (i.e., with $\theta = 1$, $\phi = Z_0^c/Z_\alpha^c$). The results are not as good in general as those which are obtained by setting $\xi = \eta = 1$. Hence we conclude that a fit of the binary critical line does not yield binary interaction parameters of any general significance.

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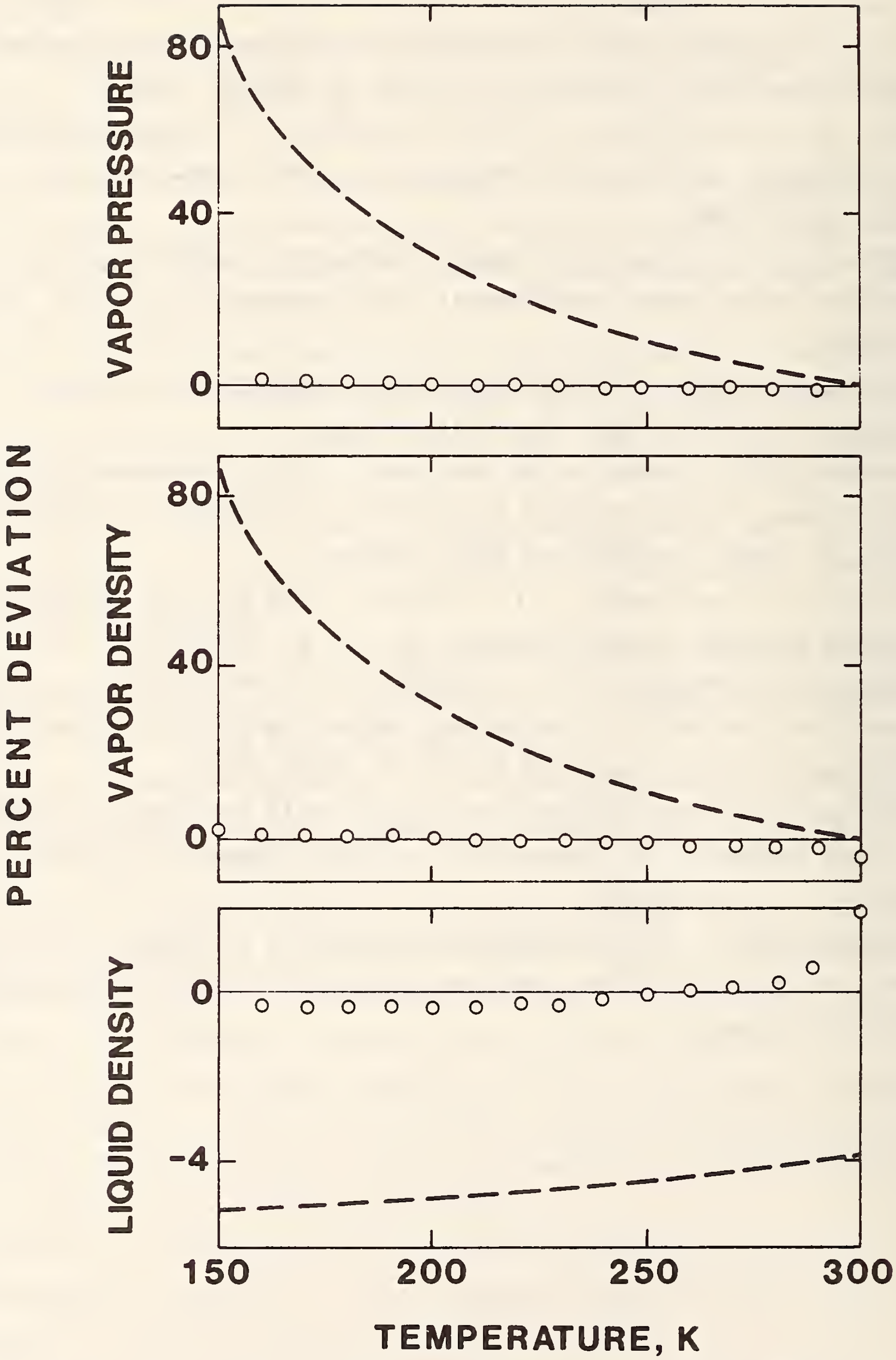

Figure 1. Percent deviations [(expt-calc) x 100/calc] for the vapor pressure, vapor density and liquid density for saturated ethane at saturation. Data from Goodwin [15]. Calculations from the extended corresponding states method with the parameter ω_α optimized, circles. Also shown as the dashed line are the results with $\theta = 1$ and $\phi = Z_o^c/Z_\alpha^c$, see equations (22)-(27).

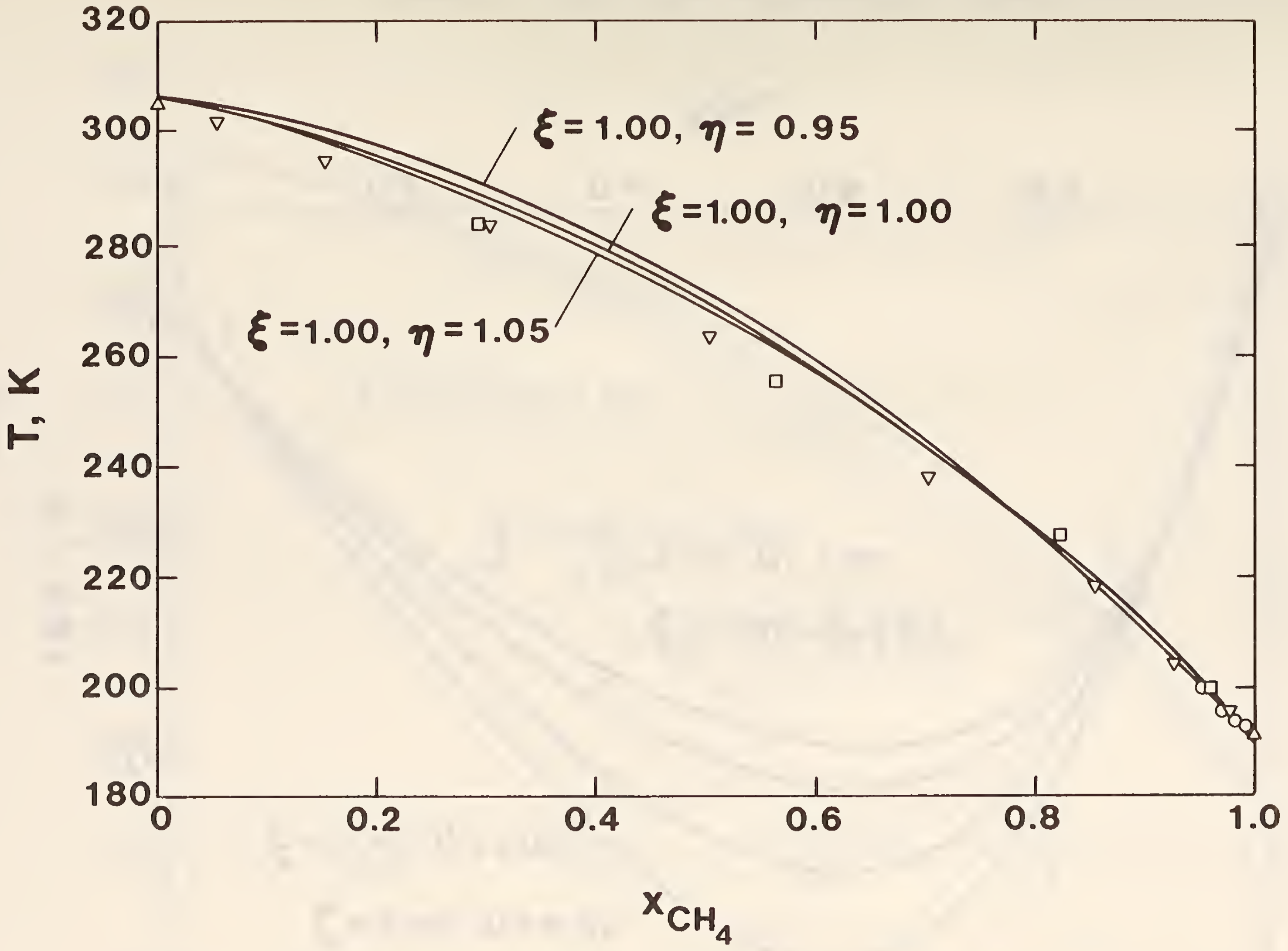

Figure 2. The methane-ethane T-x critical plot calculated via extended corresponding states showing the variation caused by the interaction parameter, η. Data [16]: ▽ Bloomer, Gani and Parent; □ Price and Kobayashi; ○ Wicheterle and Kobayashi. The values for the pures, △, are from Goodwin [15] and [19].

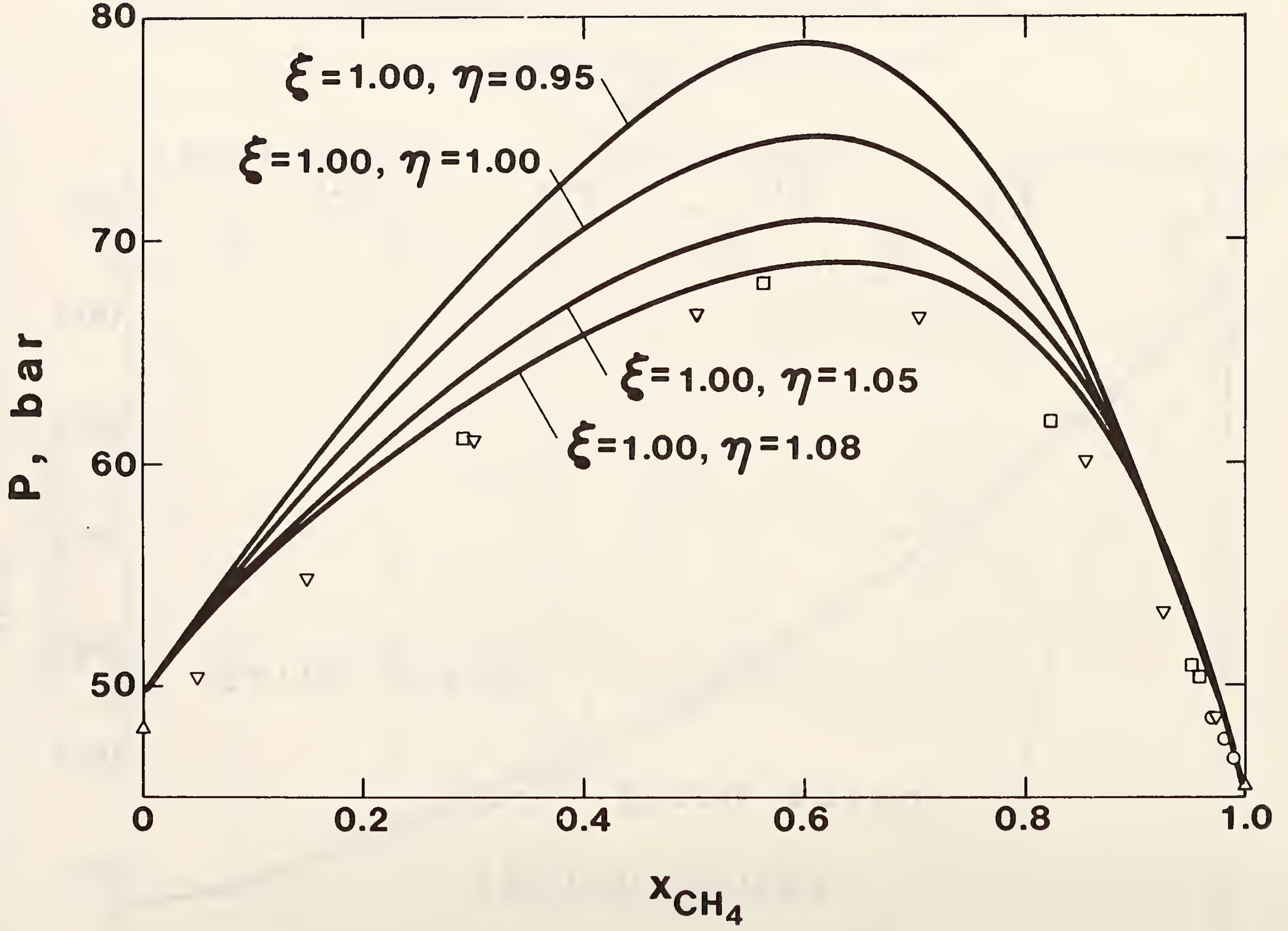

Figure 3. The p-x plot corresponding to figure 2.

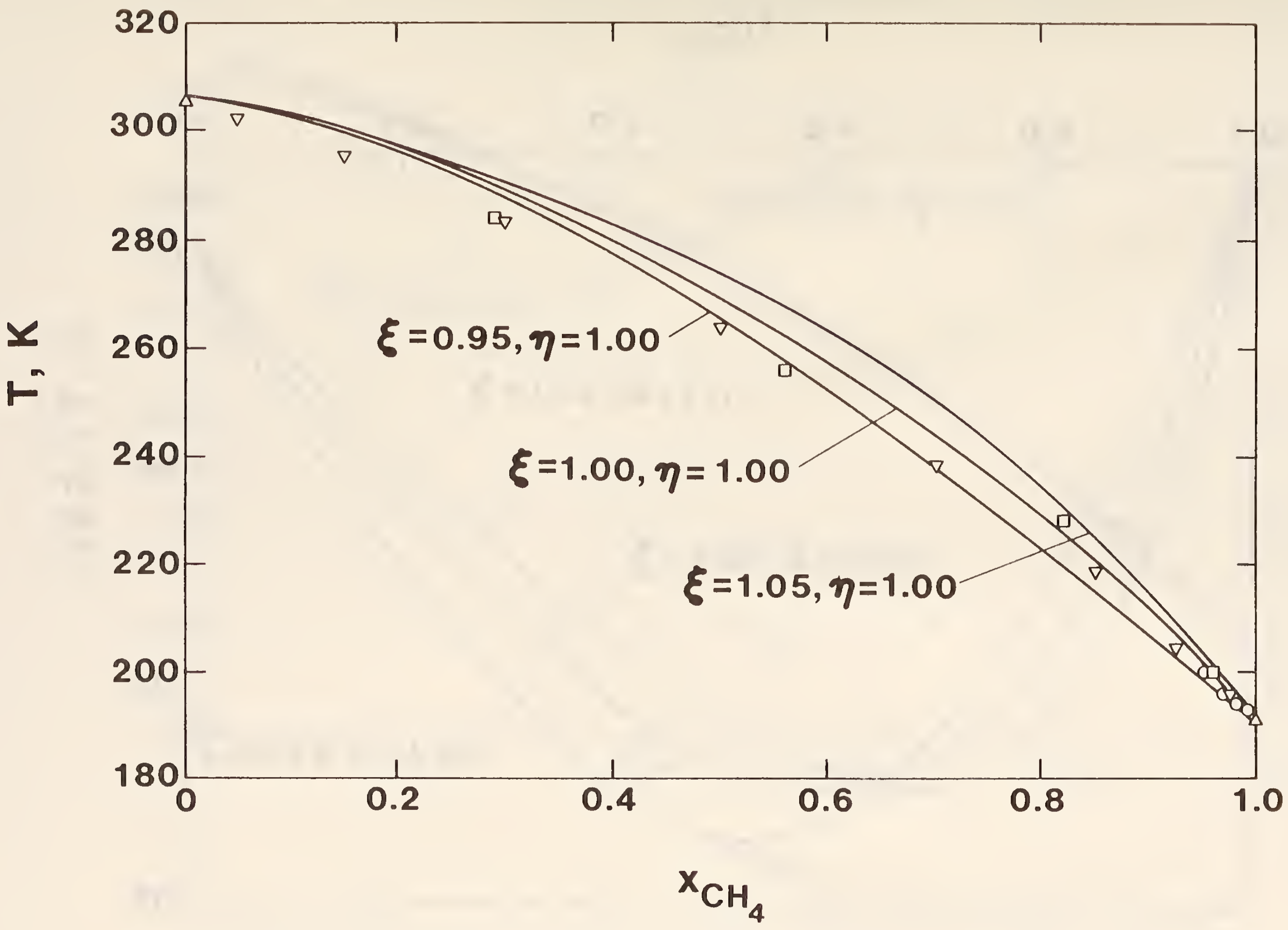

Figure 4. Variation of the parameter, ξ, for methane-ethane in the T-x plot.

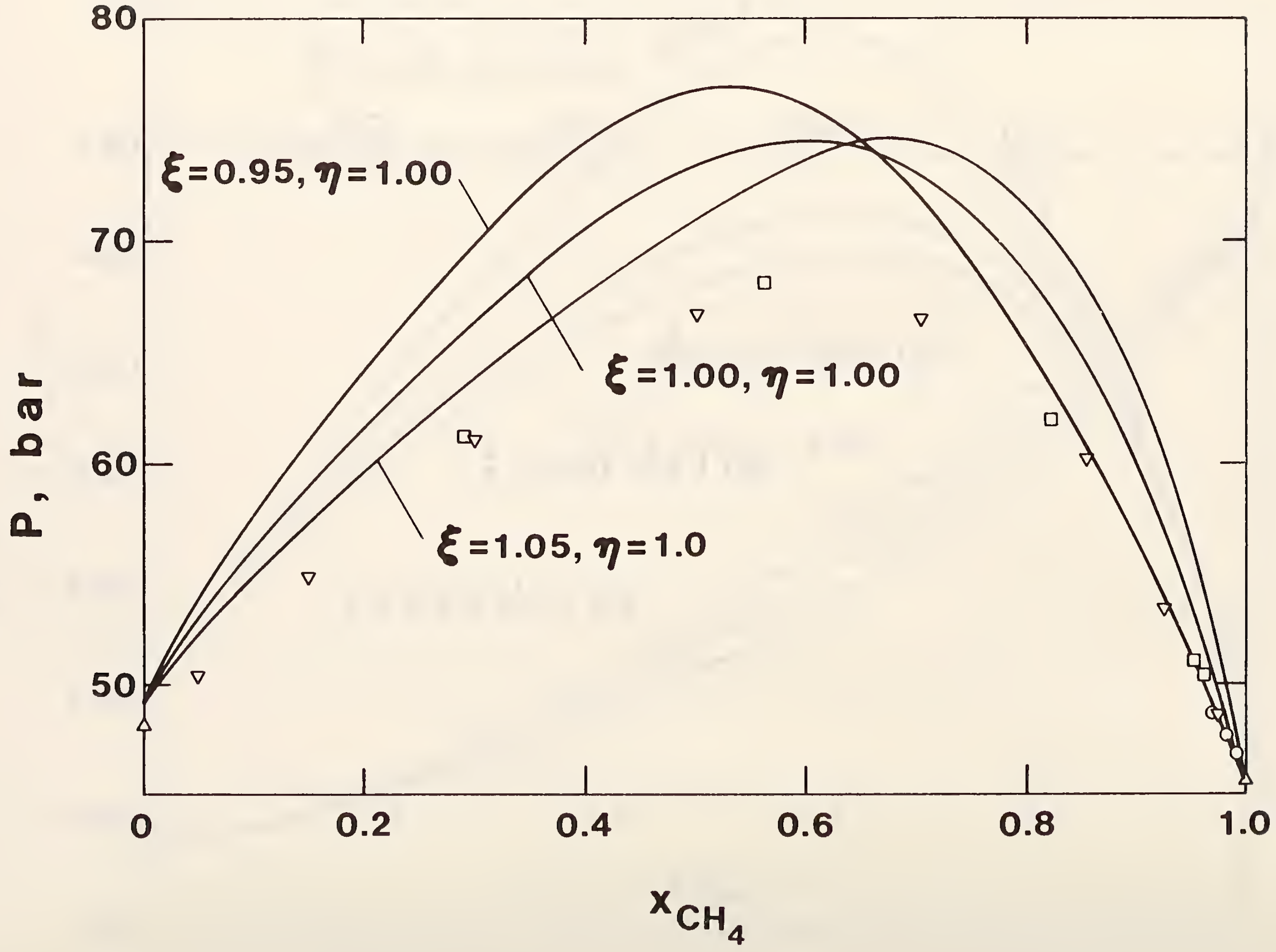

Figure 5. The p-x plot corresponding to figure 4.

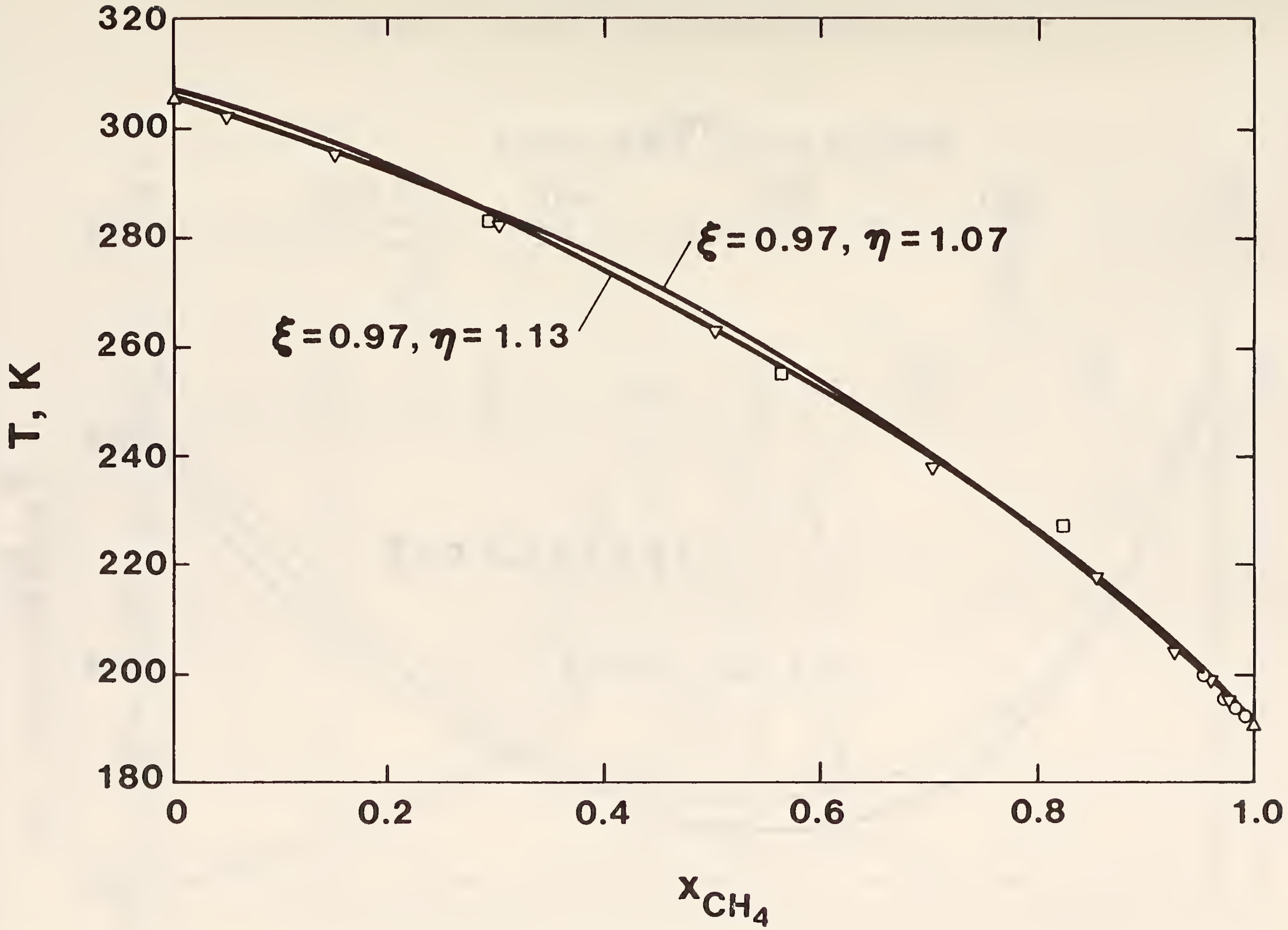

Figure 6. The T-x critical line of methane-ethane with optimized interaction parameters. The two curves correspond to extended corresponding states [$\xi = 0.97$, $\eta = 1.13$] and the classical corresponding states with $\omega_\alpha = \omega_0$ [$\xi = 0.97$, $\eta = 1.07$].

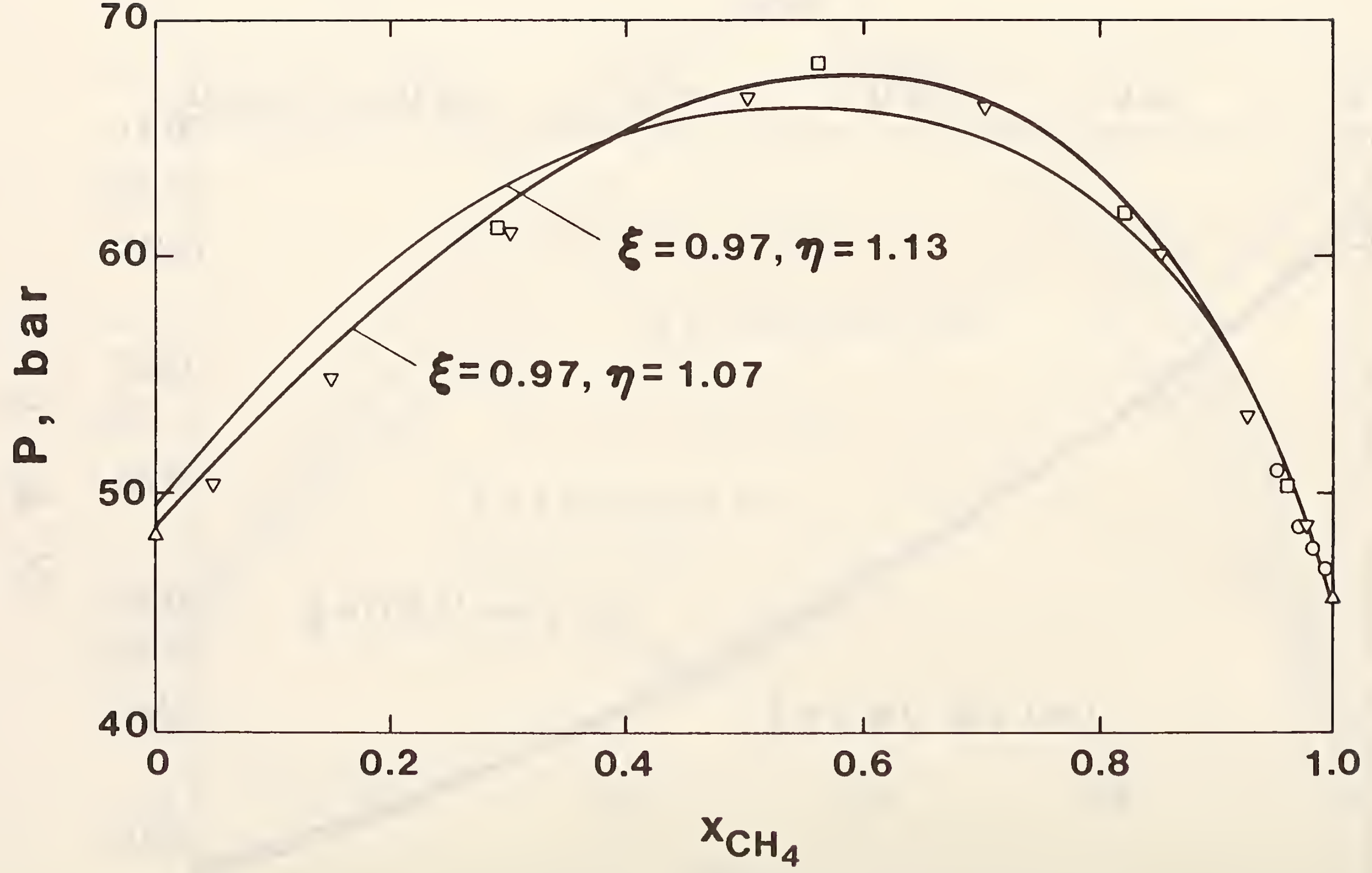

Figure 7. The p-x plot corresponding to figure 6.

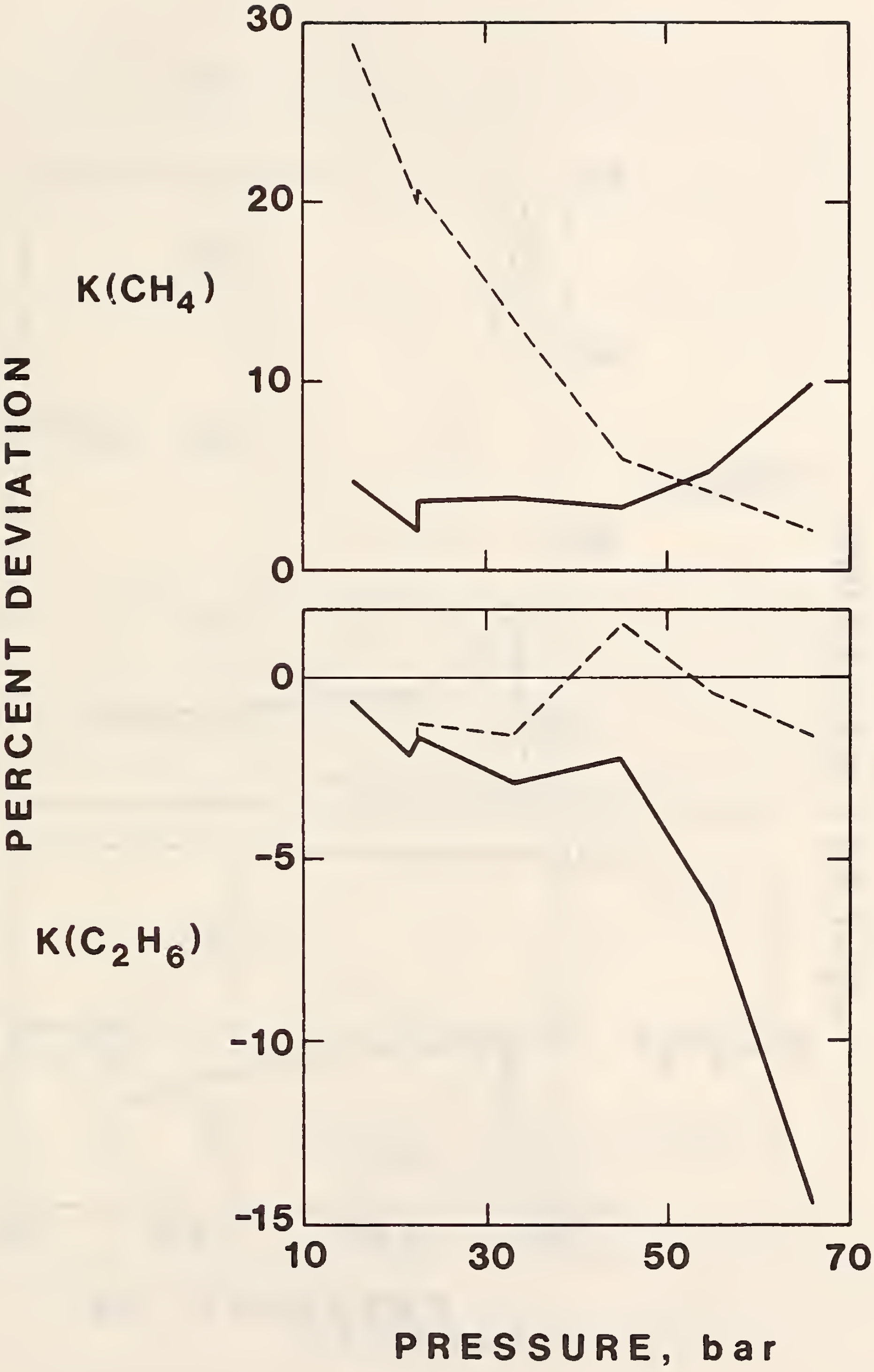

Figure 8. Methane-ethane K-value deviation plots at 250 K. Shown are the (dashed) curves with the interaction parameters from the critical line fit [$\xi = 0.97$, $\eta = 1.07$] and, for reference, with $\xi = \eta = 1.00$ as the solid curves.

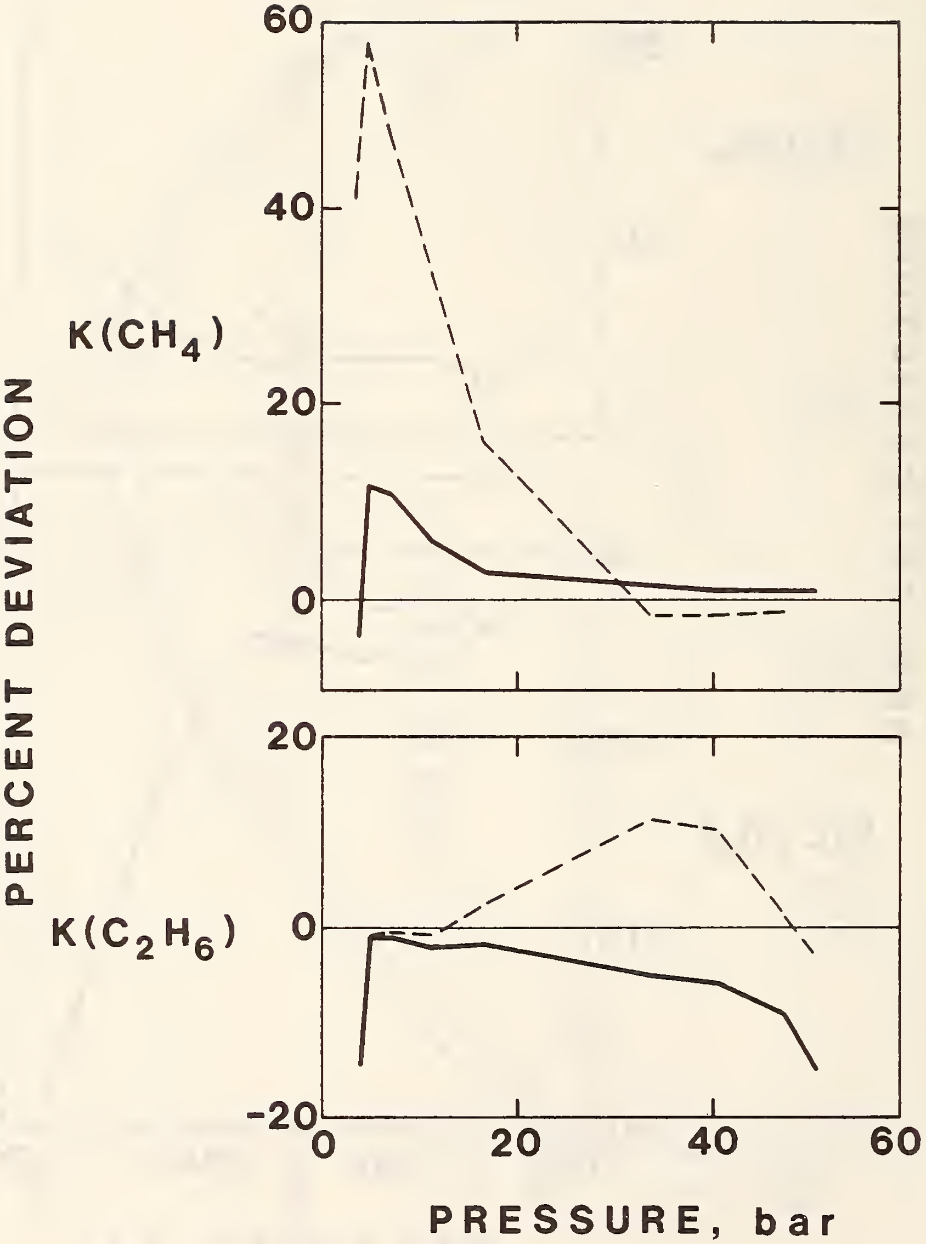

Figure 9. Methane-ethane K-values at 199.92 K.

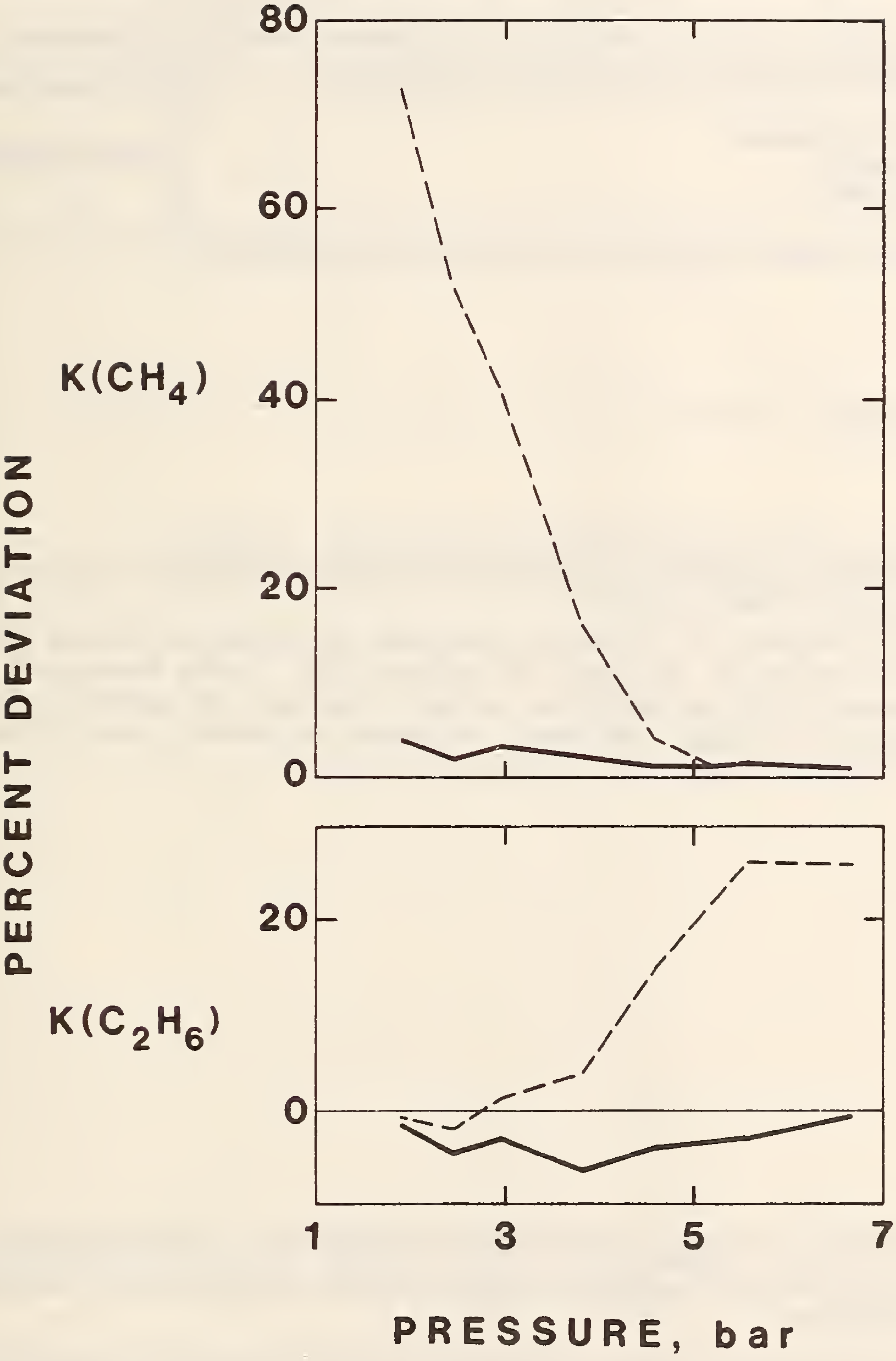

Figure 10. Methane-ethane K-values at 144.26 K.

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This Technical Note reports an informal conference on phase equilibria held at the National Bureau of Standards, Boulder, in October 1980. Talks were given on extended corresponding states, critical behavior, mixing rules and, in general, the prediction of the phase behavior of simple mixtures. A survey of methods used in industry was also presented. Suggested work for the future is given.

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