

## ABSTRACT

### DEVELOPMENT OF PSEUDOCRITICAL MIXTURE RULES APPLICABLE TO THERMODYNAMIC CALCULATIONS IN THE CRITICAL REGION

by John Douglas Stevens

Phase equilibria and other properties of fluid mixtures in the critical region may be computed thermodynamically if equations of state applicable to this region are available. Such equations of state usually have generalized forms involving two or more constants and are used in conjunction with mixture rules which express these constants as functions of composition. The eight constant Benedict-Webb-Rubin equation of state<sup>1</sup> has yielded reasonably satisfactory computations of this type.

This research work was directed toward establishing satisfactory mixture rules which may be used with a two constant reduced equation of state. The derived reduced equation of state was based on the Benedict-Webb-Rubin equation for propane. Pseudocritical mixture rules express these quantities as a function of composition. The criterion used to evaluate a mixture rule was its ability to predict conditions along the critical envelope curve. This is the boundary of the two phase region, and also represents the pressure at which the equilibrium ratios converge to unity.

Because of the complexity of the relations involved, computations were programmed on a CDC 3600 computer. Among the programs written and tested were the following: (a) Computation of compressibility factor and reduced pressure from reduced temperature and density using the corresponding states principle with propane, butane, and other hydrocarbons as reference materials. (b) Computation of derived thermodynamic properties

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including the second and third partial derivatives of free energy with respect to mole fraction at constant temperature and pressure. (c) Computation of critical envelope curves by simultaneously converging the second and third free energy derivatives to zero.

The eight constant Benedict-Webb-Rubin equation of state gave values of critical pressure, temperature, and compressibility factor for the ethane-n-heptane system which were in good agreement with Kay's<sup>2</sup> experimental data. With the two constant reduced equation of state, good agreement was obtained for a binary mixture using the following mixture rules:

$$P_{c_m} = \left[ \frac{\sum_{i=1}^2 x_i (T_{c_i}/P_{c_i})^{1/2}}{\sum_{i=1}^2 x_i (T_{c_i}/P_{c_i})} \right]^2$$

$$T_{c_m} = \left[ \frac{\sum_{i=1}^2 x_i (T_{c_i}/P_{c_i})^{1/2}}{\sum_{i=1}^2 x_i (T_{c_i}/P_{c_i})} \right]^2 \sum_{i=1}^2 x_i (T_{c_i}/P_{c_i})$$

where  $T_{c_i}$  and  $P_{c_i}$  are the critical temperature and pressure, respectively, of pure component  $i$ , and  $T_{c_m}$  and  $P_{c_m}$  are the pseudocritical temperature and pressure, respectively, of the mixture.  $x_i$  is the mole fraction of component  $i$  in the mixture.

Attempts were made to develop programs for generating pseudocritical pressures and temperatures from experimental data on true critical temperature, pressure, and density. All approaches used the critical properties of the pure components as known conditions. Using an approach which assumed cubic forms for the pseudocritical curves, it was possible to generate pairs of points on these curves. The generated points were in good agreement with the mixture rule suggested above.

<sup>1</sup>Benedict, M., G. B. Webb, and L. C. Rubin, J. Chem. Phys., 8, 334 (1940).

<sup>2</sup>Kay, W. B., Ind. Eng. Chem., 30, 459 (1938).

DEVELOPMENT OF PSEUDOCRITICAL MIXTURE RULES APPLICABLE  
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## INTRODUCTION

The chemical engineer often performs calculations requiring a knowledge of the values of thermodynamic quantities. This is especially true with mass transfer processes such as distillation and absorption where successful design of equipment is dependent on accurate vapor-liquid equilibrium data. Because vapor-liquid equilibrium properties are one of the most important thermodynamic quantities to a chemical engineer, this thesis is oriented towards obtaining a mixture rule which could be used to compute more accurate vapor-liquid equilibria in the most sensitive region, the critical region.

In the critical region, the equilibrium ratio (vapor mole fraction divided by liquid mole fraction) approaches one at the critical envelope curve (convergence pressure curve). This curve, which represents the border of the two phase region, is the locus of true critical temperatures and pressures for a multicomponent system. In order for a method of computation to be satisfactory in the critical region, it must predict the equilibrium ratio to be one, at temperatures and pressures corresponding to the critical envelope curve. Or conversely, if the equilibrium ratio is equal to one, the method must give the temperature and pressure to be equal to the critical temperature and pressure.

There are two methods currently favored for calculating vapor-liquid equilibria at high pressures. One of these methods, the convergence pressure method, involves estimation of the shape of the critical envelope curve. This is generally done for the system under consideration on the basis of data for other systems. Equilibrium ratios are then obtained from empirical equilibrium ratio charts (K-charts) using convergence pressure as a parameter. The second method, the equation of state method, is

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based on equations of state for the pure components plus a mixture rule. Equations of state are approximations of actual physical behavior and have generalized forms involving pressure, temperature, and volume (or density) plus two or more constants. Mixture rules express these constants as functions of composition. An equation of state used in conjunction with a mixture rule provides a means of computing thermodynamic quantities, including equilibrium relationships, for mixtures.

The convergence pressure method has its greatest accuracy in the critical region, but this is because it is based on experimental data in that region. However, the convergence pressure method becomes less accurate at lower pressures; it is not amenable to the calculation of other thermodynamic properties, and if extended very far from the region of the experimental data, it can lead to results which are thermodynamically impossible. The equation of state method has all of the advantages of thermodynamic consistency. The equilibrium ratios computed at low and moderate pressures are very satisfactory, but considerable errors are often encountered at high pressures near the critical region.

If a more accurate equation of state could be developed for mixtures, through the development of better mixture rules, then the equation of state method would be a much more satisfactory method for calculating equilibria. This method would then permit the calculation of other thermodynamic data, and it would require less specific experimental data than the convergence pressure technique.

The objective of this research was to obtain a better equation of state for mixtures at high pressures. The method used was to derive a reduced equation of state and then to attempt to find or develop pseudo-critical mixture rules which when used with the reduced equation of state, would yield accurate thermodynamic predictions in the critical region.

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A reduced equation of state has only two constants; in this work these were pseudocritical temperature and pressure. Pseudocritical mixture rules express pseudocritical temperature and pressure as a function of composition. The criterion used for evaluating mixture rules was to use them in conjunction with an equation of state to predict the critical envelope curve (convergence pressure curve) for a particular multicomponent system and compare these predictions with experimental data.

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## BACKGROUND

Accurate methods for predicting vapor-liquid equilibria have always been a prime requisite of the design chemical engineer. However, most methods developed to date have limitations which greatly restrict their use, and the engineer often must use a combination of methods or may even not have any acceptable method at his disposal.

### General Equilibrium Theory

A system is said to be in equilibrium if there is no apparent change in the intensive properties with respect to time. However, the intensive properties themselves, such as concentration, partial molal enthalpy, density, refractive index, etc., may be different in different phases of the system. The only requirement for equilibrium is that all potentials which cause changes should be in a well balanced state. Therefore, the equilibrium state requires that the temperature (thermal potential) and pressure (mechanical potential) be the same everywhere. In addition, a third potential, the chemical potential, should also be in a balanced state. This is equivalent to stating that the partial molal free energy be the same in all phases for all components.

The balance of the above three potentials is often referred to as the conditions for equilibrium and they may be written symbolically as

$$T_V = T_L \quad (1)$$

$$P_V = P_L \quad (2)$$

$$\bar{F}_{iV} = \bar{F}_{iL} \quad (3)$$

where  $T_V, T_L$  = temperature in the vapor and liquid phases, respectively.

$P_V, P_L$  = pressure in the vapor and liquid phases, respectively.

$\bar{F}_{iV}, \bar{F}_{iL}$  = free energy/mole for component  $i$  in the vapor and liquid phases, respectively.

Condition (3) may also be written

$$f_{iV} = f_{iL} \quad (4)$$

where  $f_{iV}, f_{iL}$  = fugacity of component  $i$  in the vapor and liquid phases, respectively.

The most practical means of expressing vapor-liquid equilibria is in terms of the equilibrium ratio or K-factor which is defined for component  $i$  as

$$K_i = y_i/x_i \quad (5)$$

where  $y_i$  = mole fraction of component  $i$  in the vapor phase.

$x_i$  = mole fraction of component  $i$  in the liquid phase.

Another constant called the vaporization equilibrium constant is sometimes used. This is defined as

$$K_v = a_{iV}/a_{iL} = (\gamma_{iV}y_i)/(\gamma_{iL}x_i) \quad (6)$$

where  $a_{iV}, a_{iL}$  = the activities of component  $i$  in the vapor and liquid phases, respectively.

$\gamma_{iV}, \gamma_{iL}$  = the activity coefficients of component  $i$  in the vapor and liquid phases, respectively.

If ideal solutions are formed in the two phases, then both activity coefficients are unity, and equation (6) reduces to equation (5). Otherwise, the relationship between the two equilibrium constants is

$$K_i = (\gamma_{iL}/\gamma_{iV})K_v \quad (7)$$

The discussion which follows refers to the equilibrium state in terms of the K-factor.

#### Corresponding States Principle

Van der Waals<sup>43</sup> first defined the term "reduced condition" and

presented the corresponding states theorem for all pure gases in 1873.

Young extended this concept to liquids in 1899.

The theorem of corresponding states claims that all pure gases, when compared at the same reduced temperature and reduced pressure, will have the same compressibility factor or, in other words, deviate from perfect gas behavior to the same degree. Reduced temperature and reduced pressure are defined as

$$T_r = T/T_c \quad (8)$$

$$P_r = P/P_c \quad (9)$$

where  $T$  = temperature of the fluid

$P$  = pressure of the fluid

$T_c$  = critical temperature of the fluid

$T_r$  = reduced temperature of the fluid

$P_c$  = critical pressure of the fluid

$P_r$  = reduced pressure of the fluid.

The compressibility factor may be written symbolically as

$$Z = P\bar{V}/RT \quad (10)$$

where  $Z$  = compressibility factor

$\bar{V}$  = volume/mole

$R$  = gas constant

Graphs of compressibility factor as a function of reduced temperature and reduced pressure are found in most thermodynamic texts.<sup>20</sup>

When the corresponding states concept is extended to mixtures, the reduced properties of mixtures based on the true critical properties of the mixture do not give the same functional relations for compressibility factors as for the pure components. In order that compressibility factors for mixtures will follow the same functional relationships as do pure

components, it is necessary to use hypothetical values for the critical properties of the mixture. These hypothetical critical properties are called pseudocritical properties. The pseudocritical temperature and pseudocritical pressure are denoted by  $T_{c_m}$  and  $P_{c_m}$ , respectively. Any property which is put into reduced form by using the pseudocritical property is said to be in the pseudoreduced condition.

#### Low and Moderate Pressure Vapor-Liquid Equilibria

If two pure substances, originally at their respective vapor pressures, are isothermally changed to pressure  $P$  and then mixed to form a two phase mixture, the thermodynamic expression for the equilibrium ratio is (Appendix I)

$$y_A/x_A = P_{AVP} v_{AVP} \gamma_{AL} / (P v_{AP} \gamma_{AV}) L \quad (11)$$

$$\text{where } L = \exp\left[\frac{1}{RT} \int_{P_{AVP}}^P \bar{V}_L dP\right]$$

$P_{AVP}$  = vapor pressure of pure component A

$P$  = total pressure of mixture

$v_{AVP}$  = fugacity coefficient of pure component A at its  
vapor pressure =  $f_{AVP}/P_{AVP}$

$v_{AP}$  = fugacity coefficient of pure component A at  
total pressure  $P$  =  $f_{AP}/P$

$\gamma_{AL}$  = activity coefficient of component A in the liquid  
phase of the mixture

$\gamma_{AV}$  = activity coefficient of component A in the vapor  
phase of the mixture

$\bar{V}_L$  = molal liquid volume of pure component A.

A similar expression may be written for component B.

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Relationship (11) involves the use of experimental vapor pressures and correction for deviations from ideal behavior. It is this relationship which is the basis for many methods of vapor-liquid equilibrium prediction.

If there are no deviations from ideal behavior in either the liquid or vapor phase and if the liquid correction factor (L) may be neglected, equation (11) reduces to Raoult's Law:

$$y_A/x_A = P_{AVP}/P \quad (12)$$

Raoult's Law is limited to the case of a mixture of perfect gases in equilibrium with a liquid phase which is an ideal solution. That is, Raoult's Law is valid when molecules of each component are of approximately the same size and when the pure components mix in both the liquid and gas phases without the complicating effects of molecular association, chemical combination, and the like. Raoult's Law neglects the effect of composition and to some extent, the effect of pressure on the behavior of a component in the vapor and liquid phases.

Fugacity coefficients  $\phi_{AVP}$  and  $\phi_{AP}$  are corrections for imperfect gas behavior due to the effect of volume of and the attraction between the molecules of the vapor. Fugacity coefficient values may be read from the fugacity charts. These are charts of  $f/P$  as a function of reduced pressure and reduced temperature. They were constructed using compressibility factor charts and should be valid as long as the corresponding states principle holds.

Souders, Selheimer, and Brown<sup>38</sup> used the fugacity charts to construct a plot of K-factor as a function of temperature and pressure. They assumed that the liquid and vapor mixtures were ideal solutions, thereby reducing equation (11) to

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$$y_A/x_A = \frac{P_{AVP} v_{AVP}}{P v_{AP}} L \quad (13)$$

Since  $v = f/P$ , equation (13) becomes

$$y_A/x_A = f_{AVP}^L/f_{AP} = f_{AL}/f_{AV} \quad (14)$$

where  $f_{AV}$  = fugacity of pure vapor A at the pressure and temperature of the system.

$f_{AL} = f_{AVP}^L$  = fugacity of pure liquid A at the pressure and temperature of the system.

K-charts were constructed for several of the hydrocarbons.

The quantities  $\gamma_{AL}$  and  $\gamma_{AV}$  are called activity coefficients and are corrections for deviations from Amagat's Law in the liquid and vapor phases, respectively. Because of the dense nature of liquid solutions,  $\gamma_{AL}$  is much more important than  $\gamma_{AV}$  at low and moderate pressures. At pressures near the critical where both phases are quite similar,  $\gamma_{AV}$  becomes a factor. The deviations from Amagat's Law behavior are due to the fact that attractions between similar molecules are different than attractions between dissimilar molecules.

Activity coefficients are composition dependent and hence, whenever they are equal to anything except unity, the K-factor is composition dependent. The methods that have been used for predicting activity coefficients are either empirical or semitheoretical, the theoretical part being the use of thermodynamic equations to direct the development of empirical rules. Many rules have been proposed, but more commonly the activity coefficients are estimated by such equations as the Wohl, Margules, van Laar, or Redlich and Kister equations.<sup>20</sup>

It should be noted that some authors<sup>37</sup> express activity coefficients as a product of two activity coefficients, each of which corrects for

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different types of deviations. This could be expressed

$$\gamma = \phi \cdot \gamma'$$

where  $\gamma$  = overall activity coefficient

$\gamma'$  = activity coefficient expressing deviations from  
Amagat's Law as a result of chemical dissimilarity

$\phi$  = activity coefficient expressing deviations from  
Amagat's Law as a result of molecular size or  
volatility.

If a system is composed of a homologous series, then  $\gamma' = 1$ .

The liquid volume correction term (L) in equation (11) is a correction for the difference between the fugacity of the liquid at the system pressure and the fugacity at the pure component's vapor pressure. This term is generally not important at low and moderate pressures although it may be calculated any time the liquid molal volume is known or an equation of state is available.

By introducing additional parameters into the corresponding states principle, more accurate fugacity predictions can be made. Pitzer<sup>30</sup> has extended the corresponding states principle by using a third parameter. Although others had previously suggested a third parameter, none of the methods proposed were as successful as Pitzer's. He called the new parameter the acentric factor, which is supposedly a measure of the deviation of the intermolecular potential function from that of simple spherical molecules. The compressibility factor Z may then be written

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

where  $\omega$  = acentric factor.

Hougen, Watson, and Ragatz<sup>20</sup> also used a three parameter approach.

They calculated equilibrium ratios as a function of the critical

compressibility factor, reduced temperature, and reduced pressure. A value of 0.27 was used for the critical compressibility factor in construction of a table and a chart, but corrections were given for values of critical compressibility factor other than 0.27. The table and chart are not accurate at high pressure and temperature because the assumption of ideal solutions in the liquid and vapor phase is no longer valid. Also, both the Pitzer and Hougen methods are limited by the accuracy of the rules used to calculate the pseudocritical properties.

Bloomer and Peck<sup>7</sup> also modified the corresponding states principle by introducing a third parameter S. This parameter takes into account the aspherical factor for nonpolar molecules. S is determined from P-V-T data and can be expressed in a simple relationship to the critical compressibility factor.

#### High Pressure Vapor-Liquid Equilibria

Two basically different approaches can be used for prediction of vapor-liquid equilibria near the critical region. These are (1) equilibria from an equation of state and (2) convergence pressure methods.

The most commonly used equation of state for prediction of high pressure equilibria is the Benedict-Webb-Rubin equation.<sup>3</sup> This equation uses eight constants to describe the vapor and liquid phase behavior of a given compound. The authors published a set of constants for each of twelve light hydrocarbons. They also suggested mixture rules for combining the eight constants to extend the equation of state to mixtures.<sup>4</sup> However, Price et al<sup>32</sup> indicate substantial deviations between experimental K-factors and those predicted by the Benedict-Webb-Rubin mixture equation. Hester<sup>17</sup> has shown that the Benedict-Webb-Rubin mixture equation also may yield highly improbable values for the pseudocritical compressibility

factor.

Benedict, Webb, Rubin, and Friend<sup>6</sup> recorded K-values of twelve hydrocarbons in a series of 32<sup>4</sup> charts called the Kellogg charts. In order to reduce the number of composition variables, these authors expressed all vapor and liquid compositions in terms of two variables, the molal average boiling points of the vapor and liquid, respectively. Each chart refers to a particular component at a particular pressure.

The Kellogg charts are reliable for many applications, but they require successive corrections for the compositions of both phases. Another disadvantage is the necessity for interpolation between charts with respect to pressure.

These 32<sup>4</sup> charts have been reduced and made easier to apply by DePriester<sup>11</sup> and Edmister and Ruby.<sup>13</sup> The DePriester charts include two for each hydrocarbon, one giving the fugacity ratio for the vapor phase, and the second, the fugacity ratio for the liquid phase. Each chart represents the relation between pressure, temperature, and composition, and thus eliminates the necessity of interpolation between charts with respect to pressure, as with the Kellogg charts. DePriester's consolidation of the information on the Kellogg charts into twenty-four charts was with little loss of accuracy. However, the charts only cover the pressure range up to 1000 psia while the Kellogg charts include pressures up to 3600 psia.

Edmister and Ruby used only six charts plus one table of vapor pressure data to cover the same range of pressure, temperature, and composition as the Kellogg charts. The Edmister and Ruby charts were derived from the Kellogg charts by correlating fugacity coefficients in terms of four reduced parameters. They are in considerably greater error than the

Kellogg and DePriester charts.

Gamson and Watson<sup>14</sup> developed equations for activity coefficients based on generalized fugacity coefficients and the pseudocritical concept. Smith and Watson<sup>37</sup> empirically modified the Gamson and Watson relationships and constructed a graphical correlation of activity coefficients as functions of the pseudocritical temperatures and pressures of the phases. These generalized correlations are applicable to systems of components of no chemical dissimilarity. On the basis of these correlations, Smith and Smith<sup>36</sup> published a set of K-charts for hydrocarbons. The generalization of the Smith and Smith charts causes some loss of accuracy for specific data. However, this generalization does allow the charts to be used for many more hydrocarbons than the Kellogg charts.

Recently Mehra and Thodos<sup>27</sup> have developed an approach which is fundamentally different from existing methods for the development of equilibrium correlations from experimental data. They predict K-factors for binary hydrocarbon systems in the critical region by using the normal boiling point ratio, the reduced vapor pressure, and the pseudoreduced vapor pressure. Good accuracy is obtained with the correlations, but the limitations to a binary hydrocarbon system limit the practicality of the method.

All of the methods presented above may be classified as theoretical. Correlations of K-factors based on experimental data were developed about the same time as the Kellogg charts and modifications thereof. These empirical correlations have the advantage of being based on experimental data and are, therefore, very accurate in the region where the experimental data was obtained. However, the experimental correlations are not amenable to the calculation of other thermodynamic properties, and the

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correlations are only valid in the range of the experimental data.

The most prominent of the empirical approaches is the convergence pressure method. The standard procedure is to predict convergence pressure based on experimental data for various binary systems and then extend the method to multicomponent systems by treating the mixture as a fictitious binary system.<sup>34,45</sup> Lenoir and White<sup>26</sup> developed an improved method using effective boiling points for predicting the convergence pressure. Once the convergence pressure is known, the K-factor is found from empirical correlations between equilibrium ratios and the estimated convergence pressure. The NGAA (Natural Gasoline Association of America) charts<sup>28</sup> were prepared for prediction of K-factors using the convergence pressure technique. The convergence pressure method is relatively convenient to use and gives acceptable results in the critical region.

#### Comparison of Vapor-Liquid Equilibrium Prediction Methods

The methods discussed above for predicting vapor-liquid equilibria are compared in Table 1. The construction of such a table is a matter of judgement and should be taken only as a general indication of the strong and weak points of the methods discussed above. Question marks mean that it is difficult to determine if the method is thermodynamically consistent. One of the aims of this research was to devise a method which would exhibit all of the properties listed in the table.

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TABLE 1. Comparison of vapor-liquid equilibrium prediction methods

| Method                  | General-<br>ized | Composition<br>Dependent | Accuracy |               |           |          | Thermo.<br>Consist.<br>Region |
|-------------------------|------------------|--------------------------|----------|---------------|-----------|----------|-------------------------------|
|                         |                  |                          | Low<br>P | Moderate<br>P | High<br>P | Critical |                               |
| Raoult's Law            | Yes              | No                       | Yes      | No            | No        | No       | Yes                           |
| Souders <u>et al.</u>   | No               | No                       | Yes      | Yes           | No        | No       | Yes                           |
| Hougen-Watson           | Yes              | No                       | Yes      | Yes           | No        | No       | Yes                           |
| B-W-R Eqn.              | No               | Yes                      | Yes      | Yes           | Yes       | Yes      | Yes                           |
| Kellogg charts          | No               | Yes                      | Yes      | Yes           | Yes       | No       | ?                             |
| DePriester              | No               | Yes                      | Yes      | Yes           | Yes       | No       | ?                             |
| Edmister-Ruby           | Yes*             | Yes                      | Yes      | Yes           | No        | No       | No                            |
| Smith-Smith             | Yes              | Yes                      | Yes      | Yes           | No        | No       | Yes                           |
| Convergence<br>Pressure | No               | Yes                      | Yes      | Yes           | No        | Yes      | No                            |

\*Separate charts are needed for methane

#### Mixture Rules

Success with the equation of state method for calculation of vapor-liquid equilibria is dependent on the accuracy of the mixture rules used. A mixture rule is some arbitrary procedure for converting an equation of state for pure compounds into an equation of state for a mixture of those compounds.

Equations of state for pure compounds are generally converted to equations of state for mixtures by some method of combining the equation of state constants. Amagat's, Dalton's, and Bartlett's rules<sup>44</sup> are simple mixture rules, but they are not applicable in the critical region. Examples of more sophisticated mixture rules are those of Benedict et al.<sup>4</sup> They converted their equation of state to mixtures by specifying rules for

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combining the eight constants ( $A_0, B_0, C_0, a, b, c, \alpha, \gamma$ ) for the pure components into corresponding constants for the mixture.

A reduced equation of state only has two constants. When the reduced equation is used for a pure compound these constants are the critical temperature and pressure of that compound. For mixtures the two equation constants are the pseudocritical temperature and pressure of the mixture. These pseudocritical quantities are generally expressed as a function of the critical properties of the pure components and the composition of the mixture. Such relationships are called pseudocritical mixture rules.

#### Pseudocritical Mixture Rules

Kay<sup>22</sup> defined the pseudocriticals for a mixture of  $n$  components as

$$T_{c_m} = \sum_{i=1}^n x_i T_{c_i} \quad (15)$$

$$P_{c_m} = \sum_{i=1}^n x_i P_{c_i} \quad (16)$$

For binary mixtures, Tang<sup>40</sup> found that a simple additive relationship was a fair approximation for critical temperature, but the pseudocritical pressure usually deviated widely from linearity. Case and Weber<sup>9</sup> also observed large deviations from Kay's rule.

Van der Waals<sup>20</sup> suggested the following pseudocritical mixture rules for use in the reduced form of his equation of state.

$$P_{c_m} = \left[ \sum_{i=1}^n x_i (T_{c_i}/P_{c_i})^{1/2} \right]^2 / \sum_{i=1}^n x_i (T_{c_i}/P_{c_i}) \quad (17)$$

$$T_{c_m} = \left[ \sum_{i=1}^n x_i (T_{c_i}/P_{c_i})^{1/2} \right]^2 / \sum_{i=1}^n x_i (T_{c_i}/P_{c_i}) \quad (18)$$

Joffe<sup>21</sup> used the van der Waals equation of state to show that the assignment of a pseudocritical temperature and pressure to a mixture is

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entirely consistent with the method of combination of equation of state constants. As a result, Joffe proposed the following relations for computing pseudocritical constants of a gas mixture:

$$(T_c/P_c)^{1/2}_m = \sum_{i=1}^n x_i (T_c/P_c)^{1/2}_i \quad (19)$$

$$(T_c/P_c)_m = (1/8) \sum_{i=1}^n \sum_{j=1}^n x_i x_j [(T_c/P_c)_i^{1/3} + (T_c/P_c)_j^{1/3}]^3 \quad (20)$$

where the double summation contains one term for each possible permutation in pairs of like and unlike components of the mixture. Joffe claimed that for five different binary gas mixtures, his proposed mixture rules yielded more accurate rules than Kay's rules. However, although Kay's rule and Joffe's rule are effective for non polar gaseous mixtures, they are in error for saturated vapors and liquids.

Leland, Chappellear, and Gamson<sup>24</sup> proposed the following mixture rules.

$$T_{c_m} = \left[ \frac{\sum_{i=1}^n \sum_{j=1}^n x_i x_j a_i a_j}{\sum_{i=1}^n \sum_{j=1}^n x_i x_j (b_i + b_j)^3} \right]^{1/\alpha} \quad (21)$$

$$P_{c_m} = \left[ \frac{T_{c_m} \sum_{i=1}^n x_i (Z_c)_i}{\sum_{i=1}^n \sum_{j=1}^n x_i x_j (b_i + b_j)^3} \right] \quad (22)$$

$$a_i = (Z_c T_c^{1+\alpha} / P_c)_i^{1/2}$$

$$b_i = (1/2)(Z_c T_c / P_c)_i^{1/3}$$

The parameter  $\alpha$  is an empirically determined function of pressure and the pseudocritical pressure as determined by Kay's rule. This mixture rule is applicable to liquids which may be approximated by simple spherical

molecules.

Stewart, Burkhardt, and Voo<sup>39</sup> simplified equation (20) to

$$(T_c/P_c)_m = 1/3 \sum_{i=1}^n x_i (T_c/P_c)_i + 2/3 \left[ \sum_{i=1}^n x_i (T_c/P_c)_i^{1/2} \right]^2 \quad (23)$$

which is used in conjunction with (19) to compute pseudocritical temperature and pressure. Hougen et al.<sup>20</sup> claim that the Stewart method reduces the average deviations by over fifty percent as compared to the results obtained with Kay's rule.

Guggenheim and McGlashan<sup>15</sup> used the reduced second virial coefficient to propose mixture rules for the pseudocritical temperature and volume. However, because use of the second virial coefficient is sufficient only where deviations from ideality are small, these mixture rules are of little use in vapor-liquid equilibrium calculations.

Prausnitz and Gunn<sup>31</sup> adjusted the mixture rules suggested by Guggenheim and McGlashan to fit experimental data for the second virial coefficient. They suggested the following rules for calculating pseudocritical temperature and pressure.

$$T_{c_m} = [\beta + (\beta^2 + rV_{c_m}\gamma)^{1/2}] / (2sV_{c_m}) \quad (24)$$

$$P_{c_m} = [RT_{c_m}/V_{c_m}] \sum_i y_i Z_{c_i} \quad (25)$$

where  $\beta = \sum_{ij} y_i y_j (V_c T_c)_{ij}$

$$\gamma = \sum_{ij} y_i y_j (V_c T_c^2)_{ij}$$

$$V_{c_m} = \sum_{ij} y_i y_j V_{c_{ij}}$$

$y_i$  = composition of component  $i$

$V_{c_m}$  = pseudocritical volume of mixture

$r, s$  = parameters which are read from a table published by

Prausnitz and Gunn.

The quantities  $T_{c_{ij}}$  and  $V_{c_{ij}}$  are called the characteristic critical temperature and volume, respectively, and are computed from

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

$$V_{c_{ij}} = 0.5(V_{c_i} V_{c_j}) - \Delta V_{c_{ij}}$$

where  $\Delta T_{c_{ij}}$ ,  $\Delta V_{c_{ij}}$  = corrections to the characteristic temperature and volume, respectively.

## THEORY

An equation of state, such as the eight constant Benedict-Webb-Rubin equation,<sup>3</sup> can be used to predict thermodynamic properties in the critical region if accurate mixture rules are available for converting the equation of state to mixtures. The factor which prohibits extensive use of such an equation is the fact that values for the eight constants must be known for each of the components in the mixture. Because these values are difficult to determine, they have been found for only a very limited number of compounds. Thus, although the equation may be very accurate for systems where all the constants are known, the equation is not completely satisfactory because it can not be generalized to mixtures of other compounds.

If an equation of state for pure compounds is put into a reduced form, it is changed to an equation with two constants, for example, critical temperature and pressure. If this reduced equation of state is applied to mixtures, the constants become the pseudocritical temperature and pressure since the true critical temperature and pressure of mixtures are known to give inaccurate reduced relationships. Pseudocritical temperature and pressure are usually expressed as a function of the critical properties of the pure components and the composition of the mixture. These relationships, called pseudocritical mixture rules, are difficult to derive because pseudocritical temperature and pressure have no actual physical significance. However, if a reduced equation of state and pseudocritical mixture rules could be found which together would give accurate thermodynamic predictions in the critical region, one could apply the reduced equation of state to many systems with only knowledge about the critical properties of the pure components. This research concerned the derivation of pseudocritical mixture rules for light hydrocarbon systems,

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but most likely such derived mixture rules could be used for many other classes of compounds.

A big advantage of making thermodynamic calculations with a reduced equation of state is that the calculations only need to be performed once for a given reduced temperature and pressure.\* Any other mixture with the same reduced temperature and pressure will have the same value for the thermodynamic quantity. Thus generalized tables or graphs can be prepared with reduced temperature and pressure as parameters.

Vapor-liquid equilibrium calculations can be made with a reduced (generalized) equation of state if the equation is applicable in both the liquid and vapor phases. A plot of the quantity, fugacity divided by mole fraction, as a function of reduced temperature and pressure can be made by using the reduced equation of state to express the fugacity quantity as a function of reduced temperature and pressure. To calculate equilibrium ratios with such a chart, the unknown quantities, temperature, pressure, or compositions, are adjusted by trial and error until the sum of compositions in the vapor and liquid phases are each unity, and the condition,

$$f_{iV} = f_{iL}$$

is satisfied for all components in the mixture. The equilibrium ratio is then computed from

$$K_1 = y_1/x_1$$

Although the construction of generalized charts has been possible for some time, such charts are of little use without accurate pseudocritical mixture rules.

\* If a variable is put into a reduced form using a pseudocritical quantity, then it is more proper to speak of the variable as being in a pseudoreduced form. However, the more common practice of denoting pseudoreduced variables as simply reduced variables is used throughout this thesis.

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One approach to obtaining a more accurate method for making thermodynamic calculations in the critical region would be to derive a reduced equation of state and then to find or develop accurate pseudocritical mixture rules for use with the reduced equation of state. The reduced equation of state could be derived using the eight constant Benedict-Webb-Rubin equation for a particular compound, for example, propane. If the corresponding states principle is valid, the derived reduced equation of state should be the same no matter what reference compound is used.

Currently available mixture rules could be evaluated by using them with the reduced equation of state to predict vapor-liquid equilibria (convergence pressure curve) in the critical region and then comparing the results with experimental data. Or conversely, pseudocritical mixture rules could be derived by beginning with experimental critical region vapor-liquid equilibrium data (i.e. an experimental convergence pressure curve) and then computing pseudocritical temperature and pressure.

#### Definitions of Critical Point and Convergence Pressure

The critical point of a binary mixture is defined as the temperature and pressure at which the vapor and liquid phases of the mixture become indistinguishable. Or, in other words, the temperature and pressure at which the K-factor equals one. If the critical points are measured for several different mixture compositions, and these points are plotted on a pressure-temperature diagram, the curve which passes through all of the critical points is called the critical envelope curve. Such a curve is illustrated in Figure 1. Points A and B represent the critical points for the two pure components, while the intermediate points represent critical points of mixtures. Curve AB, which connects all of the points, is the critical envelope curve.

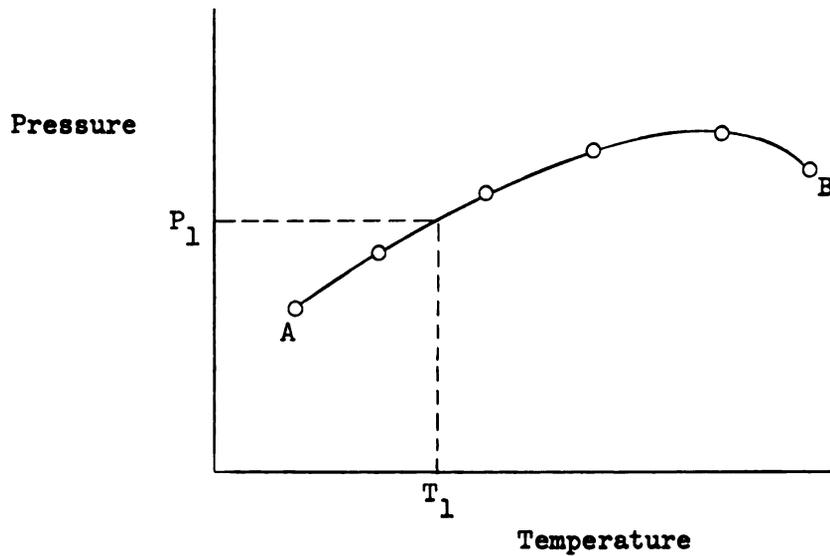


Figure 1. Illustration of a critical envelope curve

Convergence pressure is defined as the critical pressure at the temperature of the system. Thus, in Figure 1, the convergence pressure of any system at temperature  $T_1$  is the pressure  $P_1$ . Therefore, curve AB is also called the convergence pressure curve.

#### Thermodynamic Relations at the Critical Point

Because prediction of the critical envelope curve (convergence pressure curve) is equivalent to predicting the points where the K-factors equal one, it would be very desirable to have a means of calculating the critical envelope curve. This would be possible if there were thermodynamic conditions which held only at the critical point and in fact, provided a basis of definition of the true critical point. Such relationships do exist,<sup>12</sup> and they are:

$$\left(\frac{\partial^2 F}{\partial x^2}\right)_{T,P} = 0 \quad (1)$$

$$\left(\frac{\partial^3 F}{\partial x^3}\right)_{T,P} = 0 \quad (2)$$

when  $T$  and  $P$  are the true critical temperature ( $T_k$ ) and pressure ( $P_k$ ), respectively.

Relations (1) and (2) can be illustrated with a  $F$ -composition curve.

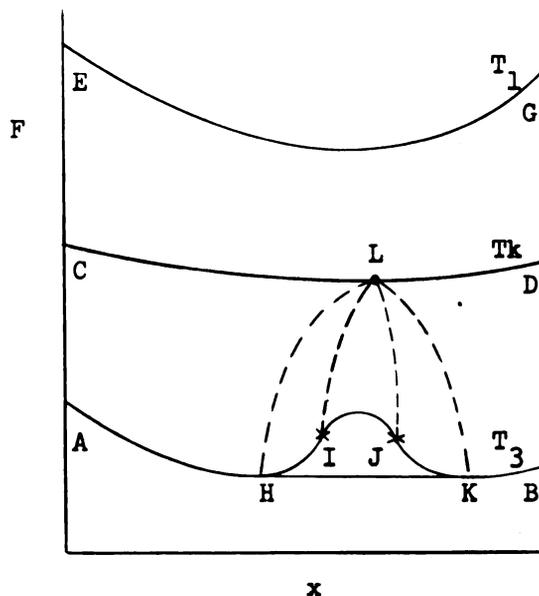


Figure 2. Free energy at constant pressure and temperature as a function of composition

In Figure 2, the  $F$ -curve at  $T_1$  ( $T_1 > T_k$ ) is concave upwards everywhere.

That is,

$$\left(\frac{\partial^2 F}{\partial x^2}\right)_{T_1, P} > 0$$

thus, all homogenous phases on curve  $EG$  are stable. On curve  $AB$  ( $T_3 < T_k$ ), segments  $AI$  and  $JB$  are concave upwards; these phases are also stable.

Between  $I$  and  $J$ , the curve is convex upwards:

$$\left(\frac{\partial^2 F}{\partial x^2}\right)_{T_3, P} < 0$$

and these phases are unstable.

Points  $I$  and  $J$  are inflection points, for which

$$\left(\frac{\partial^2 F}{\partial x^2}\right)_{T_3, P} = 0$$

and therefore, represent the limits of stability. If the temperature is varied in the direction of the critical point, the phases H, I, J, and K approach each other, and, at the critical temperature, become identical. If CD is the F-curve at the critical temperature  $T_k$ , the point L, representing the critical phase where the points H, I, J, and K coalesce, is a point of undulation at which conditions (1) and (2) hold.

By dividing the free energy  $\bar{F}$  by the gas constant R and temperature T, dimensionless free energy G is defined. That is,

$$G = \bar{F}/RT \quad (3)$$

Relationships (1) and (2) can now be written:

$$\left(\frac{\partial^2 G}{\partial x^2}\right)_{T,P} = 0 \quad (4)$$

$$\left(\frac{\partial^3 G}{\partial x^3}\right)_{T,P} = 0 \quad (5)$$

when  $T = T_k$

$P = P_k$

Because the temperature is  $T_k$  and the pressure is  $P_k$  on a convergence pressure curve, conditions (4) and (5) hold at any interior point on that curve. It should be realized that the derivatives in (4) and (5) are equal to zero because of a physical condition of free energy at the true critical point and not because of a mathematical definition. Therefore, fourth and higher order derivatives of free energy are not necessarily equal to zero at the critical point.

#### Expression for Free Energy

A general expression for computing dimensionless free energy G can be derived for a binary mixture at temperature T and pressure P by using the path in Figure 3. Note that the free energy expression need only be derived for one of the phases, since the amount of free energy is the same

in both the liquid and vapor phases. The path shown in Figure 3 is for the vapor phase.

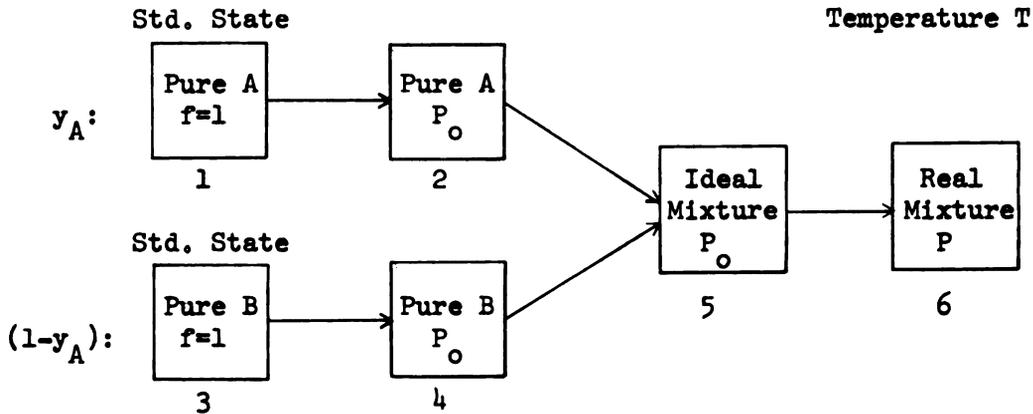


Figure 3. Path for calculation of the free energy of a binary mixture at temperature T and pressure P.

Using the path in Figure 3, it is shown in Appendix II that the expression for G is

$$G = \ln P + y_A \ln y_A + (1 - y_A) \ln(1 - y_A) + Z - 1 - \ln Z + \int_0^D [(P/RT - D)/D^2] dD \quad (6)$$

where D = density.

The first three terms represent the free energy of a mixture of perfect gases at pressure P. The last four terms are a measure of the non-ideality of the imperfect gas mixture. It should be observed that by following the path of Figure 3, it is not necessary to be concerned with nonideal solutions since the gases are in the perfect gas state when they are mixed.

#### Corresponding States Theorem for Mixtures

One of the basic assumptions made in this work was that the corresponding states theorem was applicable to mixtures. That is, it was assumed that two parameters (reduced temperature and pressure) were sufficient

to represent the state of the mixture. The following discussion concerns the theoretical support available for applying this theory to pure compounds and to mixtures.

After van der Waals<sup>43</sup> proposed the corresponding states principle in the late nineteenth century, many years elapsed before enough knowledge was gained about molecular behavior to support the hypothesis theoretically. During this period, the belief that the state of a system could be represented by just two parameters had only empirical justification. With the advent of classical statistical mechanics, a means was obtained to give the proposal theoretical support.

Hirschfelder, Curtiss, and Bird<sup>18</sup> applied classical mechanics to spherical nonpolar gases to show that reduced pressure is a unique function of reduced temperature and volume. Pitzer<sup>29</sup> showed a similar result for liquids while Guggenheim and McGlashan<sup>15</sup> extended the treatment to mixtures of slightly imperfect gases. In these three works the primary assumption was that the energy of interaction between any two molecules was representable by the same general function of two parameters. That is, the expression for the potential energy was of the form

$$\psi(r) = \epsilon f(r/\sigma)$$

where  $\epsilon$  and  $\sigma$  are characteristic of the molecular species and  $f$  is the same general function for all molecules. The Lennard-Jones potential is of this two parameter form and represents an approximation to this general function. In each of the works mentioned above the authors were able to show that reduced temperature was a function of  $\epsilon$  and reduced volume a function of  $\sigma$ .

By establishing that the reduced pressure of a mixture of slightly imperfect gases was representable by a single reduced temperature and

volume, Guggenheim and McGlashan<sup>15</sup> provided support to the hypothesis that the corresponding states principle could be extended to mixtures by treating a mixture as if it were a pure compound. Rules which use critical properties of the pure components of a mixture to compute values of reduced temperature and volume (or any other pair of the variables, pressure, temperature, volume) for a mixture are called pseudocritical mixture rules. The development of pseudocritical mixture rules for pressure and temperature was one of the primary goals of this research.

The theoretical support for the corresponding states theorem is very limited. However, it is reasonable to assume that certain classes of compounds (e.g. hydrocarbons) will have a common function  $f$ . If this is the case, the corresponding states theorem appears to have reasonable theoretical justification for its use with mixtures within that class of compounds. A third parameter approach as discussed under Background is one method of extending the corresponding states principle to a variety of classes of compounds. This third parameter serves to make adjustments for differences in the function  $f$  between classes of compounds.

For mixtures, the expressions for reduced temperature, density, and pressure become:

$$T_r = T/T_{c_m}$$

$$D_r = D/D_{c_m}$$

$$P_r = P/P_{c_m}$$

where  $T_{c_m}$ ,  $D_{c_m}$ ,  $P_{c_m}$  = pseudocritical temperature, density, and pressure, respectively.

#### Equation of State

The need for an equation of state is apparent from the last term in equation (6). The Benedict-Webb-Rubin equation of state<sup>3</sup> gives excellent

representation of the critical properties of pure light hydrocarbons. This equation is applicable to both the liquid and vapor phases with the same set of equation constants. The form of the Benedict-Webb-Rubin equation for pure components is

$$P = RTD + (B_0 RT - A_0 - C_0/T^2)D^2 + (bRT - a)D^3 + \alpha \alpha D^6 + (cD^3/T^2) (1 + \gamma D^2) \exp(-\gamma D^2) \quad (7)$$

where  $A_0$ ,  $B_0$ ,  $C_0$ ,  $a$ ,  $b$ ,  $c$ ,  $\alpha$ ,  $\gamma$  = Benedict-Webb-Rubin equation constants which are dependent on the substance the equation is to describe.

Benedict et al.<sup>3</sup> suggested that  $C_0$  be expressed as a function of temperature, if it was hoped that the equation of state would represent vapor pressures at the subatmospheric level. In this way the equation of state was made extremely accurate at very low pressure as well as in the critical pressure region. The importance of this property to this research was that any mixture rule which was devised could be used at lower pressures if the equation of state was also applicable in that region. Therefore,  $C_0$  was expressed as a function of temperature. This expression is equation (1) on page 115.

Assuming the corresponding states theorem is valid, the expressions for reduced temperature, density and pressure can be substituted into equation (7) to give a reduced equation of state. Similarly, equation (7) can be substituted into equation (6) and the resulting expression put into reduced form by the reduced relationships listed above. The analytical expressions for  $(\partial^2 G/\partial x^2)_{T,P}$  and  $(\partial^3 G/\partial x^3)_{T,P}$ , in terms of reduced parameters, can then be used to evaluate or derive pseudocritical mixture rules in the critical region by using the thermodynamic conditions that  $(\partial^2 G/\partial x^2)_{T,P}$  and  $(\partial^3 G/\partial x^3)_{T,P}$  equal zero at the critical point.

Experimental critical point data can be used as a check on the results computed from available mixture rules or it can be used as the basis for deriving pseudocritical mixture rules.

## STATEMENT OF THE MATHEMATICAL PROBLEM

This chapter summarizes, in mathematical form, relationships used in this thesis. The discussion is divided into four sections: (1) the search for an equation of state on which to base the derivation of a reduced equation of state, (2) evaluation of published pseudocritical mixture rules, (3) generation of pseudocritical temperature and pressure values on which a new pseudocritical mixture rule could be based, and (4) a numerical method for checking analytically derived derivatives. The method of solution, as attempted in this research, is also discussed.

### Evaluation of Equations of State

In this section two equations of state were evaluated for their ability to predict convergence pressure curves. Each equation was used to compute critical temperature, pressure, and density values for a particular binary system. These computed values were then compared with experimental data. The equation which made the best predictions was used as the basis for the derivation of the reduced equation of state.

The van der Waals<sup>43</sup> and Benedict-Webb-Rubin<sup>3</sup> equations of state were combined with mixture rules recommended by van der Waals and Benedict et al. to form equations of state for mixtures. That is,

van der Waals:

Equation of state  
for pure compounds  
 $P = P(T, D, a, b)$

+

Mixture rules  
 $a = a(x)$   
 $b = b(x)$

→

Equation of state  
for mixtures  
 $P = P(T, D, x)$

B-W-R:

|   |
|---|
| Equation of state<br>for pure compounds<br>$P = P(T, D, a, b, c, A_0,$<br>$B_0, C_0, \alpha, \gamma)$ |
|---|

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|   |
|---|
| Equation of state<br>for mixtures<br>$P = P(T, D, x)$ |
|---|

|   |
|---|
| Mixture rules<br>$a = a(x)$<br>⋮<br>⋮<br>$\alpha = \gamma(x)$ |
|---|

The general expression for dimensionless free energy  $G$  is (page 26):

$$G = \ln P + x \ln x + (1-x)\ln(1-x) + Z - 1 - \ln Z + \int_0^D [(P/RT - D)D^2]dD \quad (1)$$

By noting that  $P = P(T, D, x)$

$$Z = Z(P, T, D, x)$$

$$\text{then } G = G(T, D, x) \quad (2)$$

for both equations of state.

From the expression for  $G$ , the derivatives  $(\partial^2 G / \partial x^2)_{T,P}$  and  $(\partial^3 G / \partial x^3)_{T,P}$  may be derived analytically. This gives equations of the form

$$G'' = G''(T, D, x) \quad (3)$$

$$G''' = G'''(T, D, x) \quad (4)$$

$$\text{where } G'' = (\partial^2 G / \partial x^2)_{T,P}$$

$$G''' = (\partial^3 G / \partial x^3)_{T,P}$$

It has been shown that at the critical point,  $G''$  and  $G'''$  equal zero. Since the objective in this part of the thesis was to calculate the critical temperature, pressure, and density, equations (3) and (4) were solved simultaneously for the value of  $T$  and  $D$  which made  $G''$  and  $G'''$  equal zero for a given composition ( $x$ ). Because the computed values were the

critical temperature and density,  $T$  and  $D$  were actually  $T_k$  and  $D_k$ , respectively. The critical pressure was then computed from

$$P_k = P_k(T_k, D_k, x)$$

This procedure was repeated for several values of  $x$  and the results were compared with the experimental critical point data.

Because equations (3) and (4) were complex expressions, computer programs were written which used the Newton-Raphson<sup>42</sup> convergence method to find a value of  $T$  and  $D$  which made  $G''$  and  $G'''$  equal to zero. The partial derivatives required in the Newton-Raphson method were estimated numerically.

#### Evaluation of Published Pseudocritical Mixture Rules

This section of the research used a reduced equation of state in conjunction with available pseudocritical mixture rules to compute critical temperature, pressure, and density values for a particular binary system. The mixture rules were evaluated on the basis of how well their critical point predictions compared with experimental data.

The Benedict-Webb-Rubin equation of state for propane (i.e. the constants  $a$ ,  $b$ , ...,  $\gamma$  were those for propane) was used as the basis for the reduced equation of state. By making the substitutions

$$T = T_c T_r$$

$$P = P_c P_r$$

$$D = D_c D_r$$

where  $T_c$ ,  $P_c$ ,  $D_c$  = critical temperature, pressure, and density of the reference compound (propane).

$T_r$ ,  $P_r$ ,  $D_r$  = reduced temperature, pressure, and density, respectively,

the equation of state becomes

$$P_r = P_r(T_r, D_r) \quad (5)$$

By the corresponding states theorem, the function which expresses  $Pr$  in terms of  $Tr$  and  $Dr$  is the same general function for all pure compounds and mixtures of those compounds. Thus, although equation (5) was derived using the Benedict-Webb-Rubin constants and the critical constants for propane, this equation is valid for other compounds as well.

When equation (5) is applied to mixtures the reduced pressure, temperature, and density are computed from

$$Pr = P/Pc_m$$

$$Tr = T/Tc_m$$

$$Dr = D/Dc_m$$

where  $Pc_m$ ,  $Tc_m$ ,  $Dc_m$  = pseudocritical pressure, temperature, and density, respectively.

Therefore, equation (5) written for mixtures is

$$P/Pc_m = Pr(T/Tc_m, D/Dc_m) \quad (6)$$

If the Benedict-Webb-Rubin equation of state is substituted into equation (1) and the resulting expression put into reduced form, the expression for computing  $G$  of a mixture becomes:

$$G = G(T/Tc_m, D/Dc_m, x) \quad (7)$$

$$\text{from which } G'' = G''(T/Tc_m, D/Dc_m, x) \quad (7)$$

$$G''' = G'''(T/Tc_m, D/Dc_m, x) \quad (8)$$

Equations (6), (7), and (8) are now equations with only  $Tc_m$  and  $Pc_m$  as constants since

$$Dc_m = Pc_m / RTc_m Zc$$

where  $Zc$  = critical compressibility factor (equal to the same value for all compounds).

Pseudocritical mixture rules generally express  $Tc_m$  and  $Pc_m$  as functions of composition and the critical properties of the pure components.

Using published expressions for  $P_{c_m}$  and  $T_{c_m}$ , equations (7) and (8) were solved simultaneously for the values of  $T$  (i.e.  $T_k$ ) and  $D$  (i.e.  $D_k$ ) which made  $G''$  and  $G'''$  equal to zero. The method of computation and evaluation of results was the same as used in the evaluation of equations of state.

#### Generation of a Pseudocritical Mixture Rule

This part of the research concerns the attempt to generate curves of  $P_{c_m}$  as a function of  $x$  and  $T_{c_m}$  as a function of  $x$  from experimental  $T_k$ ,  $P_k$ , and  $Z_r$  data. Three different approaches were used.

I. This approach used expressions for  $T_k(x)$ ,  $Z_r(x)$ , and  $P_k(x)$  where, for the pure components, ( $x = 0, 1.0$ ), the following was true

$$T_k = T_c$$

$$P_k = P_c$$

$$Z_k = Z_c$$

In addition, the fact that  $G''$  equals zero at the critical point was also used.

The use of experimental data and the free energy condition to compute  $T_{c_m}$ ,  $P_{c_m}$ , and  $D_r$  is illustrated by the flow diagram of Figure 4. For all of the flow diagrams in this chapter, it is assumed that  $T_c$  and  $P_c$  are known for the pure components ( $x = 0, 1.0$ ), but this fact is not shown on the diagrams. Also,  $T_k$ ,  $P_k$ , and  $Z_r$  are known functions of  $x$ . The diagrams illustrate only the general overall calculation procedure, excluding many of the minor details. Linear interpolation or extrapolation was used to adjust the variables in Figure 4.

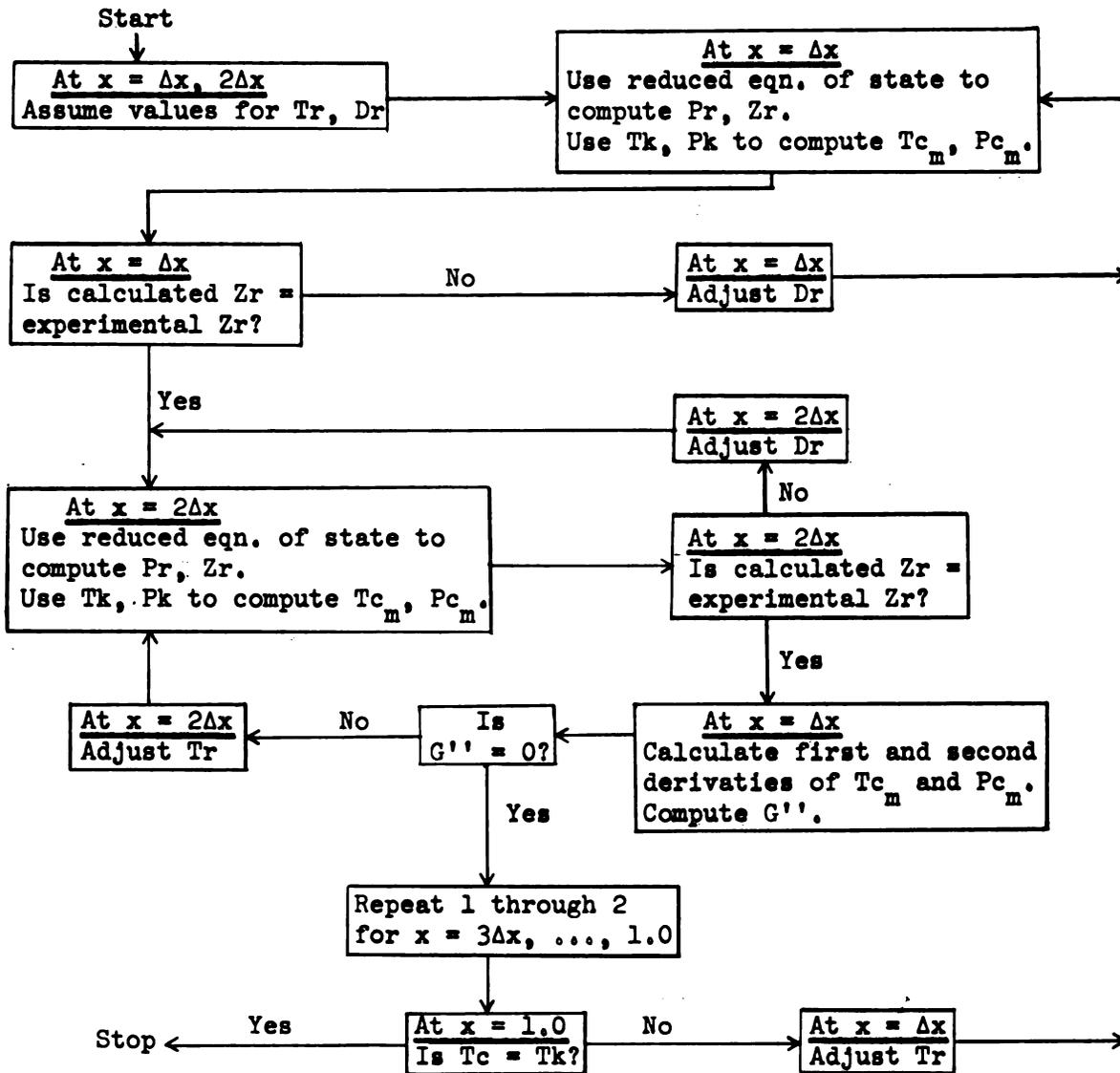


Figure 4. Flow diagram for calculation of  $T_{c_m}$ ,  $P_{c_m}$ , and  $D_r$  using experimental  $T_k$ ,  $P_k$ , and  $Z_r$  data

II. In this approach the experimental  $Z_r$  data was not used. Instead, the second free energy condition at the critical point, that  $(\partial^3 G / \partial x^3)_{T,P}$  is equal to zero, was employed. Figure 5 shows a flow diagram for the calculations in this approach.

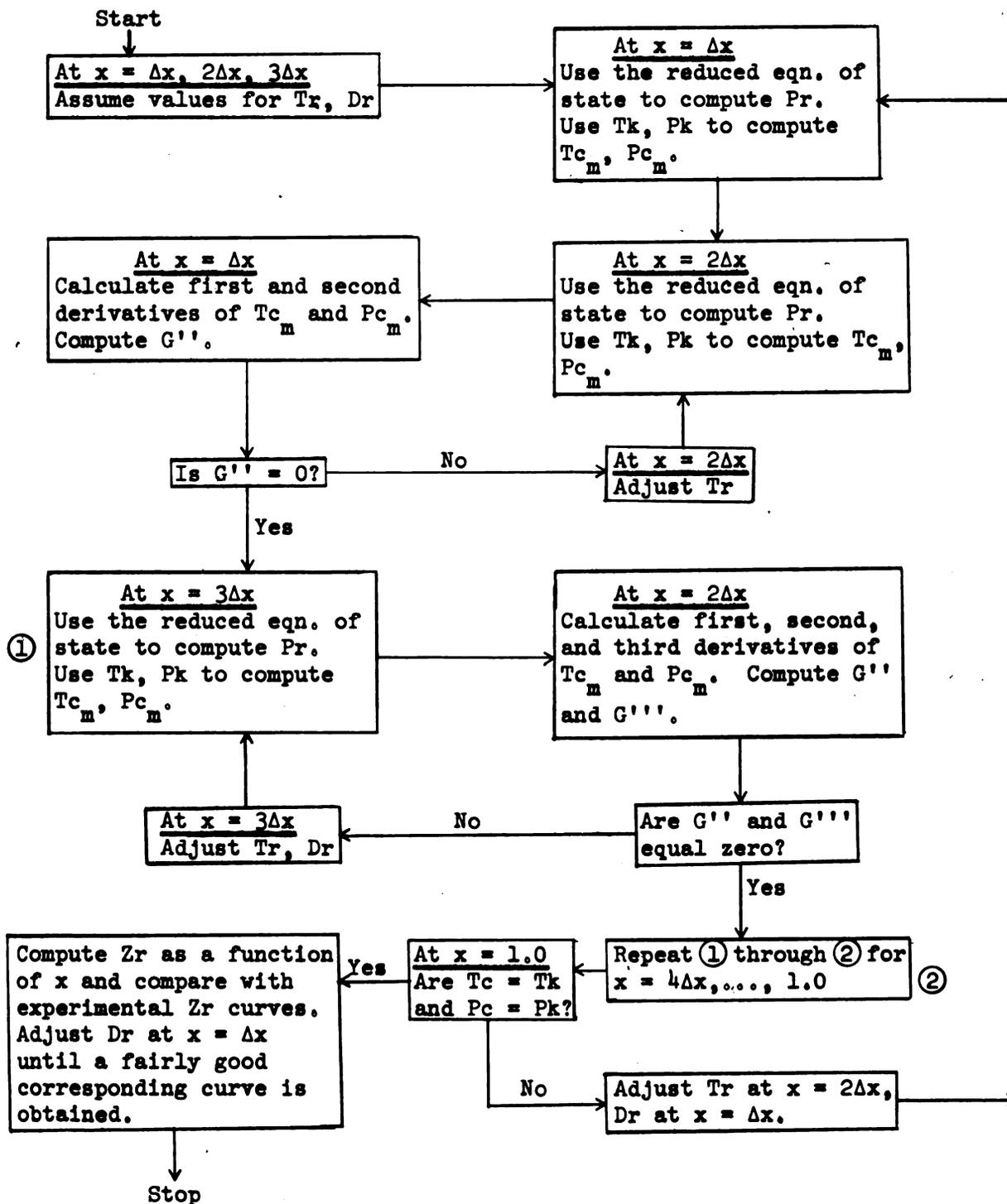


Figure 5. Flow diagram for calculation of  $T_{c_m}$  and  $P_{c_m}$  using experimental  $T_k$  and  $P_k$  data

The major problem with this approach was in finding a convergence method which would find values of  $Tr_{x+\Delta x}$  and  $Dr_{x+\Delta x}$  that would make  $G_x''$  and  $G_x'''$  equal to zero. The two methods which were used were the Newton-Raphson method<sup>42</sup> and a method which assumed  $G''$  and  $G'''$  to be linear functions of  $Tr$  and  $Dr$ . The linear method is described in detail on page 107.

III. In this part of the research, the form of the  $Tc_m$  and  $Pc_m$  curves was assumed to be cubic. Using the values of  $Tc$  and  $Pc$  for the pure compounds, values of  $Tc_m$  and  $Pc_m$  were computed at two intermediate values of  $x$ . The calculation flow diagram appears in Figure 6. The method used to adjust  $Tr$  and  $Dr$  was the Newton-Raphson method.

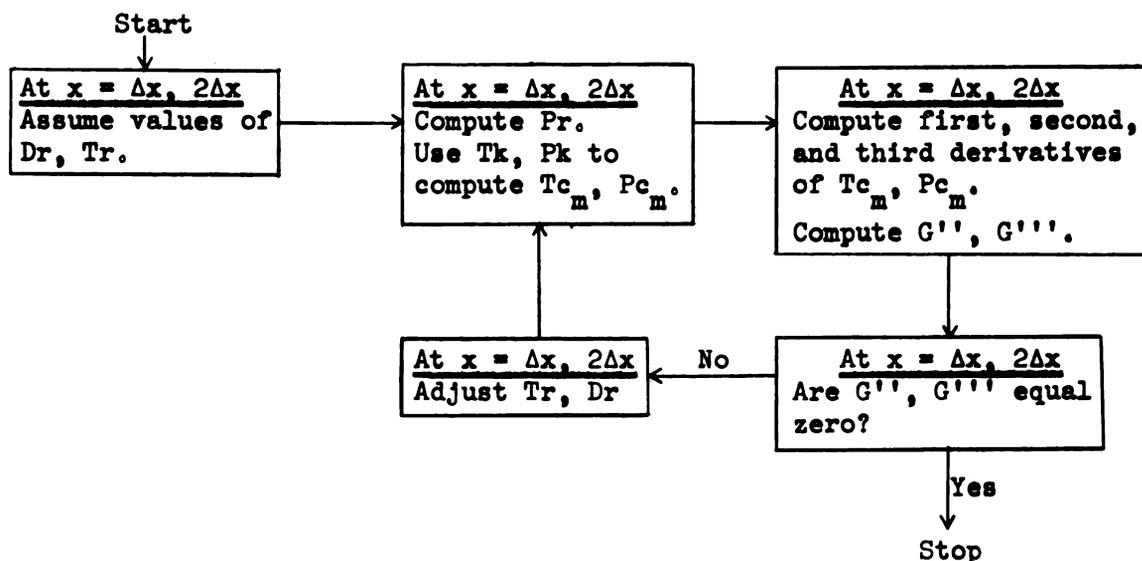


Figure 6. Flow diagram for calculation of  $Tc_m$  and  $Pc_m$  assuming the form of these curves to be cubic.

#### Numerical Check on Analytical Derivatives

Because of the complexity of the equations for  $G''$  and  $G'''$ , a program was written which numerically checked the analytical expressions.

For a function  $F(T,D,x)$ , the derivative with respect to  $x$  at constant  $T$

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Figure 7

and P can be derived as follows:

$$\begin{aligned}
 (\partial F/\partial x)_{T,P} &= (\partial F/\partial x)_{T,D} + (\partial F/\partial D)_{T,x} (\partial D/\partial x)_{T,P} \\
 (\partial D/\partial x)_{T,P} &= -(\partial P/\partial x)_{T,D}/(\partial P/\partial D)_{T,x} = -(\partial P/\partial x)_{T,D} (\partial D/\partial P)_{T,x} \\
 (\partial F/\partial x)_{T,P} &= (\partial F/\partial x)_{T,D} - (\partial F/\partial P)_{T,x} (\partial P/\partial x)_{T,D}
 \end{aligned} \tag{9}$$

where F can be G, G', or G''.

The flow diagram used to compute these derivatives numerically is shown in Figure 7.

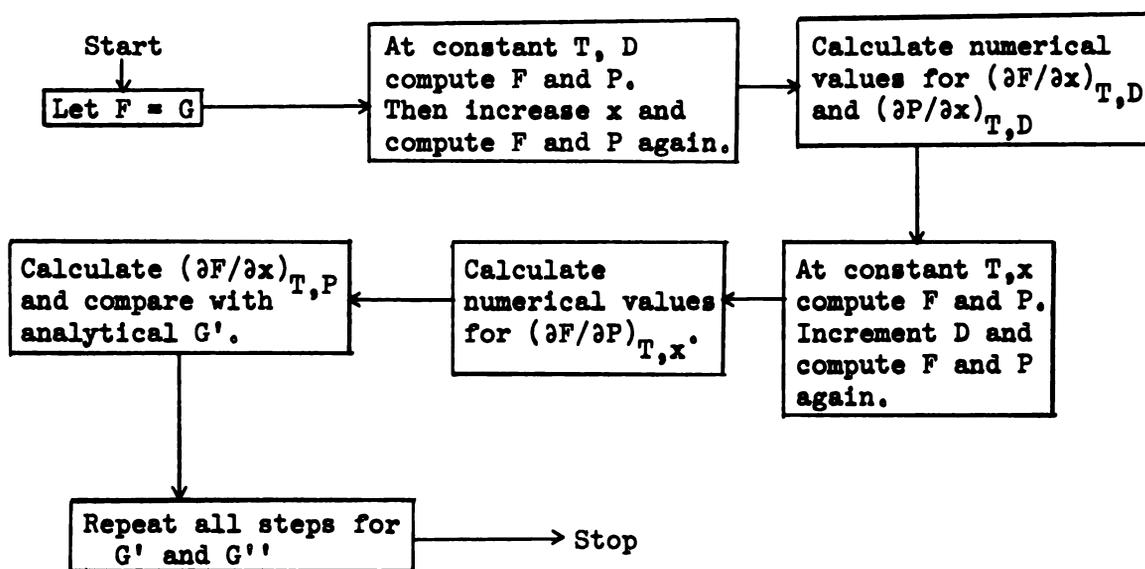


Figure 7. Flow diagram for calculations in the program for checking analytical derivatives

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## EXPERIMENTAL WORK

### Experimental Procedure

This research involved extensive use of automatic digital computers. During the course of the work two computers were used.

For the first year of work, the Michigan State University MISTIC computer was used. Input and output for this computer was by means of paper tape. Printed copies of the tapes were obtained from a teletype machine.

After the first year of work on this problem, Michigan State University purchased a Control Data Corporation 3600 Computer. This computer used Fortran programming language and was approximately eighty times faster than the MISTIC computer. The procedure for running a program on this machine was (1) to construct the Fortran program, (2) to punch the program on IBM cards using a card punch, and (3) to submit the program at the Computer Center for running.

For both computers, the basic steps which eventually led to a correctly operating program were the same. The first step was to decide what the program was to accomplish. Next, the mathematical formulas and techniques which were needed to obtain this goal were derived. The program was written in such a way that the computer would perform exactly the desired mathematical operations. The computer program was then run, and results were obtained. If these results were correct, or at least appeared correct, this whole process was a relatively simple one. However, if the program did not work properly, the process of removing errors was often very time consuming, especially if the program was long. For long programs, the procedure was to construct the program by parts. This

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allowed a constant check on each part of the program as it was constructed.

With programs such as were written for this project, another element was involved in the correction process. Because many of the convergence methods were derived specifically for this project, there was always the chance that the basic equations had been derived incorrectly, or that even the method was not applicable to this research.

If a method did fail to work, considerable time was spent trying to evaluate why the method failed, and whether there were any changes which could be made to correct the method. Often it was possible to alter the method to obtain a working program, but often no usable results were obtained.

#### Experimental Critical Point Vapor-Liquid Equilibrium Data

W. B. Kay's data for the ethane-n-heptane system<sup>23</sup> were the specific experimental equilibrium data used. These data appear in Table 2. Values for critical compressibility factor ( $Z_k$ ) were computed from  $Z_k = P_k/RT_kD_k$ . The pseudocritical compressibility factor ( $Z_{c_m}$ ) was assumed to be a straight line between the critical compressibility factor of the two pure components. Prausnitz and Gunn<sup>31</sup> made a similar assumption for the acentric factor  $\omega$  and obtained results that were in good agreement with experimental data. Because  $Z_{c_m}$  is a linear function of  $\omega$ , the straight line assumption for  $Z_{c_m}$  has some justification. Reduced compressibility ( $Z_r$ ) at the true critical point was then calculated from

$$Z_r = Z_k/Z_{c_m} .$$

Because the MISTIC library routine for a least squares fit of the data did not yield satisfactory results, a special program was written for fitting the data. In this program the method of least squares was

TABLE 2. Experimental data for ethane-n-heptane system at the true critical point (23:463)

| Weight Percent |                | Mole Percent   |                | Tk    | Pk   | Dk                    |
|----------------|----------------|----------------|----------------|-------|------|-----------------------|
| C <sub>2</sub> | C <sub>7</sub> | C <sub>2</sub> | C <sub>7</sub> | °F    | psi  | lbs./ft. <sup>3</sup> |
| 0              | 100            | 0              | 100            | 513.3 | 396  | 14.653                |
| 9.78           | 90.22          | 26.54          | 73.46          | 468.2 | 682  | 16.22                 |
| 29.91          | 70.09          | 58.71          | 41.29          | 373.9 | 1106 | 16.62                 |
| 50.24          | 49.76          | 77.09          | 22.91          | 276.8 | 1263 | 17.43                 |
| 70.22          | 29.78          | 88.71          | 11.29          | 189.8 | 1132 | 16.97                 |
| 90.22          | 9.78           | 96.83          | 3.15           | 120.3 | 850  | 15.48                 |
| 100            | 0              | 100            | 0              | 90.1  | 712  | 13.736                |

modified in order that the curve would exactly fit the data for pure ethane and n-heptane. This exact fit for the properties of the pure components was desirable because, by definition, the reduced temperature and pressure are unity at the critical point. That is,

$$T_r = T_k/T_c = 1$$

$$P_r = P_k/P_c = 1$$

All degrees of polynomials up to six were fitted to the data and then evaluated on the basis of how well they predicted the data points. In all cases the fourth degree polynomials gave the best fit. The temperature curve was expressed as a function of mole fraction ethane. However, the pressure and reduced compressibility factor curves were expressed as a function of weight fraction ethane because better fits were obtained using this variable. A computer program was written which computed Tk, Pk, and Zr for any value of x.

#### Evaluation of Equations of State

Because of their well known capabilities in both the vapor and liquid phases, the van der Waals<sup>43</sup> and Benedict-Webb-Rubin<sup>3</sup> equations of state were selected to be evaluated for their ability to predict vapor-liquid

equilibria in the critical region. The form of the van der Waals equation for a binary system (ethane-n-heptane) is:

$$P = RTD/(1 - bD) - aD^2 \quad (1)$$

where  $a = [xa_1^{1/2} + (1 - x)a_2^{1/2}]^2$  = van der Waals constant a

for the mixture,

$b = xb_1 + (1 - x)b_2$  = van der Waals constant b for the

mixture,

$a_1, b_1$  = van der Waals constants for pure ethane,

$a_2, b_2$  = van der Waals constants for pure n-heptane,

x = mole fraction ethane.

The Benedict-Webb-Rubin mixture equation is the same as equation (7) on page 29 except that the constants for the mixture are found by the following mixture rules:

$$B_o = xB_{o1} + (1 - x)B_{o2}$$

$$A_o = [xA_{o1}^{1/2} + (1 - x)A_{o2}^{1/2}]^2$$

and likewise for  $C_o$  and  $\gamma$ .

$$a = [xa_1^{1/3} + (1 - x)a_2^{1/3}]^3$$

and likewise for b, c, and  $\alpha$ .

where subscript 1 represents ethane

subscript 2 represents n-heptane.

Each equation of state was substituted into the general expression for dimensionless free energy G (equation (6), page 26). The derivatives  $(\partial^2 G / \partial x^2)_{T,P}$  and  $(\partial^3 G / \partial x^3)_{T,P}$  were analytically derived for both equations of state. Computer programs were written which simultaneously solved the  $G''$  and  $G'''$  equations for the value of T and D which made the expressions

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equal to zero. The Newton-Raphson convergence method<sup>42</sup> was used in the calculations.

These values of  $T$  and  $D$  were actually  $T_k$  and  $D_k$  because  $G''$  and  $G'''$  are equal to zero only at the critical point. The critical pressure  $P_k$  was computed from the equation of state. These data from the two equations were compared with Kay's experimental data for the ethane-n-heptane system.<sup>23</sup> As a result of this comparison, the Benedict-Webb-Rubin equation of state was selected as the basis for the reduced equation of state.

#### Derivation of the Reduced Equation of State

The reduced equation of state was derived using the Benedict-Webb-Rubin<sup>3</sup> equation of state for propane. This equation would be equation (7) on page 29 with the constants ( $a, b, \dots, \gamma$ ) those for propane. By making the following substitutions:

$$T = T_c T_r$$

$$D = D_c D_r$$

$$P = P_c P_r$$

where  $T_c, D_c, P_c$  = critical temperature, density, and pressure of propane,

an equation with only two constants can be derived. If  $T_{c_m}$  and  $P_{c_m}$  are selected to be those two constants, then  $D_{c_m}$  can be computed from  $D_{c_m} = P_{c_m} / RT_{c_m} Z_c$  where  $Z_c$  has the same value for all compounds, according to the corresponding states principle. Thus, the reduced equation of state expresses reduced pressure as a function of reduced temperature and density and has only pseudocritical temperature and pressure as constants. Computer programs were written which computed  $P_r$  and  $Z_r$  given  $T_r, D_r$ , and the Benedict-Webb-Rubin equation constants and the critical constants for the reference compound (e.g. propane).

## Derivation of the Analytical Expressions for the Critical Point Free Energy Relationships

Using the general expression for dimensionless free energy  $G$  (equation (6), page 26), the equation for  $G$ , when  $P$  is expressed by the Benedict-Webb-Rubin equation of state, was derived. The expression for  $G$  was then put into reduced form (i.e. made a function of two constants) by making the above listed substitutions for  $T$ ,  $D$ , and  $P$ . The analytical equations for  $(\partial^2 G / \partial x^2)_{T,P}$  and  $(\partial^3 G / \partial x^3)_{T,P}$  were then derived. Computer programs were written in order that  $G''$  and  $G'''$  could be calculated on a digital computer.

## Evaluation of Available Pseudocritical Mixture Rules

Three available pseudocritical mixture rules were evaluated by using them in conjunction with the reduced equation of state to compute the temperature, pressure, and compressibility factor of the ethane-n-heptane system at the point where the K-factor was unity (convergence pressure curve). The mixture rules tested were:

1. Kay's rule<sup>22</sup>

$$T_{c_m} = xT_{c_1} + (1 - x)T_{c_2}$$

$$P_{c_m} = xP_{c_1} + (1 - x)P_{c_2}$$

where  $x$  = mole fraction ethane

subscript 1 represents ethane

subscript 2 represents n-heptane

2. Van der Waals' combinations<sup>43</sup>

$$(T_c/P_c)_m = x(T_c/P_c)_1 + (1 - x)(T_c/P_c)_2$$

$$(T_c/P_c^{1/2})_m = x(T_c/P_c^{1/2})_1 + (1 - x)(T_c/P_c^{1/2})_2$$

3. Joffe's rule<sup>21</sup>

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$$(Tc/Pc^{1/2})_m = x(Tc/Pc^{1/2})_1 + (1 - x)(Tc/Pc^{1/2})_2$$

$$(Tc/Pc)_m = x^2(Tc/Pc)_1 + (1 - x)^2(Tc/Pc)_2 \\ + 1/4[(Tc/Pc)_1^{1/3} + (Tc/Pc)_2^{1/3}]^3 x(1 - x)$$

The procedure for each  $x$  was to use the expressions for  $Tc_m$  and  $Pc_m$  in the generalized equations for  $G''$  and  $G'''$  and then solve  $G''$  and  $G'''$  simultaneously for the value of  $T$  (i.e.  $T_k$ ) and  $D$  (i.e.  $D_k$ ) which made  $G''$  and  $G'''$  equal zero.  $P_k$  was computed from the reduced equation of state. The mixture rules were evaluated on the basis of how well the values of  $T_k$ ,  $P_k$ , and  $D_k$ , for several values of  $x$ , compared with Kay's experimental data.<sup>23</sup>

Computer programs were written for the evaluation of the three mixture rules. The Newton-Raphson convergence method<sup>42</sup> was used in the three programs.

#### Generation of Pseudocritical Mixture Rules

Three different approaches were used in an attempt to generate curves of  $Tc_m$  as a function of  $x$  and  $Pc_m$  as a function of  $x$ .

I. In this approach Kay's experimental critical point data<sup>23</sup> were used along with the condition that  $G''$  equals zero at the critical point, to compute curves of  $Tc_m$  and  $Pc_m$  as a function of composition. A computer program was written for use on the MISTIC computer, and it followed the calculation flow diagram in Figure 4, page 36. In addition, several variations of this approach were tried. The size of the increment  $\Delta x$  was varied, although 0.05 was the most commonly used value. Also, the computer program was changed to begin at the other end of the composition range (i.e. pure

n-heptane). Finally, butane was used as a reference compound instead of propane. This meant that the Benedict-Webb-Rubin constants were those for butane.

To aid in obtaining convergence, expressions for the maximum possible values of  $Dr$ , given  $Tr_{\max}$  and  $Zr$ , were used to put some bound on new guesses of  $Tr$  and  $Dr$ .

A check program was written by another person for checking results from this approach.

II. In this part of the research the experimental reduced compressibility factor data for the true critical point were not used. Instead, the condition used was that the third partial derivative of free energy with respect to composition, at constant temperature and pressure, was equal to zero at the critical point. This part was begun on the MISTIC computer, but the arrival of the Control Data 3600 Computer made it necessary to rewrite all programs in Fortran programming language. Following the flow diagram in Figure 5, page 37, computer programs were written for computing  $Tc_m$  and  $Pc_m$  at successive values of composition. The Fortran program was called Program LINEAR and is listed and described in Appendix VI.

Because the equations for  $G''$  and  $G'''$  are functions of both  $Tr$  and  $Dr$ , the generation of values for  $Tr$  and  $Dr$  required a simultaneous convergence process for the two variables. The major problem connected with this part of the research was the development of such a convergence process.

The first convergence scheme used was a process which assumed that  $G''$  and  $G'''$  were linear functions of  $Tr$  and  $Dr$ . The details of this convergence scheme are discussed in the description of subroutine CONVERG

in Appendix VI.

A variation of the linear convergence method was also used. Since three sets of guesses for (Tr,Dr) were needed to predict a new set of guesses, the convergence scheme was changed so that the three sets of guesses included the last set and the best two previous sets. Before, the immediate past three sets had been used.

Since the programs written for this approach had failed because of lack of convergence, two methods were used to obtain better initial guesses for Tr and Dr at  $x_2$ ,  $x_3$ , and  $x_4^*$ , for use in Program LINEAR. The first method changed six variables ( $Tr_2$ ,  $Tr_3$ ,  $Tr_4$ ,  $Dr_2$ ,  $Dr_3$ ,  $Dr_4$ )\*\* simultaneously until  $G''$  was equal to zero at  $x_2$  and  $x_3$ , and  $G'''$  was equal to zero at  $x_3$ . These six variables were changed to meet these three conditions by a method of steepest descent.

The method of steepest descent involved calculating the partial derivative of a function  $\phi$  (defined as the sum of the squares of  $G_2''$ ,  $G_3''$ , and  $G_3'''$ ) with respect to each variable while the other variables were held constant. These slopes were used to compute the estimated changes in each of the six variables necessary to make  $\phi$  equal to zero. The equations used were

$$\rho = -\phi / [(\partial\phi/\partial XX_1)^2 + (\partial\phi/\partial XX_2)^2 + \dots + (\partial\phi/\partial XX_6)^2] \quad (1)$$

$$\Delta XX_1 = (\partial\phi/\partial XX_1)\rho, \text{ etc.}$$

where  $XX_1$  represents a dummy variable used for interpolation and

\*Subscripts on x represent a numbering system on successive values of x beginning with  $x_1 = 0$ ,  $x_2 = \Delta x$ , etc.

\*\* Subscripts on variables other than x represent the values of these variables at the value of x which has the same subscript.

extrapolation instead of Tr or Dr. There is one XX variable for each of  $Tr_2, Tr_3, Tr_4, Dr_2, Dr_3, Dr_4$ .  $\rho$  is a proportionality factor.

To speed convergence, a minimization procedure was used. This procedure used the slope of the  $\rho$  versus  $\phi$  curve at  $\rho = 0$  and the value of  $\phi$  at some other  $\rho$  value to fit a quadratic equation to these data points. The calculated minimum of this equation was used to compute the next values of  $\rho$ . Except for a variation in the minimization procedure, the above convergence method is approximately the same as one described by Booth<sup>8</sup>. Because the speed of convergence was extremely slow with this method, several programs were prepared in an attempt to find the reason for this slowness. These included (1) programs for learning more about the  $\phi$  versus  $\rho$  curve and (2) a program for determining the best increment of XX to use in the numerical differentiation calculations.

The second method used an approach similar to the Newton-Raphson method<sup>42</sup> to simultaneously vary the variables ( $Tr_2, Tr_3, Tr_4, Dr_2, Dr_3, Dr_4$ ) until  $G''$  and  $G'''$  were zero at  $x_2$  and  $x_3$ . Since the fact that  $Tr = 1$  and  $Pr = 1$  at  $x = 0 = x_1$  was also used, four points were available to compute up to third derivatives of Tr and Pr. Because the six variables ( $Tr_2, Tr_3, Tr_4, Dr_2, Dr_3, Dr_4$ ) were varied to satisfy only four requirements ( $G'' = 0$  and  $G''' = 0$  at  $x_2$  and  $x_3$ ), an infinite number of solutions was possible. This permitted other requirements, such as non-negativity and well behaved curves, to be satisfied.

The computed sets of starting data were then used as initial values in Program LINEAR.

III. The third approach assumed a cubic form for the  $Tc_m$  and  $Pc_m$  curves as a function of  $x$ . The computer program written for this section follows the calculation flow diagram in Figure 6, page 38. This program

was called Program TOTRANGE and is listed in Appendix VII. The Newton-Raphson convergence method<sup>42</sup> was used for solving a system of four equations and four unknowns in the program.

#### Check for the Analytical Derivatives

A check program was written to check the equations for  $G''$  and  $G'''$ . This program, called Program CHECK, follows the flow diagram in Figure 7 on page 39. It is listed and described in Appendix VIII.

#### Chronological Order of the Research Work

To provide greater continuity to the description of the research work, the discussion does not necessarily follow the same chronological pattern in which the work was done. The work was actually performed in the following order:

1. Generation of pseudocritical mixture rules.
2. Evaluation of published pseudocritical mixture rules.
3. Evaluation of equations of state.

Also, the placing of the computer programs in the appendices should not detract from the fact that they constituted the bulk of the research work. They have been included in the appendices to give continuity to the remainder of the report.

## RESULTS AND DISCUSSION

### Fitting of Curves to Experimental Data

Early in the research work it was necessary to fit polynomials to the experimental critical point data of Kay<sup>23</sup> to adapt this data for use on a digital computer. Critical temperatures were expressed as a function of mole fraction, but critical pressures and reduced compressibility factors were expressed as functions of weight fraction because this variable yielded better fits. The polynomials which resulted are:

$$T_k = (973.0 - 186.4392126x + 200.413825x^2 - 558.3704113x^3 + 121.195736x^4)/1.8 \quad (1)$$

$$P_k = (396. + 3051.927387W - 1199.746006W^2 - 4263.827785W^3 + 2727.646362W^4)/14.696 \quad (2)$$

$$Z_r = 1.0 + 4.030611284W - 6.695218637W^2 + 1.855922080W^3 + 0.8086852915W^4 \quad (3)$$

where  $x$  = mole fraction ethane

$W$  = weight fraction ethane =  $30.06x/[30.06x + 100.17(1-x)]$

$T_k$  = critical temperature, °K

$P_k$  = critical pressure, atm.

$Z_r$  = critical reduced compressibility factor.

Table 3 lists computed values of  $T_k$ ,  $P_k$ ,  $Z_k$ , and  $Z_r$  at .05 increments of mole fraction ethane. One-half weight fraction ethane is approximately 0.769 mole fraction ethane.

TABLE 3. Critical temperature, pressure, compressibility factor, and reduced compressibility factor as computed from a least squares fit of Kay's data

| x    | Tk (°K)   | Pk (Atm.) | Zk        | Zr        |
|------|-----------|-----------|-----------|-----------|
| .00  | 540.53888 | 26.946107 | .25919000 | 1.0000000 |
| .05  | 535.60000 | 30.154282 | .27526831 | 1.0610586 |
| .10  | 530.99107 | 33.552553 | .29164371 | 1.1231494 |
| .15  | 526.49458 | 37.148395 | .30825131 | 1.1860199 |
| .20  | 521.90313 | 40.946990 | .32500224 | 1.2493263 |
| .25  | 517.01940 | 44.949864 | .34177661 | 1.3126070 |
| .30  | 511.65618 | 49.152915 | .35841401 | 1.3752466 |
| .35  | 505.63639 | 53.543590 | .37470164 | 1.4364310 |
| .40  | 498.79300 | 58.096802 | .39035853 | 1.4950881 |
| .45  | 490.96911 | 62.769114 | .40501526 | 1.5498112 |
| .50  | 482.01792 | 67.490348 | .41818773 | 1.5987603 |
| .55  | 471.80272 | 72.151619 | .42924455 | 1.6395395 |
| .60  | 460.19689 | 76.588316 | .43736661 | 1.6690452 |
| .65  | 447.08393 | 80.556178 | .44150205 | 1.6832977 |
| .70  | 432.35742 | 83.698999 | .44032381 | 1.6772835 |
| .75  | 415.92108 | 85.507451 | .43221376 | 1.6448994 |
| .80  | 397.68867 | 85.275775 | .41533654 | 1.5792384 |
| .85  | 377.58410 | 82.083934 | .38796487 | 1.4738291 |
| .90  | 355.54134 | 74.900183 | .34947786 | 1.3264226 |
| .95  | 331.50450 | 63.108845 | .30315790 | 1.1495795 |
| 1.00 | 305.42776 | 48.448557 | .26395000 | 1.0000000 |

## Equations of State for Mixtures

The van der Waals<sup>43</sup> and Benedict-Webb-Rubin<sup>3</sup> equations of state for mixtures were evaluated on the basis of their ability to predict convergence pressure curves and critical compressibility factors. Prediction of these quantities was used as a basis for evaluation because good prediction indicates computational accuracy in the critical region.

The prediction of convergence pressure curves is of particular interest because the curves are used in the convergence pressure method of predicting vapor-liquid equilibria. Because of a shortage of critical point data, the shape of convergence pressure curves is generally estimated from data for other systems. This is illustrated in Figure 8 which is a typical convergence pressure diagram published by Hadden.<sup>16</sup> In this diagram only three of the curves are substantiated by experimental data.

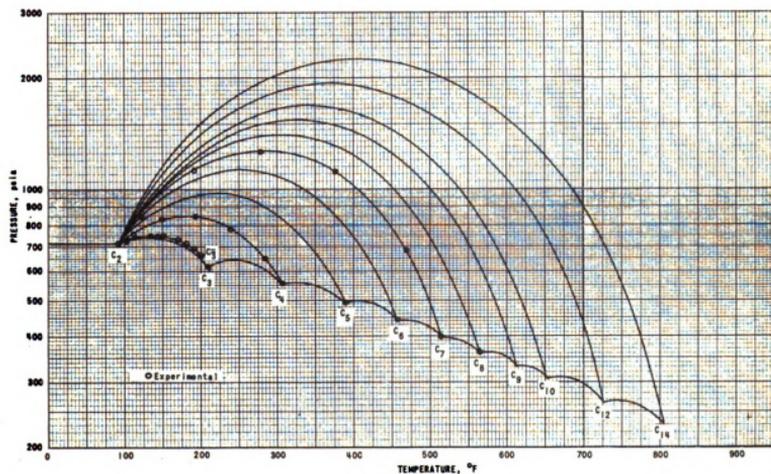


Figure 8. Convergence pressure data - ethane lightest component

The convergence pressure curves shown in Figure 8 are plots of pressure as a function of temperature. Throughout the remainder of this discussion, convergence pressure data will be plotted on two separate graphs. These graphs will be temperature and pressure as a function of composition. Because composition is a common parameter, the two separate plots are equivalent to a single plot such as in Figure 8.

Using the van der Waals equation plus the rules recommended by van der Waals for computing equation constants for a mixture, the critical state properties shown in Table 4 were obtained. Table 5 lists similar results obtained by using the Benedict-Webb-Rubin equation of state with the combination rules recommended by Benedict et al. for mixtures.

Figures 9, 10, and 11 are plots of the critical temperature, pressure, and compressibility factors, respectively, as a function of composition. The critical temperatures predicted by both equations of state agree very well with Kay's data (Table 2, page 42). The van der Waals equation was in considerably greater error in predicting pressures than the Benedict-Webb-Rubin equation. Table 4 shows the maximum percent pressure deviation for the van der Waals equation to be over 34 percent. The Benedict-Webb-Rubin equation was also in good agreement with known compressibility factors while the van der Waals agreement was relatively poor.

Overall, the Benedict-Webb-Rubin equation of state for mixtures was in good agreement with Kay's experimental data. However, it should be realized that Kay's data were probably used in the empirical derivation of the Benedict-Webb-Rubin equation of state, and this could account for the excellent agreement. Nevertheless, the excellent results obtained with the Benedict-Webb-Rubin equation indicate that this equation of state is capable of being applied to pure compounds and mixtures with

TABLE 4. Values of critical density, temperature, pressure, and compressibility factor as predicted by the van der Waals equation of state for mixtures

| x    | Dk<br>(moles/liter) | Tk<br>(°K) | Dev. From<br>Data (%) | Pk<br>(atm.) | Dev. From<br>Data (%) | Zk         |
|------|---------------------|------------|-----------------------|--------------|-----------------------|------------|
| 0.05 | 1.6824284           | 535.07767  | -0.10                 | 28.771692    | - 4.59                | 0.38942833 |
| 0.10 | 1.7487094           | 529.26780  | -0.32                 | 30.642235    | - 8.67                | 0.40340651 |
| 0.15 | 1.8202682           | 523.07300  | -0.65                 | 32.575061    | -12.31                | 0.41687237 |
| 0.20 | 1.8977382           | 516.45669  | -1.04                 | 34.567900    | -15.58                | 0.42975245 |
| 0.25 | 1.9818530           | 509.37809  | -1.48                 | 36.616655    | -18.54                | 0.44195956 |
| 0.30 | 2.0734668           | 501.79175  | -1.93                 | 38.714764    | -21.24                | 0.45338962 |
| 0.35 | 2.1735777           | 493.64714  | -2.37                 | 40.852363    | -23.70                | 0.46391771 |
| 0.40 | 2.2833569           | 484.88813  | -2.79                 | 43.015181    | -25.96                | 0.47339314 |
| 0.45 | 2.4041839           | 475.45271  | -3.16                 | 45.183084    | -28.02                | 0.48163320 |
| 0.50 | 2.5376893           | 465.27276  | -3.47                 | 47.328168    | -29.87                | 0.48841521 |
| 0.55 | 2.6858055           | 454.27419  | -3.72                 | 49.412284    | -31.52                | 0.49346673 |
| 0.60 | 2.8508254           | 442.37753  | -3.87                 | 51.383840    | -32.91                | 0.49645332 |
| 0.65 | 3.0354679           | 429.49938  | -3.93                 | 53.173772    | -33.99                | 0.49696389 |
| 0.70 | 3.2429407           | 415.55484  | -3.89                 | 54.690577    | -34.66                | 0.49449366 |
| 0.75 | 3.4769817           | 400.46158  | -3.72                 | 55.814443    | -34.73                | 0.48842613 |
| 0.80 | 3.7418245           | 384.14547  | -3.41                 | 56.390708    | -33.87                | 0.47801771 |
| 0.85 | 4.0419409           | 366.54679  | -2.92                 | 56.223212    | -31.51                | 0.46239363 |
| 0.90 | 4.3811148           | 347.62230  | -2.23                 | 55.067867    | -26.48                | 0.44057674 |
| 0.95 | 4.7592177           | 327.32166  | -1.26                 | 52.623445    | -16.61                | 0.41160868 |

TABLE 4. Values of critical density, temperature, pressure, and compressibility factor as predicted by the van der Waals equation of state for mixtures

| x    | Dk<br>(moles/liter) | Tk<br>(°K) | Dev. From<br>Data (%) | Pk<br>(atm.) | Dev. From<br>Data (%) | Zk         |
|------|---------------------|------------|-----------------------|--------------|-----------------------|------------|
| 0.05 | 1.6824284           | 535.07767  | -0.10                 | 28.771692    | - 4.59                | 0.38942833 |
| 0.10 | 1.7487094           | 529.26780  | -0.32                 | 30.642235    | - 8.67                | 0.40340651 |
| 0.15 | 1.8202682           | 523.07300  | -0.65                 | 32.575061    | -12.31                | 0.41687237 |
| 0.20 | 1.8977382           | 516.45669  | -1.04                 | 34.567900    | -15.58                | 0.42975245 |
| 0.25 | 1.9818530           | 509.37809  | -1.48                 | 36.616655    | -18.54                | 0.44195956 |
| 0.30 | 2.0734668           | 501.79175  | -1.93                 | 38.714764    | -21.24                | 0.45338962 |
| 0.35 | 2.1735777           | 493.64714  | -2.37                 | 40.852363    | -23.70                | 0.46391771 |
| 0.40 | 2.2833569           | 484.88813  | -2.79                 | 43.015181    | -25.96                | 0.47339314 |
| 0.45 | 2.4041839           | 475.45271  | -3.16                 | 45.183084    | -28.02                | 0.48163320 |
| 0.50 | 2.5376893           | 465.27276  | -3.47                 | 47.328168    | -29.87                | 0.48841521 |
| 0.55 | 2.6858055           | 454.27419  | -3.72                 | 49.412284    | -31.52                | 0.49346673 |
| 0.60 | 2.8508254           | 442.37753  | -3.87                 | 51.383840    | -32.91                | 0.49645332 |
| 0.65 | 3.0354679           | 429.49938  | -3.93                 | 53.173772    | -33.99                | 0.49696389 |
| 0.70 | 3.2429407           | 415.55484  | -3.89                 | 54.690577    | -34.66                | 0.49449366 |
| 0.75 | 3.4769817           | 400.46158  | -3.72                 | 55.814443    | -34.73                | 0.48842613 |
| 0.80 | 3.7418245           | 384.14547  | -3.41                 | 56.390708    | -33.87                | 0.47801771 |
| 0.85 | 4.0419409           | 366.54679  | -2.92                 | 56.223212    | -31.51                | 0.46239363 |
| 0.90 | 4.3811148           | 347.62230  | -2.23                 | 55.067867    | -26.48                | 0.44057674 |
| 0.95 | 4.7592177           | 327.32166  | -1.26                 | 52.623445    | -16.61                | 0.41160868 |

TABLE 5. Values of critical density, temperature, pressure, and compressibility factor as predicted by the Benedict-Webb-Rubin equation of state for mixtures

| x    | Dk<br>(moles/liter) | Tk<br>(°K) | Dev. From<br>Data (%) | Pk<br>(atm.) | Dev. From<br>Data (%) | Zk         |
|------|---------------------|------------|-----------------------|--------------|-----------------------|------------|
| 0.05 | 2.1988824           | 537.15117  | +0.29                 | 30.070395    | -0.28                 | 0.31021027 |
| 0.10 | 2.3149502           | 532.15117  | +0.37                 | 33.151584    | -1.20                 | 0.32739387 |
| 0.15 | 2.4500561           | 528.36886  | +0.36                 | 36.481434    | -1.80                 | 0.34338080 |
| 0.20 | 2.6163878           | 523.19314  | +0.25                 | 40.140257    | -1.97                 | 0.35729879 |
| 0.25 | 2.8679907           | 516.98032  | -0.01                 | 44.445773    | -1.12                 | 0.36525341 |
| 0.30 | 3.3478922           | 508.45078  | -0.63                 | 50.428554    | +2.60                 | 0.36097049 |
| 0.35 | 3.6516231           | 500.59817  | -1.00                 | 55.910509    | +4.42                 | 0.37267804 |
| 0.40 | 3.9338281           | 492.32922  | -1.30                 | 61.427057    | +5.73                 | 0.38645976 |
| 0.45 | 4.2240173           | 483.37107  | -1.55                 | 67.004787    | +6.75                 | 0.39986654 |
| 0.50 | 4.5331285           | 473.56804  | -1.75                 | 72.554512    | +7.50                 | 0.41181255 |
| 0.55 | 4.8684388           | 462.77669  | -1.91                 | 77.918854    | +7.99                 | 0.42140233 |
| 0.60 | 5.2362520           | 450.84712  | -2.03                 | 82.860462    | +8.19                 | 0.42767423 |
| 0.65 | 5.6425121           | 437.61983  | -2.12                 | 87.034909    | +8.04                 | 0.42947664 |
| 0.70 | 6.0924091           | 422.93209  | -2.18                 | 89.953776    | +7.47                 | 0.42537825 |
| 0.75 | 6.5884252           | 406.63972  | -2.23                 | 90.945384    | +6.36                 | 0.41362313 |
| 0.80 | 7.1243169           | 388.67510  | -2.27                 | 89.144539    | +4.54                 | 0.39226573 |
| 0.85 | 7.6667710           | 369.19415  | -2.22                 | 83.630094    | +1.88                 | 0.36000691 |
| 0.90 | 8.0986986           | 348.88235  | -1.87                 | 74.057359    | -1.13                 | 0.31936664 |
| 0.95 | 8.0519223           | 328.97245  | -0.76                 | 61.997280    | -1.76                 | 0.28518659 |

Figure 9. Critical temperature as a function of mole fraction ethane

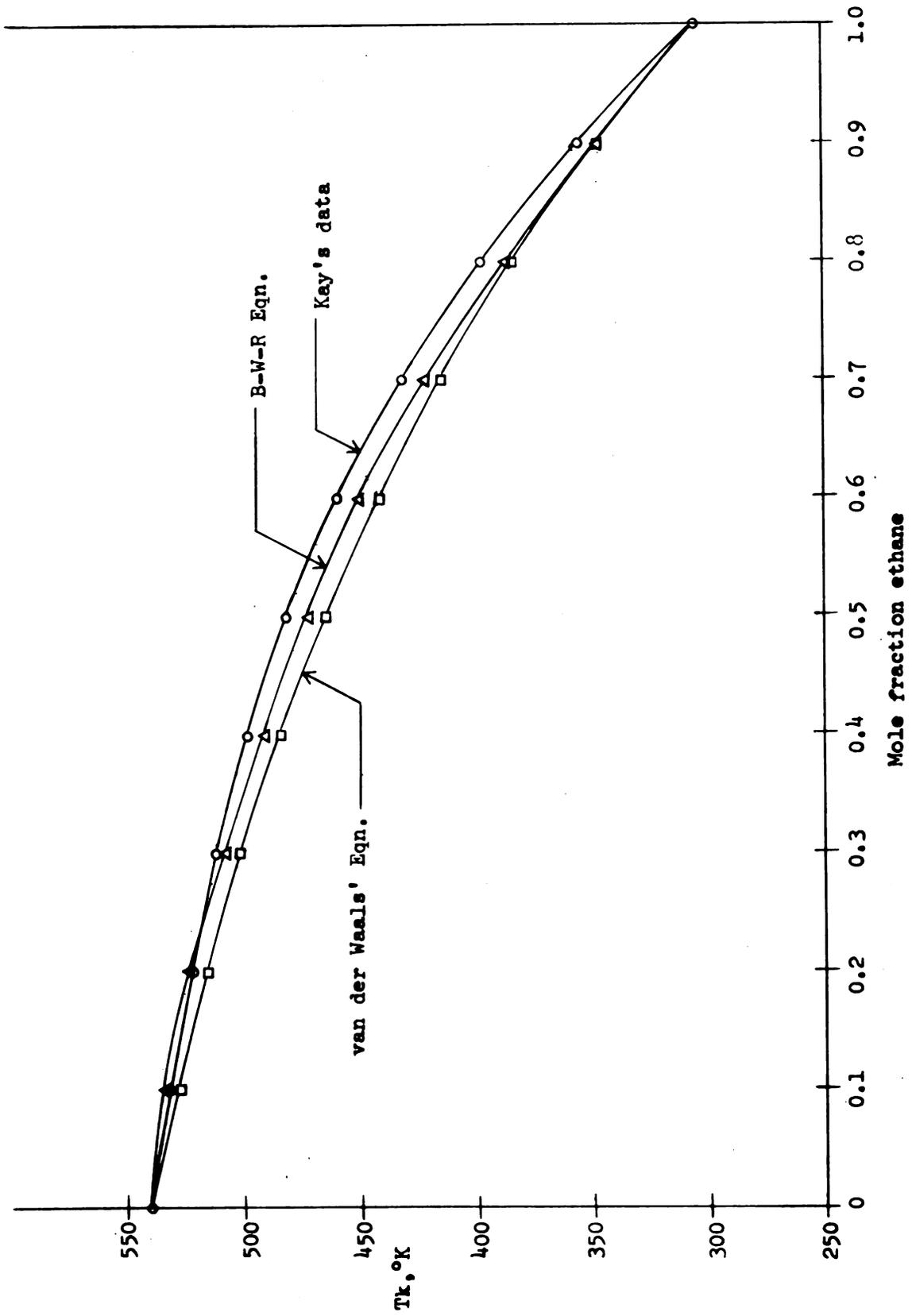


Figure 10. Critical pressure as a function of mole fraction ethane

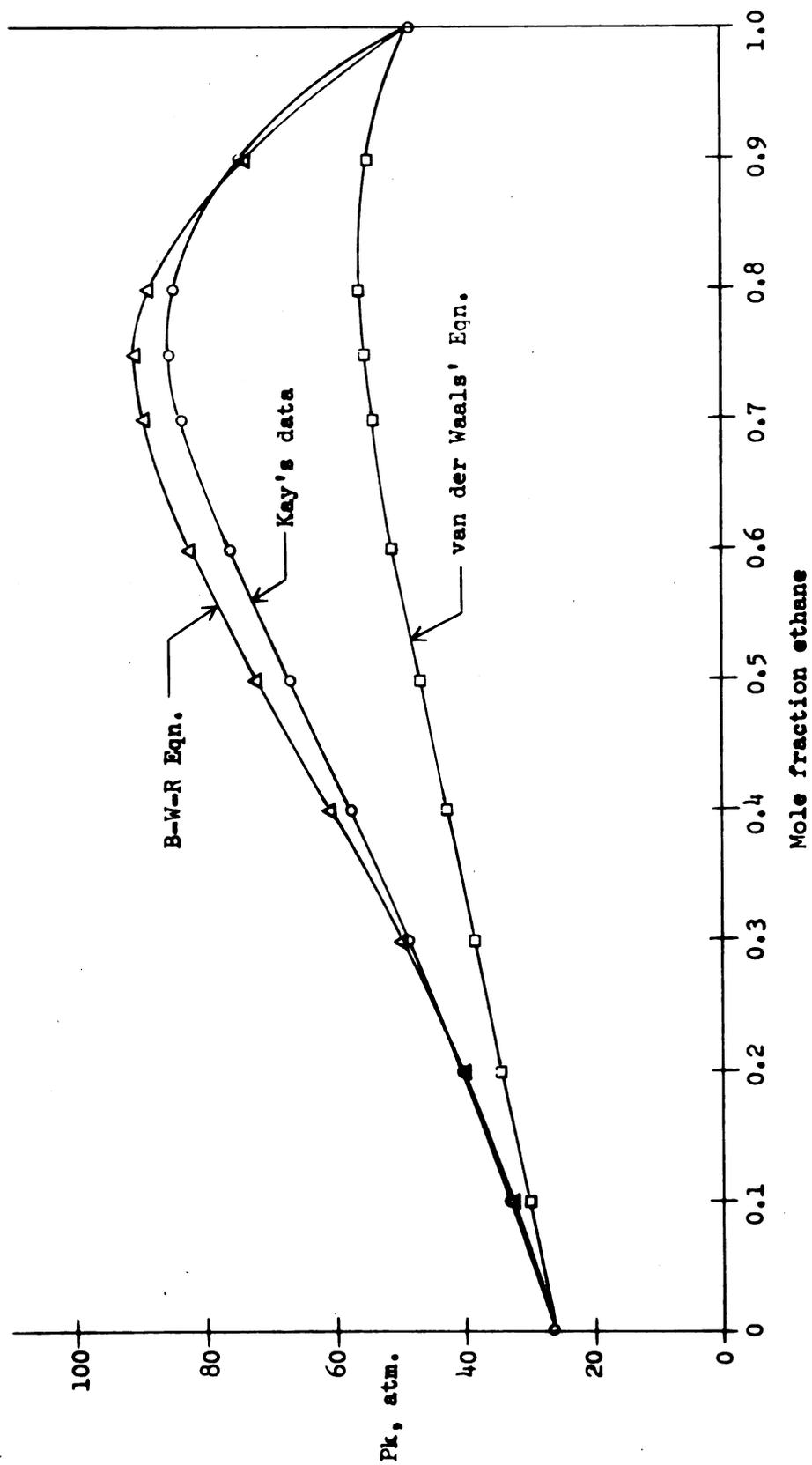
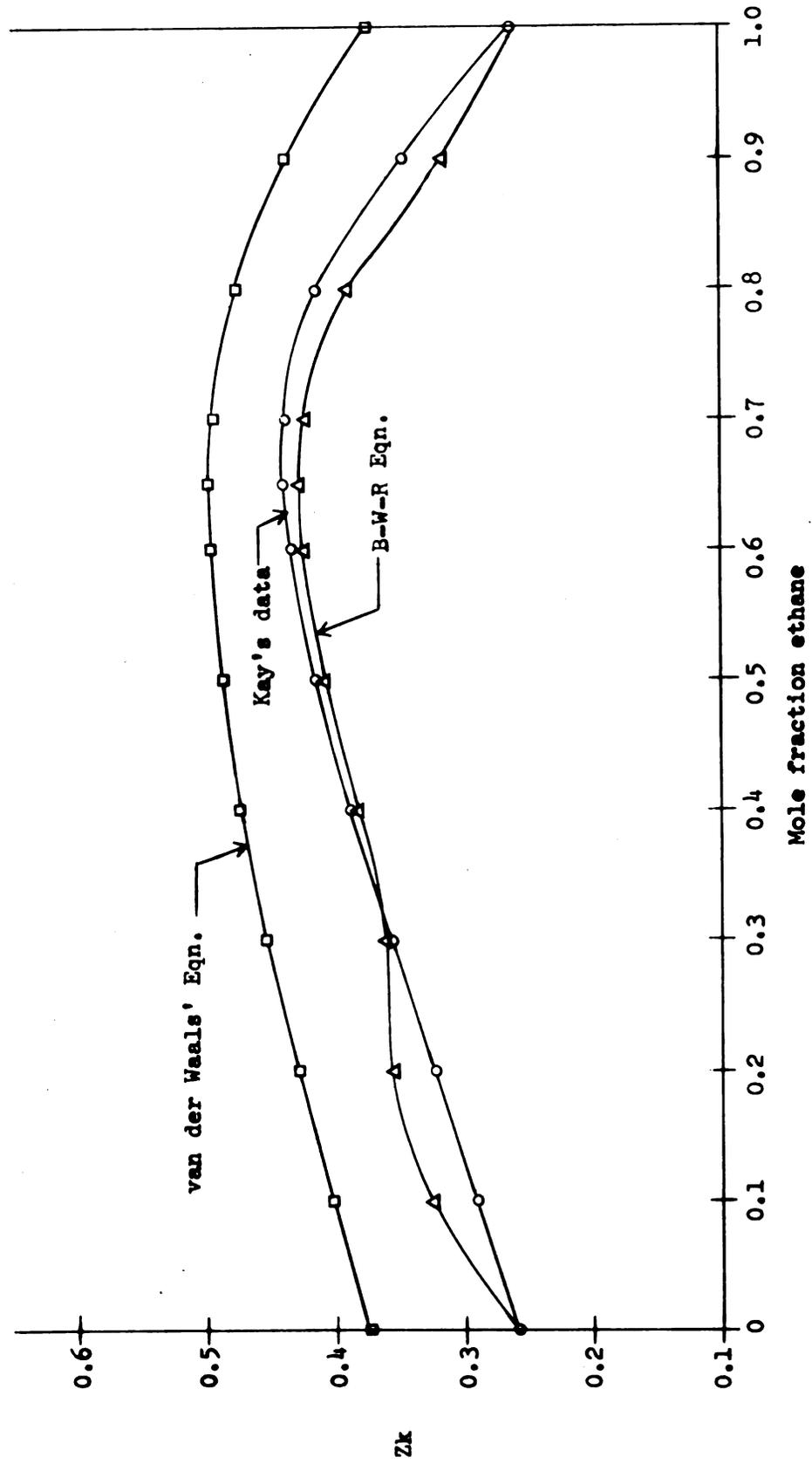


Figure 11. Critical compressibility as a function of mole fraction ethane



approximately the same accuracy.

### Generalized Equation of State

A generalized equation of state expressing reduced pressure in terms of reduced temperature and density was derived. The form of the equation was based on the Benedict-Webb-Rubin equation of state. The resulting reduced equation is

$$Pr = fTrDr + (gTr - h - i/Tr^2)Dr^2 + (jTr - k)Dr^3 + lDr^6 + (mDr^3/Tr^2)(1. + nDr^2)\exp(-nDr^2) \quad (4)$$

where constants  $f$  through  $n$  are the reduced equation of state constants and are defined in Appendix III. According to the corresponding states principles, these constants should be the same for all compounds. However, in reality, these constants do vary slightly depending on the reference compound used to compute them. In this research propane was used as the reference compound unless otherwise noted.

### Generalized Equations for Free Energy and its First Three Derivatives

Because the second and third derivatives of free energy ( $G$ ) with respect to composition, are equal to zero at the critical point, it was desirable to have generalized expressions for these quantities. The generalized expression for  $G$  was found to be

$$G = \ln P_{c,m} Pr + x \ln x + (1. - x)\ln(1. - x) + Z - 1. - \ln Z + [(g - h/Tr - i/Tr^3)Dr + (j - k/Tr)Dr^2/2 + (l/Tr)Dr^5/5 + (mDr^2/2Tr^3)[(2 - 2\exp(-nDr^2))/nDr^2 - \exp(-nDr^2)]]/f \quad (5)$$

Details of the above generalization appears in Appendix III. The equations for  $G''$  and  $G'''$  and the procedure for obtaining them are shown in Appendices III, IV, and V.

## Evaluation of Published Mixture Rules

Using the derived generalized equation of state and generalized expressions for  $G''$  and  $G'''$ , Kay's,<sup>22</sup> van der Waals',<sup>43</sup> and Joffe's<sup>21</sup> mixture rules were evaluated for their ability to predict critical state properties. Tables 6, 7, and 8 list the predicted values of critical temperature, pressure, and compressibility factor obtained with each of the three mixture rules. These results are plotted as functions of composition in Figures 12, 13, and 14. The critical temperature agreement was very good in all cases. The maximum temperature percent deviation was 4.67 percent; this occurred with Kay's rule. The predicted critical pressures were best with van der Waals' mixture rule and poorest with Kay's rule. Joffe's rule, although slightly poorer than van der Waals' combinations, was nevertheless in good agreement with Kay's data. Figure 14 shows only fair agreement with the experimental compressibility factors. Van der Waals' and Joffe's rules are approximately equivalent in their ability to match the experimental compressibility factors.

Overall, the van der Waals' mixture rule appears to be the best of the three mixture rules evaluated. In fact, the critical temperature and pressure predictions made by using the van der Waals mixture rule in the generalized equation of state were about as good as the predictions made from the Benedict-Webb-Rubin equation of state for mixtures. The average critical temperature error was 1.16 percent using the van der Waals rule with the generalized equation and 1.32 percent using the Benedict-Webb-Rubin equation for mixtures. The average critical pressure error was 5.41 percent with the reduced equation of state plus van der Waals' rule and 4.25 percent with the eight constant Benedict-Webb-Rubin equation.

The relatively good temperature and pressure agreement obtained with

TABLE 6. Critical temperatures, pressures, and compressibility factors and critical reduced densities obtained from the generalized equation of state using Kay's mixture rule

| x    | Dr        | Tk<br>(°K) | Dev. From<br>Data (%) | Pk<br>(atm.) | Dev. From<br>Data (%) | Zk         |
|------|-----------|------------|-----------------------|--------------|-----------------------|------------|
| 0.05 | 0.9231651 | 540.88146  | +0.99                 | 32.081979    | +6.39                 | 0.32837705 |
| 0.10 | 0.8836010 | 541.73942  | +2.02                 | 37.429280    | +11.55                | 0.37630737 |
| 0.15 | 0.8713950 | 542.17612  | +2.98                 | 43.160219    | +16.18                | 0.41434263 |
| 0.20 | 0.8769442 | 541.54189  | +3.76                 | 49.348115    | +20.52                | 0.44449636 |
| 0.25 | 0.8946219 | 539.36347  | +4.32                 | 55.981493    | +24.54                | 0.46834217 |
| 0.30 | 0.9206883 | 535.32072  | +4.63                 | 62.975014    | +28.12                | 0.48701430 |
| 0.35 | 0.9524494 | 529.23324  | +4.67                 | 70.179159    | +31.07                | 0.50125431 |
| 0.40 | 0.9878553 | 521.03687  | +4.46                 | 77.385910    | +33.20                | 0.51146354 |
| 0.45 | 1.0252945 | 510.75449  | +4.03                 | 84.331900    | +34.35                | 0.51774698 |
| 0.50 | 1.0634892 | 498.46689  | +3.41                 | 90.701008    | +34.39                | 0.51994559 |
| 0.55 | 1.1014103 | 484.29001  | +2.65                 | 96.126566    | +33.23                | 0.51766700 |
| 0.60 | 1.1381447 | 468.36458  | +1.77                 | 100.194502   | +30.82                | 0.51032823 |
| 0.65 | 1.1726882 | 450.86204  | +0.85                 | 102.454443   | +27.18                | 0.49722998 |
| 0.70 | 1.2036582 | 432.00446  | -0.08                 | 102.451997   | +22.41                | 0.47769174 |
| 0.75 | 1.2289241 | 412.08810  | -0.92                 | 99.797548    | +16.71                | 0.45128334 |
| 0.80 | 1.2451643 | 391.48666  | -1.56                 | 94.275043    | +10.55                | 0.41815902 |
| 0.85 | 1.2473405 | 370.59239  | -1.85                 | 85.955295    | + 4.72                | 0.37940017 |
| 0.90 | 1.2277400 | 349.64951  | -1.66                 | 75.221599    | + 0.43                | 0.33717536 |
| 0.95 | 1.1715345 | 328.45734  | -0.92                 | 62.618319    | - 0.78                | 0.29508380 |

TABLE 7. Critical temperatures, pressures, and compressibility factors and critical reduced densities obtained from the generalized equation of state using van der Waals' combinations

| x    | Dr        | Tk<br>(°K) | Dev. From<br>Data (%) | Pk<br>(atm.) | Dev. From<br>Data (%) | Zk         |
|------|-----------|------------|-----------------------|--------------|-----------------------|------------|
| 0.05 | 0.9768298 | 537.45599  | +0.35                 | 30.644440    | +1.63                 | 0.30624680 |
| 0.10 | 0.9633264 | 534.36914  | +0.64                 | 34.488729    | +2.79                 | 0.33903493 |
| 0.15 | 0.9581024 | 531.05083  | +0.87                 | 38.532570    | +3.73                 | 0.36912509 |
| 0.20 | 0.9595236 | 527.30369  | +1.03                 | 42.815067    | +4.46                 | 0.39668929 |
| 0.25 | 0.9664084 | 522.95364  | +1.15                 | 47.359121    | +5.36                 | 0.42184106 |
| 0.30 | 0.9779152 | 517.78913  | +1.20                 | 52.168630    | +6.14                 | 0.44459261 |
| 0.35 | 0.9933872 | 511.65693  | +1.19                 | 57.221872    | +6.87                 | 0.46484445 |
| 0.40 | 0.0122475 | 504.36183  | +1.12                 | 62.461497    | +7.51                 | 0.48236720 |
| 0.45 | 1.0339289 | 495.71973  | +0.97                 | 67.781420    | +7.99                 | 0.49677399 |
| 0.50 | 1.0578205 | 485.55437  | +0.73                 | 73.011208    | +8.18                 | 0.50748858 |
| 0.55 | 1.0832113 | 473.70934  | +0.40                 | 77.899690    | +7.97                 | 0.51371798 |
| 0.60 | 1.1092170 | 460.06761  | -0.03                 | 82.102129    | +7.20                 | 0.51444616 |
| 0.65 | 1.1346673 | 444.58183  | -0.56                 | 85.179809    | +5.74                 | 0.50847929 |
| 0.70 | 1.1579352 | 427.31567  | -1.17                 | 86.627134    | +3.50                 | 0.49459062 |
| 0.75 | 1.1766970 | 408.4842   | -1.79                 | 85.944862    | +0.51                 | 0.47181998 |
| 0.80 | 1.1876393 | 388.49618  | -2.31                 | 82.766929    | -2.94                 | 0.43993903 |
| 0.85 | 1.1861305 | 367.86444  | -2.57                 | 77.008248    | -6.18                 | 0.39996076 |
| 0.90 | 1.1656461 | 347.09784  | -2.37                 | 68.949631    | -7.94                 | 0.35445651 |
| 0.95 | 1.1152699 | 326.45019  | -1.52                 | 59.191060    | -6.21                 | 0.30786518 |

TABLE 8. Critical temperatures, pressures, and compressibility factors and critical reduced densities obtained from the generalized equation of state using Joffe's mixture rule

| x    | Dr        | Tk<br>(°K) | Dev. From<br>Data (%) | Pk<br>(atm.) | Dev. From<br>Data (%) | Zk         |
|------|-----------|------------|-----------------------|--------------|-----------------------|------------|
| 0.05 | 0.9727908 | 537.69519  | +0.39                 | 29.889297    | -0.88                 | 0.29790306 |
| 0.10 | 0.9514143 | 534.84787  | +0.73                 | 32.996463    | -1.66                 | 0.32403773 |
| 0.15 | 0.9362428 | 531.88385  | +1.02                 | 36.302932    | -2.28                 | 0.34880851 |
| 0.20 | 0.9265177 | 528.69177  | +1.30                 | 39.843636    | -2.69                 | 0.37217648 |
| 0.25 | 0.9214978 | 525.16053  | +1.57                 | 43.650313    | -2.89                 | 0.39417022 |
| 0.30 | 0.9206871 | 521.17216  | +1.86                 | 47.751547    | -2.85                 | 0.41477934 |
| 0.35 | 0.9238190 | 516.59494  | +2.17                 | 52.171467    | -2.56                 | 0.43393137 |
| 0.40 | 0.9308000 | 511.27742  | +2.50                 | 56.926158    | -2.01                 | 0.45148343 |
| 0.45 | 0.9416647 | 505.04261  | +2.87                 | 62.016929    | -1.20                 | 0.46720848 |
| 0.50 | 0.9565450 | 497.68220  | +3.25                 | 67.418917    | -0.11                 | 0.48076944 |
| 0.55 | 0.9756409 | 488.95109  | +3.63                 | 73.062511    | +1.26                 | 0.49167708 |
| 0.60 | 0.9991835 | 478.56353  | +3.99                 | 78.803787    | +2.89                 | 0.49922584 |
| 0.65 | 1.0273678 | 466.19395  | +4.27                 | 84.379008    | +4.75                 | 0.50240232 |
| 0.70 | 1.0602174 | 451.48901  | +4.42                 | 89.338656    | +6.74                 | 0.49976437 |
| 0.75 | 1.0973090 | 434.10254  | +4.37                 | 92.962654    | +8.72                 | 0.48930956 |
| 0.80 | 1.1371929 | 413.77168  | +4.04                 | 94.17901     | +10.44                | 0.46841056 |
| 0.85 | 1.1761194 | 390.45139  | +3.41                 | 91.567138    | +11.25                | 0.43404523 |
| 0.90 | 1.2048942 | 364.48466  | +2.52                 | 83.588143    | +11.60                | 0.38386639 |
| 0.95 | 1.1985574 | 336.58129  | +1.53                 | 69.258505    | +9.74                 | 0.31938622 |

Figure 12. Critical temperature as a function of mole fraction ethane

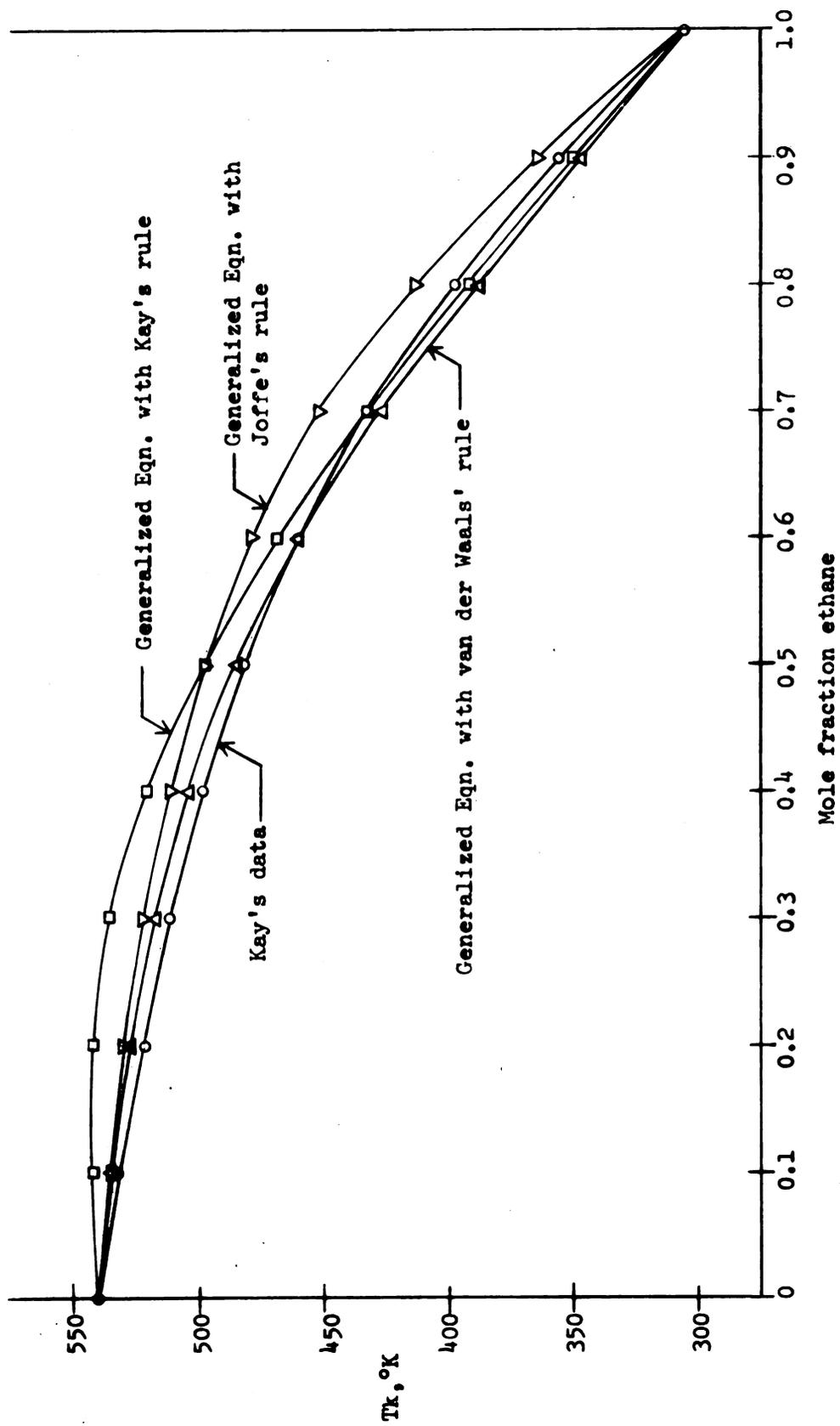




Figure 13. Critical pressure as a function of mole fraction ethane

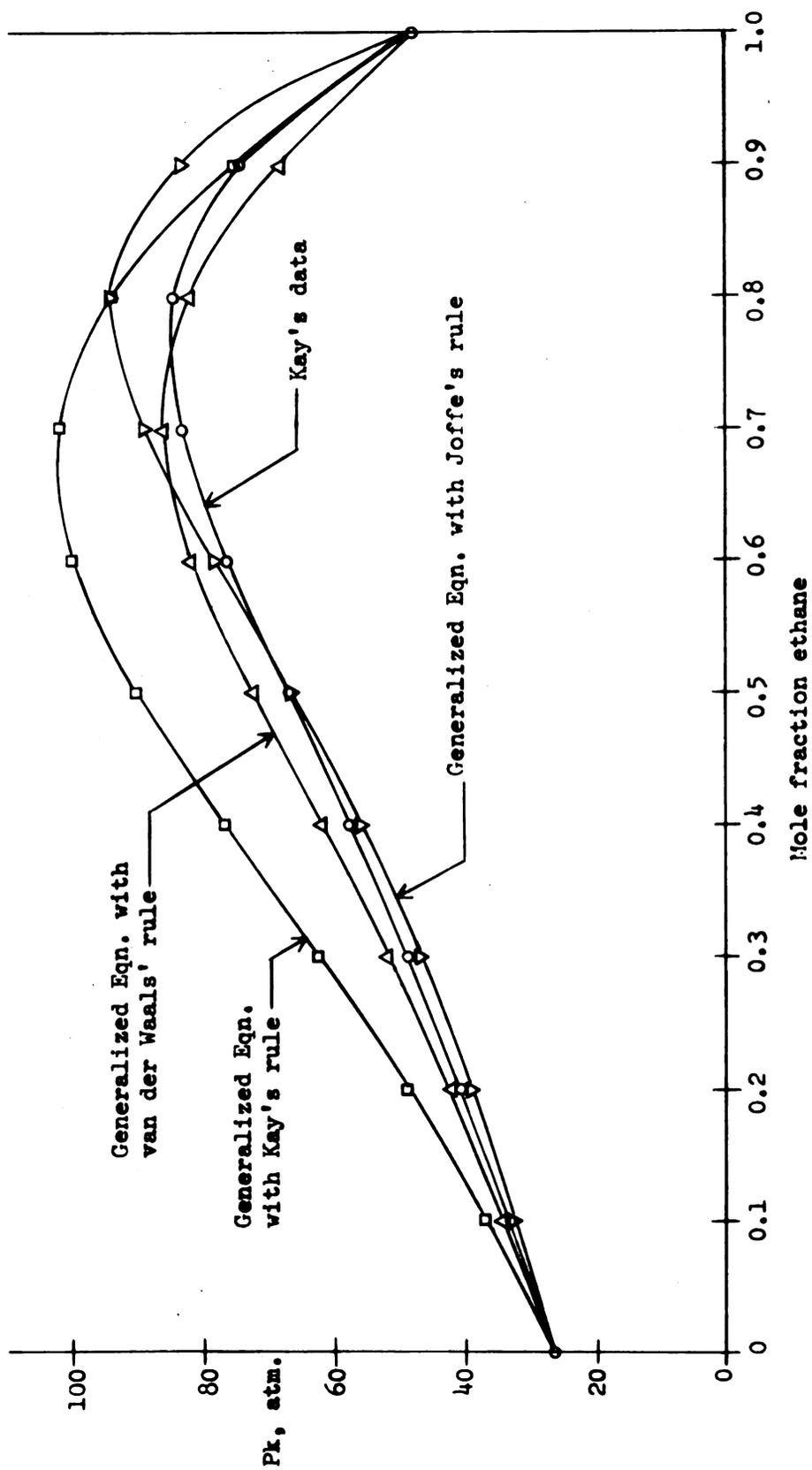
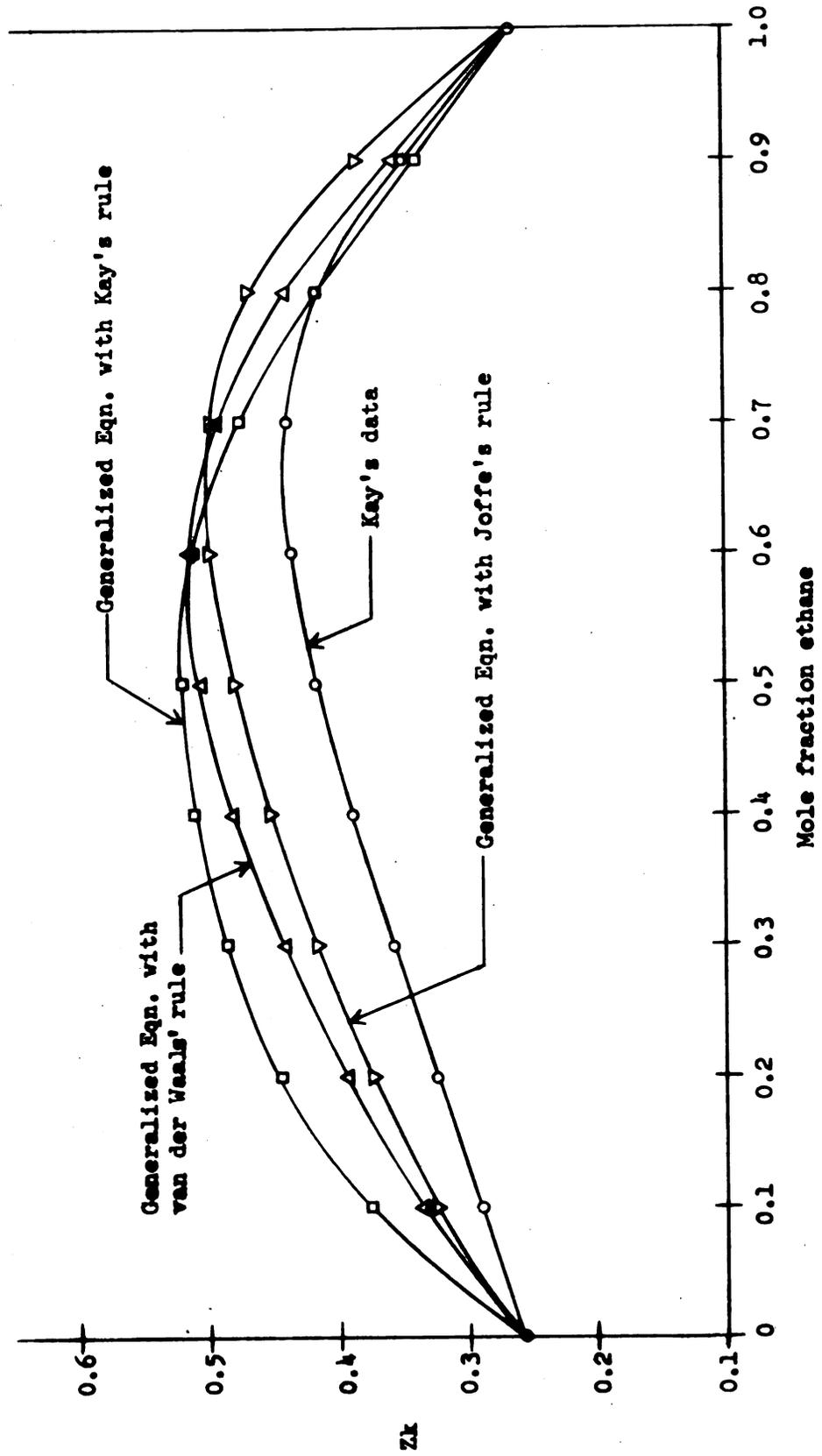




Figure 14. Critical compressibility as a function of mole fraction ethane



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the van der Waals' combinations indicates that this mixture rule may be very satisfactory for vapor-liquid equilibrium calculations. However, the poorer compressibility factor agreement indicates that the predicted densities are in error from the experimental densities. This lack of agreement means that the mixture rule probably would not be entirely satisfactory for predicting other thermodynamic quantities from a generalized equation of state.

#### Generation of Pseudocritical Mixture Rules

The results from the first two approaches which were used to compute  $T_{c_m}$  and  $P_{c_m}$  values were not completely satisfactory. They are listed along with a discussion of the data in Appendix IX.

By assuming the curves of  $T_{c_m}$  and  $P_{c_m}$  to be cubic (Program TOTRANGE), values of  $T_{c_m}$  and  $P_{c_m}$  were computed at two intermediate values of composition. Table 9 lists the results from program TOTRANGE for two pairs of  $x$  values. The pairs used were  $x = 0.6215, 0.8723$  (approximately symmetrical with respect to weight fraction) and  $x = 0.333, 0.667$  (symmetrical with respect to mole fraction).

TABLE 9. Values of pseudocritical temperature and pressure as computed by program TOTRANGE

| $x$    | $T_c$        | $P_c$          | Graph Symbol |
|--------|--------------|----------------|--------------|
| 0.333  | 454.11823 °K | 28.445853 atm. | △            |
| 0.667  | 378.39011    | 35.058287      | △            |
| 0.6215 | 394.77462    | 35.821393      | □            |
| 0.8723 | 336.30273    | 43.010320      | □            |

Figures 15 and 16 are plots of pseudocritical temperatures and

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pressures as a function of composition. Figure 15 shows the  $T_{c_m}$  curves from program TOTRANGE and van der Waals' mixture rule to be nearly linear. The generated pseudocritical pressure curve (Figure 16) is reasonably close to the curve predicted by the van der Waals' mixture rule, but both of these curves deviate considerably from linearity (Kay's rule).

Using the computed reduced compressibility factors from program TOTRANGE, the values of critical compressibility factor were calculated and plotted in Figure 17. The agreement with Kay's data is only fair but it is better than the agreement obtained using van der Waals' mixture rule in the generalized equation of state. Errors were undoubtedly introduced because the computations in program TOTRANGE involved fitting a third degree polynomial to only four points and then taking up to third derivatives of this polynomial. This numerical procedure would explain the variation of the values at  $x = 0.6215$  and  $x = 0.667$  in Figures 15, 16, and 17.

If more accurate pseudocritical curves could be generated by using smaller increments of composition then, theoretically, the computed curve should come closer to the data curve in Figure 17.

#### Differentiation Check

The results of a program written to numerically check the expressions for  $G^{(1)}$  and  $G^{(2)}$  are shown in Table 10. Agreement to at least three significant figures was obtained between the numerical and mathematical calculations of the derivatives.

Figure 15. Pseudocritical temperatures computed from program TOTRANGE as a function of mole fraction ethane

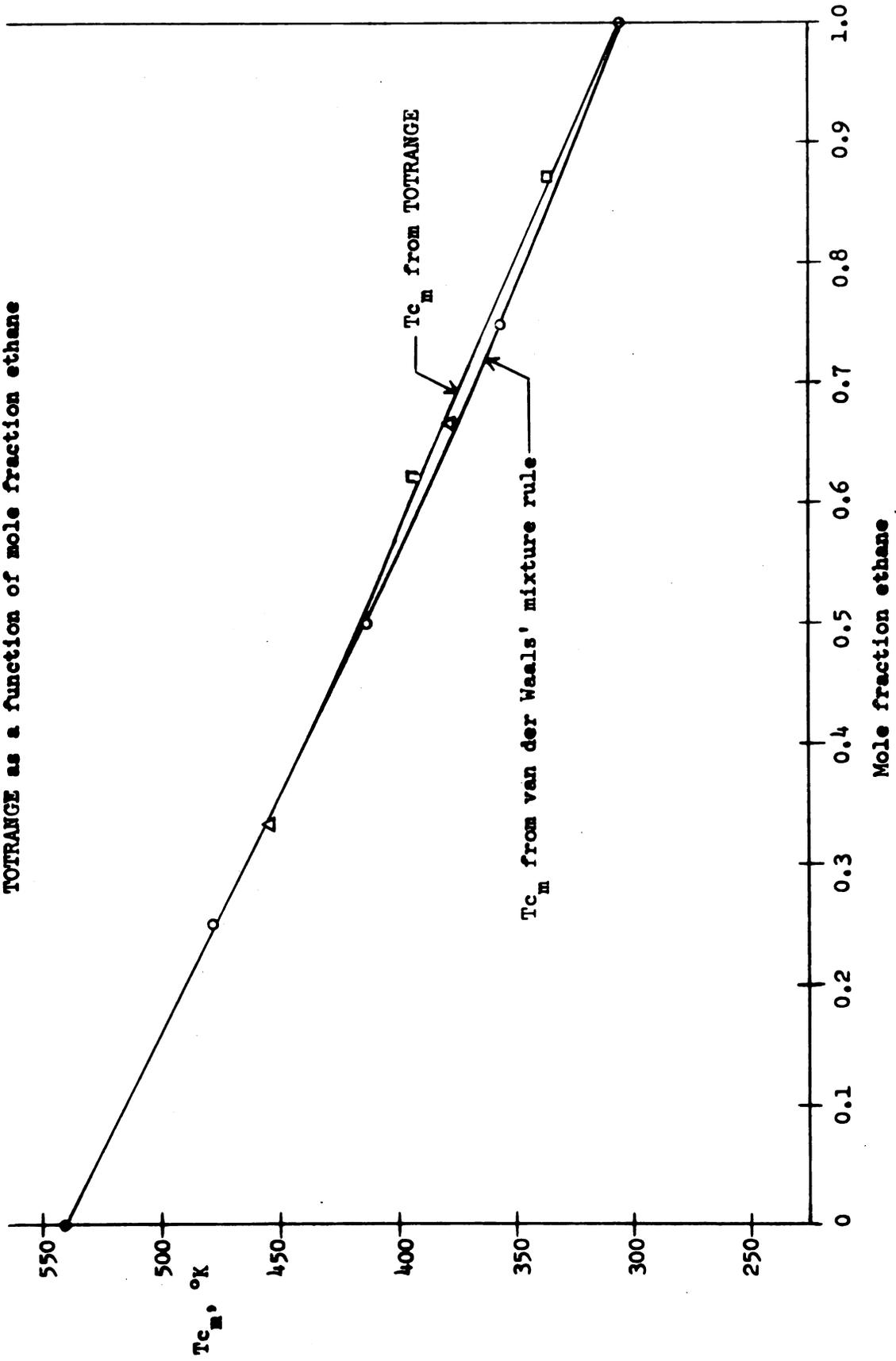


Figure 16. Pseudocritical pressures computed from program TOTRANGE as a function of mole fraction ethane

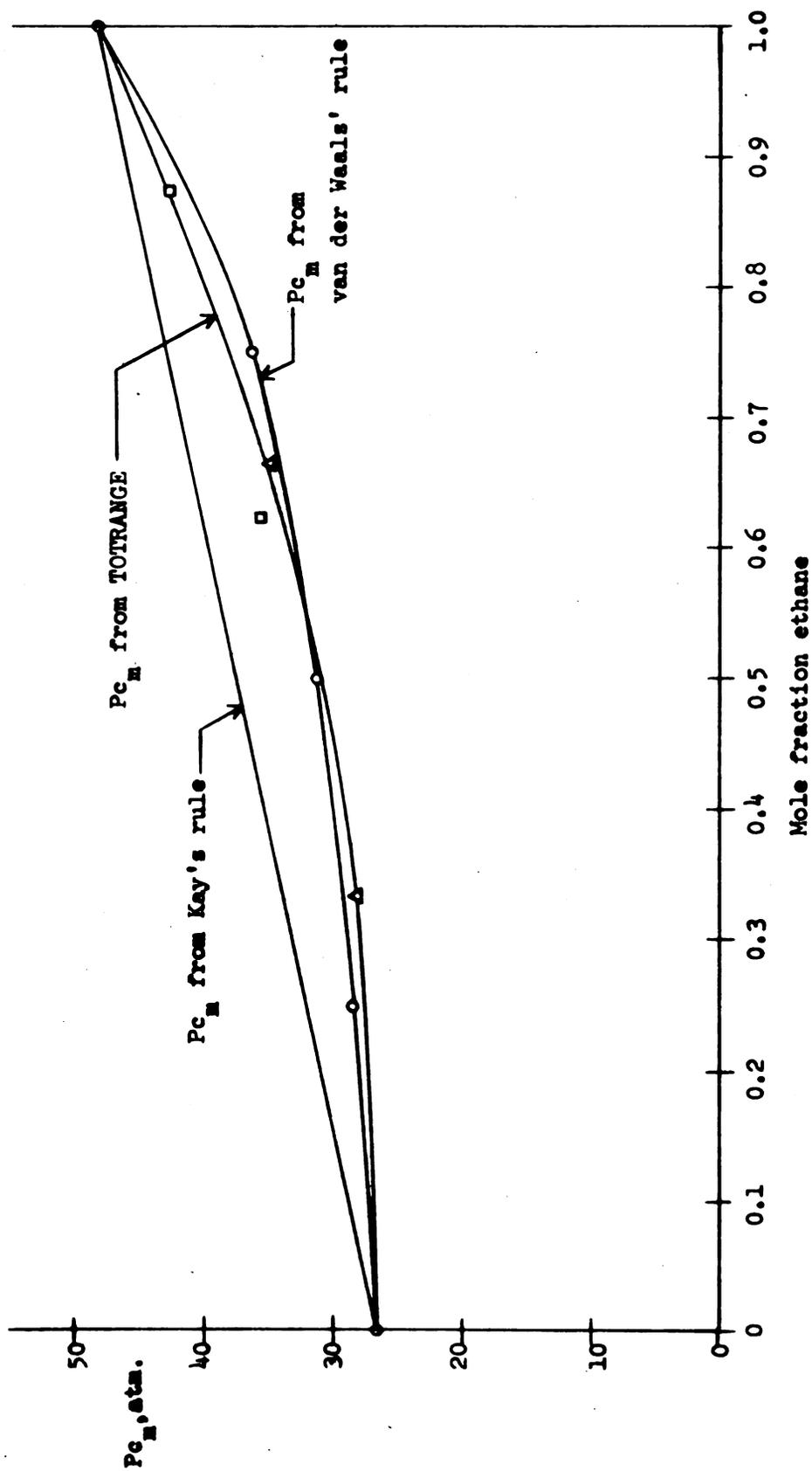


Figure 17. Critical compressibility factors as computed from program TOTRANGE as a function of mole fraction ethane

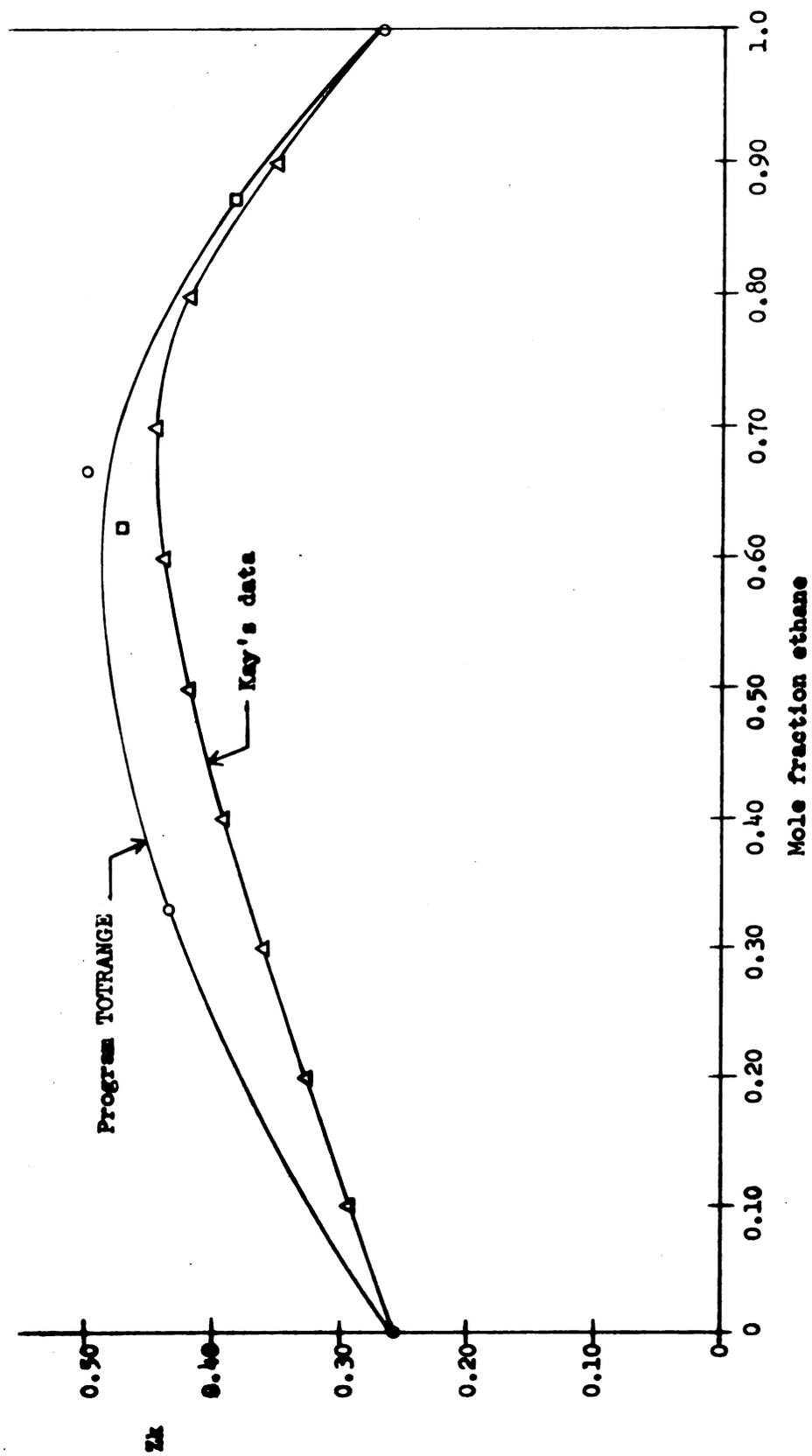


TABLE 10. Results from program CHECK for three values of composition

|                 | $G'$         | $G''$       | $G'''$       |
|-----------------|--------------|-------------|--------------|
| <b>x = 0.10</b> |              |             |              |
| Numerical       | -6.431077905 | 7.704937921 | -3.798404175 |
| Analytical      | -6.431534010 | 7.705581635 | -3.798455510 |
| <b>x = 0.50</b> |              |             |              |
| Numerical       | 1.101609680  | 6.944423760 | 2.148565989  |
| Analytical      | 1.101493811  | 6.944451400 | 2.148572376  |
| <b>x = 0.90</b> |              |             |              |
| Numerical       | 7.040336664  | 3.936850926 | 4.290774979  |
| Analytical      | 7.040051734  | 3.937199652 | 4.289405663  |

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## CONCLUSIONS

Using the eight constant Benedict-Webb-Rubin equation of state for a reference compound, an expression for reduced pressure in terms of reduced temperature and density was derived. This expressed, in equation form, relationships which usually appear only in tables and charts. Reduced expressions were also derived for the second and third partial derivatives of free energy with respect to mole fraction at constant temperature and pressure.

Computer programs were written and tested for use on the Control Data Corporation 3600 digital computer. Included were programs which performed the following: (1) Calculation of reduced pressure and compressibility factor using the reduced equation of state. (2) Calculation of derived thermodynamic quantities including the second and third partial derivatives of free energy. (3) Computation of critical envelope curves by simultaneously converging the second and third partial derivatives of free energy to zero. (4) Computation of pseudocritical temperature and pressure curves using free energy conditions at the critical point and experimental critical envelope curve data. (5) Numerical calculation for checking analytically derived expressions for the second and third free energy derivatives.

A method was devised to compute convergence pressure curves which previously had been available only from experimental data. The eight constant Benedict-Webb-Rubin equation of state made excellent predictions of the critical envelope curve for the ethane-n-heptane system. However, using the following mixture rules

$$P_{c_m} = \left[ \frac{\sum_{i=1}^n x_i (T_c/P_c)^{1/2}_i}{\sum_{i=1}^n x_i (T_c/P_c)_i} \right]^2$$

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$$T_{c_m} = \left[ \sum_{i=1}^n x_i (T_c/P_c)^{1/2}_i \right]^2 / \sum_{i=1}^n x_i (T_c/P_c)_i$$

in conjunction with the two constant reduced equation of state, results were obtained that were about as good as those from the eight constant Benedict-Webb-Rubin equation.

Using experimental critical envelope curve data, cubic curves of pseudocritical temperature and pressure were generated which were in good agreement with the above mixture rules. When the critical compressibility factor curves were computed from the generated pseudocritical curves, the results were closer to the experimental data than those computed using the above mixture rules.

## SUGGESTIONS FOR FURTHER STUDY

The excellent convergence pressure curve agreement obtained with the van der Waals mixture rule, when used with the generalized equation of state, reveals a slightly different approach which may yield more success with computational methods which progress across the composition range in small increments. This new approach would require changing the experimental critical temperature and pressure data to fit the convergence pressure curve predicted by the van der Waals combinations (Figures 12, 13) when used with the generalized equation. Equations for  $G''$  and  $G'''$  could be used, as in program LINEAR, to generate pseudocritical temperature and pressure curves. These generated curves should be approximately the same as the pseudocritical curves predicted by the van der Waals mixture rule. As the calculation proceeded across the composition range, at least three possibilities might occur:

1. The generated curves could begin to deviate greatly from the pseudocritical curves computed from the van der Waals combinations. This would indicate the magnification of an error. This might be corrected by beginning in the middle of the composition range and progressing towards the two ends.

2. The generated curves may be very close to the van der Waals mixture rule curve, yet at some point the calculations might not converge. This would indicate that a better convergence method was needed.

3. The computations may proceed across the entire composition range. In this case, relaxation techniques may be applicable to change the experimental data back to Kay's data.

A study should also be made to determine how accurately the

generalized equation of state with van der Waals' mixture rule will predict vapor-liquid equilibria. This computation would require fugacity and vapor pressure calculations. The results could then be compared with experimental vapor-liquid equilibrium data.

## NOMENCLATURE

|   |   |
|---|---|
| a   | = Activity  |
| $A_0, B_0, C_0, a,$<br>b, c, $\alpha, \gamma$ | = Constants in Benedict-Webb-Rubin equation of state  |
| d   | = Differential operator   |
| D   | = Molal density, moles/unit volume  |
| Dc  | = Critical molal density of a pure component, moles/<br>unit volume   |
| $Dc_m$  | = Pseudocritical molal density of a mixture, moles/<br>unit volume  |
| Dk  | = Critical molal density of a binary mixture, moles/<br>unit volume   |
| Dr  | = Reduced molal density   |
| f   | = Fugacity  |
| $f, g, h, i, j,$<br>k, l, m, n                | = Constants in the reduced Benedict-Webb-Rubin equation<br>of state   |
| F   | = Gibbs free energy   |
| $\bar{F}$                                     | = Free energy/mole  |
| G   | = $\bar{F}/RT$ of a binary mixture of two gases, referred to<br>standard states of unit fugacity for the pure<br>components, which have been mixed in a perfect gas<br>state at the temperature of the system |
| K   | = Equilibrium ratio or K-factor, $y/x$  |
| $K_v$   | = Vaporization equilibrium ratio, $a_v/a_L$   |
| L   | = Liquid volume correction term   |
| P   | = Total pressure, atm.  |
| Pc  | = Critical pressure of pure component, atm.   |
| $Pc_m$  | = Pseudocritical pressure of a mixture, atm.  |
| $P_0$   | = A low pressure such that gases exhibit perfect gas<br>behavior, atm.  |
| Pr  | = Reduced pressure  |

|                            |   |
|----------------------------|---|
| R                          | = Gas constant, (liter·atm.)/(g-mole·K°)                    |
| T                          | = Temperature, °K   |
| T <sub>c</sub>             | = Critical temperature of pure component, K°                |
| T <sub>c<sub>m</sub></sub> | = Pseudocritical temperature of a mixture, °K               |
| T <sub>k</sub>             | = Critical temperature of a binary mixture, °K              |
| Tr                         | = Reduced temperature                                       |
| V                          | = Volume  |
| $\bar{V}$                  | = Unit volume/mole  |
| $\bar{V}_0$                | = Unit volume/mole under perfect gas conditions             |
| x                          | = Mole fraction ethane                                      |
| x                          | = Mole fraction in the liquid phase                         |
| y                          | = Mole fraction in the vapor phase                          |
| Z                          | = Compressibility factor, $\bar{P}\bar{V}/RT$               |
| Z <sub>c</sub>             | = Critical compressibility factor of pure component         |
| Z <sub>c<sub>m</sub></sub> | = Pseudocritical compressibility factor of a binary mixture |
| Z <sub>k</sub>             | = Critical compressibility factor of a binary mixture       |
| Z <sub>r</sub>             | = Reduced compressibility factor                            |

## GREEK SYMBOLS

|               |   |
|---------------|---|
| $\Delta$      | = Finite change of a property; a positive value indicates an increase         |
| $\partial$    | = Partial differential operator   |
| $\gamma$      | = Overall activity coefficient  |
| $\gamma_{Ay}$ | = Activity coefficient of component A in vapor phase at a mole fraction of y  |
| $\gamma_{Ax}$ | = Activity coefficient of component A in liquid phase at a mole fraction of x |
| $\nu$         | = Fugacity coefficient  |

## SUBSCRIPTS

|     |                                      |
|-----|--------------------------------------|
| A   | = Component A                        |
| B   | = Component B                        |
| i   | = Component i                        |
| j   | = Component j                        |
| L   | = Liquid phase                       |
| P   | = Total pressure                     |
| V   | = Vapor phase                        |
| VPA | = Vapor pressure of pure component A |
| VPB | = Vapor pressure of pure component B |

## SUPERSCRIPITS

|     |   |
|-----|---|
| '   | = First derivative with respect to mole fraction ethane at constant temperature and pressure  |
| ''  | = Second derivative with respect to mole fraction ethane at constant temperature and pressure |
| ''' | = Third derivative with respect to mole fraction ethane at constant temperature and pressure  |
| °   | = Standard state  |

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APPENDIX I

Derivation of an Equilibrium Ratio Expression for a Two Phase Mixture

Temperature T

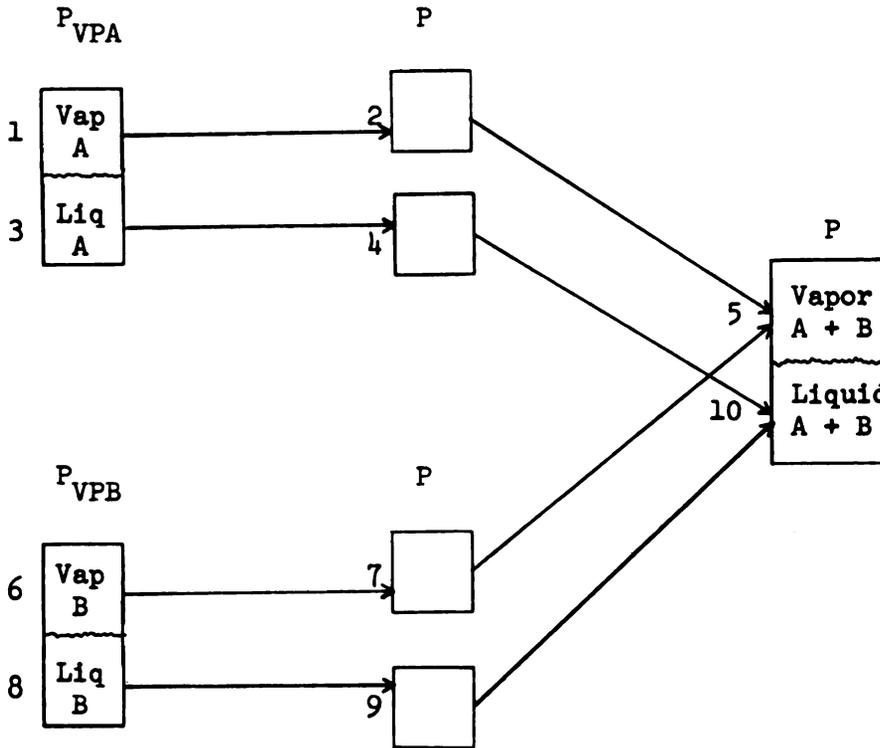


Figure 18. Formation of a two phase mixture at temperature  $T$  and pressure  $P$

For component A in Figure 18:

$$\bar{F}_1 = \bar{F}_3 \quad (1)$$

$$\text{and } \bar{F}_5 = \bar{F}_{10} \quad (2)$$

Subtracting (2) from (1)

$$\bar{F}_1 - \bar{F}_5 = \bar{F}_3 - \bar{F}_{10} \quad (3)$$

Letting  $\Delta\bar{F}_{i-j}$  represent  $\bar{F}_i - \bar{F}_j$ , (3) can be written

$$\Delta\bar{F}_{1-5} = \Delta\bar{F}_{3-10}$$

$$\text{or } \Delta\bar{F}_{1-2} + \Delta\bar{F}_{2-5} = \Delta\bar{F}_{3-4} + \Delta\bar{F}_{4-10} \quad (4)$$

Step

Step

Step

Step

Step 1-2 By definition  $d\bar{F} = RT d \ln f$

$$\Delta\bar{F}_{1-2} = RT \ln (f_2/f_1) = RT \ln(f_{AP}/f_{AVP}) \quad (5)$$

Step 2-5  $\Delta\bar{F}_{2-5} = RT \ln(f_5/f_2) = RT \ln[(f_5/f^\circ)/(f_2/f^\circ)]$

where  $f^\circ$  represents the fugacity in the standard state. Let

$$f^\circ = f_2$$

Since  $a = f/f^\circ$

$$\text{then } \Delta\bar{F}_{2-5} = RT \ln a_5$$

By definition  $a_5 = \gamma_{AV}y_A$

$$\text{Therefore } \Delta\bar{F}_{2-5} = RT \ln(\gamma_{AV}y_A) \quad (6)$$

Step 3-4 By definition  $d\bar{F} = \bar{V}_L dP - \bar{S}dT$

$$\text{or } [d\bar{F} = \bar{V}_L dP]_T$$

$$\Delta\bar{F}_{3-4} = \int_{P_{AVP}}^P \bar{V}_L dP \quad (7)$$

Step 4-10 Using an argument similar to that used to derive equation (6)

$$\Delta\bar{F}_{4-10} = RT \ln(\gamma_{AL}x_A) \quad (8)$$

Inserting (5), (6), (7), and (8) into (4):

$$RT \ln(f_{AP}/f_{AVP}) + RT \ln(\gamma_{AV}y_A) = \int_{P_{AVP}}^P \bar{V}_L dP + RT \ln(\gamma_{AL}x_A)$$

$$\text{or } y_A/x_A = [P_{AVP}v_{AVP}\gamma_{AL}/(Pv_{AP}\gamma_{AV})]L \quad (9)$$

$$\text{where } L = \exp[(1/RT) \int_{P_{AVP}}^P \bar{V}_L dP]$$

$$v = f/P$$

APPENDIX II

Derivation of Relationships for Calculating Free Energy of a Binary Mixture at Temperature T and Pressure P

Let the standard states be the vapor of the pure components at unit fugacity at the temperature of the system. For purposes of this calculation assume the following path.

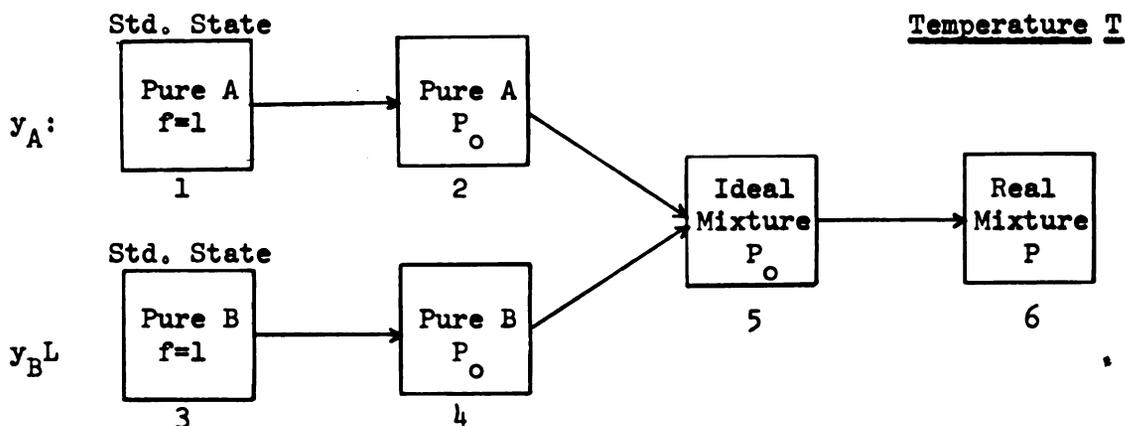


Figure 19. Path for calculation of the free energy of a binary mixture at temperature T and pressure P

$$\Delta \bar{F}_{TOT} = (\bar{F}_{mix} \text{ at } T \text{ and } P) - (y_A \bar{F}_A^\circ + y_B \bar{F}_B^\circ)$$

$$\Delta \bar{F}_{TOT} = y_A (\Delta \bar{F}_{1-2} + \Delta \bar{F}_{2-5}) + y_B (\Delta \bar{F}_{3-4} + \Delta \bar{F}_{4-5}) + \Delta \bar{F}_{5-6} \quad (1)$$

$$\Delta \bar{F}_{1-2} = RT \ln(f_2/f_1) = RT \ln(P_0/1) = RT \ln P_0$$

likewise,  $\Delta \bar{F}_{3-4} = RT \ln P_0$

$$\Delta \bar{F}_{2-5} = RT \ln y_A$$

$$\Delta \bar{F}_{4-5} = RT \ln y_B$$

$$\Delta \bar{F}_{5-6} = \int_{P_0}^P \bar{V} dP$$

Integrating by parts,

$$\Delta \bar{F}_{5-6} = \bar{V}P \Big|_{P_0}^P - \int_{\bar{V}_0}^{\bar{V}} P d\bar{V}$$

where  $\bar{V}_0$  = molal volume at pressure  $P_0$

The Benedict-Webb-Rubin equation of state may be written

$$P = RT/\bar{V} + A$$

where  $A = f(T, \bar{V})$  and represents the balance of the equation of state.

$$\Delta \bar{F}_{5-6} = \bar{V}P - \bar{V}_0 P_0 - \int_{\bar{V}_0}^{\bar{V}} (RT/\bar{V} + A) d\bar{V}$$

$$\Delta \bar{F}_{5-6} = \bar{V}P - \bar{V}_0 P_0 - RT \ln(\bar{V}/\bar{V}_0) - \int_{\bar{V}_0}^{\bar{V}} A d\bar{V}$$

But,  $A = P - RT/\bar{V}$

$$\text{Therefore } \int_{\bar{V}_0}^{\bar{V}} A d\bar{V} = \int_{\bar{V}_0}^{\bar{V}} (P - RT/\bar{V}) d\bar{V}$$

$$\bar{V} = 1/D$$

$$d\bar{V} = (-1/D^2) dD$$

$$\int_{\bar{V}_0}^{\bar{V}} A d\bar{V} = - \int_0^D [(P - RTD)/D^2] dD$$

Let

$$I = \int_0^D [(P - RTD)/D^2] dD$$

Thus,

$$\Delta \bar{F}_{5-6} = \bar{V}P - \bar{V}_0 P_0 - RT \ln(\bar{V}/\bar{V}_0) + I$$

From the perfect gas law,  $\bar{V}_0 P_0 = RT$

$$\Delta \bar{F}_{5-6} = \bar{V}P - RT - RT \ln \bar{V} + RT \ln(RT) - RT \ln P_0 + I$$

Substituting into (1)

$$\begin{aligned}\Delta \bar{F}_{\text{TOT}} &= y_A RT \ln P_o + y_B RT \ln P_o + y_A RT \ln y_A + y_B RT \ln y_B \\ &+ \bar{V}P - RT - RT \ln \bar{V} + RT \ln(RT) - RT \ln P_o + I\end{aligned}$$

Since  $y_A + y_B = 1$

$$y_A RT \ln P_o + y_B RT \ln P_o = RT \ln P_o$$

$$\Delta \bar{F}_{\text{TOT}} = y_A RT \ln y_A + y_B RT \ln y_B + \bar{V}P - RT - RT \ln(\bar{V}/RT) + I$$

Adding and subtracting  $RT \ln P$

$$\Delta \bar{F}_{\text{TOT}} = RT \ln P + y_A RT \ln y_A + y_B RT \ln y_B + RT(Z - 1 - \ln Z) + I$$

By definition

$$G = \bar{F}/RT$$

But using the above stated standard states

$$\Delta \bar{F}_{\text{TOT}} = (\bar{F}_{\text{mix}} \text{ at } T \text{ and } P)$$

Therefore  $G = \Delta \bar{F}_{\text{TOT}}/RT$

or  $G = \ln P + y_A \ln y_A + (1 - y_A) \ln(1 - y_A) + Z - 1 - \ln Z$

$$+ (1/RT) \int_0^D [(P - RTD)/D^2] dD \quad (2)$$

### APPENDIX III

#### Derivation of the Equations for G'' and G'''

Benedict-Webb-Rubin equation of state:

$$P = RDT + (B_0 RT - A_0 - C_0/T^2)D^2 + (bRT - a)D^3 + aaD^6 + (cD^3/T^2)(1 + \gamma D^2)\exp(-\gamma D^2) \quad (1)$$

Making the following substitutions into (1):

$$\begin{aligned} P &= P_c P_r, & T &= T_c T_r, & D &= D_c D_r, \\ P_c P_r &= R T_r T_c D_r D_c + (B_0 R T_c T_r - A_0 - C_0/T_r^2 T_c^2) D_r^2 D_c^2 \\ &+ (b R T_c T_r - a) D_r^3 D_c^3 + aa D_r^6 D_c^6 + (c D_r^3 D_c^3 / T_r^2 T_c^2) \\ &(1 + \gamma D_r^2 D_c^2) \exp(-\gamma D_r^2 D_c^2) \end{aligned} \quad (2)$$

Let

$$\begin{aligned} f &= R T_c D_c / P_c \\ g &= B_0 R T_c D_c^2 / P_c \\ h &= A_0 D_c^2 / P_c \\ i &= C_0 D_c^2 / T_c^2 P_c \\ j &= b R T_c D_c^3 / P_c \\ k &= a D_c^3 / P_c \\ l &= aa D_c^6 / P_c \\ m &= c D_c^3 / T_c^2 P_c \\ n &= \gamma D_c^2 \end{aligned}$$

Therefore

$$P_r = f T_r D_r + (g T_r - h - i/T_r^2) D_r^2 + (j T_r - k) D_r^3 + l D_r^6 + (m D_r^3 / T_r^2) (1 + n D_r^2) \exp(-n D_r^2) \quad (3)$$

This is the reduced form of the Benedict-Webb-Rubin equation of state.

From the discussion of free energy (Appendix II), it was shown that

$$G = \ln P + y_A \ln y_A + (1 - y_A) \ln(1 - y_A) + Z - 1 - \ln Z + (1/RT) \int_0^D [(P - RTD)D^2] dD \quad (4)$$

Letting  $y_A = x =$  mole fraction ethane and substituting (1) into (4)

$$G = \ln P + x \ln x + (1 - x) \ln(1 - x) + Z - 1 - \ln Z + (1/RT) [(B_0 RT - A_0 - C_0/T^2)D + (bRT - a)D^2/2 + aD^5/5 + (cD^2/2T^2)(2/\gamma D^2 - [2 \exp(-\gamma D^2)]/\gamma D^2 - \exp(-\gamma D^2))] \quad (5)$$

Putting (5) into reduced form

$$G = \ln P_{c,m} Pr + x \ln x + (1 - x) \ln(1 - x) + Z - 1 - \ln Z + (B_0 - A_0/RTcTr - C_0/RTr^3Tc^3)DcDr + (b - a/RTcTr)Dc^2Dr^2/2 + aDc^5Dr^5/5RTcTr + (cDr^2Dc^2/2RTc^3Tr^3)[(2 - 2\exp(-\gamma Dc^2Dr^2))/\gamma Dc^2Dr^2 - \exp(-\gamma Dc^2Dr^2)] \quad (6)$$

Note:

$$B_0 Dc = g/f$$

$$A_0 Dc/RTc = h/f$$

$$C_0 Dc/RTc^3 = i/f$$

$$bDc^2/2 = j/2f$$

$$aDc^2/2RTc = k/2f$$

$$aDc^5/5RTc = l/5f$$

$$cDc^2/2RTc^3 = m/2f$$

$$c/2\gamma RTc^3 = m/2nf$$

$$\gamma Dc^2 = n$$

Then,

$$G = \ln P_{c,m} Pr + x \ln x + (1 - x) \ln(1 - x) + Z - 1 - \ln Z + [(g - h/Tr - i/Tr^3)Dr + (j - k/Tr)Dr^2/2 + (l/Tr)Dr^5/5 + (mDr^2/2Tr^3)[(2 - 2\exp(-nDr^2))/nDr^2 - \exp(-nDr^2)]]/f \quad (7)$$

Let

$$T_o = 1./Tr \quad (8)$$

$$T_o' = -Tr'/Tr^2 \quad (9)$$

$$T_o'' = 2(Tr')^2/Tr^3 - Tr''/Tr^2 \quad (10)$$

$$T_o''' = -T_o[3(T_o'Tr'' + T_o''Tr') + T_o'Tr'''] \quad (11)$$

$$T_n = 1./Tr^3 = T_o^3 \quad (12)$$

$$T_n' = 3T_o^2T_o' \quad (13)$$

$$T_n'' = 6T_o(T_o')^2 + 3T_o^2T_o'' \quad (14)$$

$$T_n''' = 3[2T_o' + 6T_oT_o'T_o'' + T_o^2T_o'''] \quad (15)$$

$$G = x \ln x + (1.-x)\ln(1.-x) + Z - 1. - \ln Z + \ln Pc_m Pr \\ + [(g - hT_o - iT_n)Dr + (j - kT_o)Dr^2/2 + 1T_oDr^5/5 \\ + mT_n/n + (m/2n)T_n \exp(-nDr^2)(-2 - nDr^2)]/f \quad (16)$$

$$G' = \left(\frac{\partial G}{\partial x}\right)_{T,P} = \ln[x/(1. - x)] + Z' - Z'/Z + [(g - hT_o - iT_n)Dr' \\ - (hT_o' + iT_n')Dr + (j - kT_o)DrDr' - kT_o'Dr^2/2 + 1T_oDr^4Dr' \\ + 1T_o'Dr^5/5 + mT_n'/n + (m/2n) \cdot \exp(-nDr^2) \\ (-2T_n' - nDr^2T_n' + 2nDrDr'T_n + 2n^2Dr^3Dr'T_n)]/f \quad (17)$$

$$G'' = \left(\frac{\partial^2 G}{\partial x^2}\right)_{T,P} = 1./(x - x^2) + Z'' - Z''/Z + (Z'/Z)^2 + [gDr'' \\ - h(T_oDr'' + T_o'Dr + 2T_o'Dr') - i(T_nDr'' + T_n'Dr + 2T_n'Dr') \\ + j[DrDr'' + (Dr')^2] - k[T_oDrDr'' + T_o'Dr^2/2 + 2T_o'DrDr' \\ + T_o(Dr')^2] + 1[2T_o'Dr^4Dr' + T_o'Dr^5/5 + 4T_oDr^3(Dr')^2 \\ + T_oDr^4Dr''] + mT_n''/n + (m/2n)\exp(-nDr^2)(-2T_n'' - nDr^2T_n'' \\ + 4nDrDr'T_n' + 2nDrDr''T_n + 2n(Dr')^2T_n + 4n^2Dr^3Dr'T_n' \\ + 2n^2Dr^3Dr''T_n + 2n^2Dr^2(Dr')^2T_n - 4n^3Dr^4 \cdot (Dr')^2T_n]/f \quad (18)$$

$$\begin{aligned}
G'''' &= \left(\frac{\partial^3 G}{\partial x^3}\right)_{T,P} \\
&= (2x - 1.)/(x - x^2)^2 + Z'''' - Z''''/Z + 3Z'Z''/Z^2 \\
&\quad - 2(Z'/Z)^3 + [gDr'''' - h(T_0 Dr'''' + T_0'''' Dr + 3Dr' T_0''') \\
&\quad + 3Dr'' T_0'') - i(T_n Dr'''' + T_n'''' Dr + 3T_n' Dr'' + 3T_n'' Dr') \\
&\quad + j(Dr Dr'''' + 3Dr' Dr''') - k(T_0 Dr Dr'''' + T_0'''' Dr^2/2 \\
&\quad + 3T_0 Dr' Dr'' + 3T_0' Dr Dr'' + 3T_0'' Dr Dr' + 3T_0''' (Dr')^2) \\
&\quad + 1(3T_0'''' Dr^4 Dr' + 12T_0'''' Dr^3 (Dr')^2 + 3T_0'''' Dr^4 Dr'' \\
&\quad + 12 T_0'''' Dr^2 (Dr')^3 + 12 T_0'''' Dr^3 Dr' Dr'' + T_0'''' Dr^4 Dr'''' \\
&\quad + T_0'''' Dr^5/5 + mT_n''''/n + (m/2n)\exp(-nDr^2)(-2T_n'''' \\
&\quad - nDr^2 T_n'''' + 6nDr Dr' T_n'''' + 6nDr Dr'' T_n'''' + 6n(Dr')^2 T_n'''' \\
&\quad + 2nDr Dr'' T_n'''' + 6nDr' Dr'' T_n'''' + 6n^2 Dr^3 Dr' T_n'''' + 6n^2 \cdot \\
&\quad Dr^3 Dr'' T_n'''' + 6n^2 Dr^2 (Dr')^2 T_n'''' + 2n^2 Dr^3 Dr'''' T_n'''' \\
&\quad + 6n^2 Dr^2 Dr' Dr'' T_n'''' - 12 n^3 Dr^4 (Dr')^2 T_n'''' - 12 n^3 Dr^4 \cdot \\
&\quad Dr' Dr'' T_n'''' - 20n^3 Dr^3 (Dr')^3 T_n'''' + 8n^4 Dr^5 (Dr')^3 T_n'''' )]/f \quad (19)
\end{aligned}$$

See Appendix IV for derivation of equations for  $Dr'$ ,  $Dr''$ , and  $Dr''''$ .

See Appendix V for derivation of equations for  $Z$ ,  $Z'$ ,  $Z''$ , and  $Z''''$ .

APPENDIX IV

Derivation of Equations for  $Dr'$ ,  $Dr''$ , and  $Dr'''$

Taking the derivative with respect to  $x$  of equation III-3:

$$\begin{aligned} Pr' = & [fDr + (g + 2i/Tr^3)(Dr^2 + jDr^3 - (2mDr^3/Tr^3)(1. + nDr^2) \\ & \exp(-nDr^2))] \cdot Tr' + [fTr + (gTr - h - i/Tr^2)2Dr + (jTr - k)3Dr^2 \\ & + 6(1)Dr^5 + (3mDr^2/Tr^2)(1. + nDr^2)\exp(-nDr^2) \\ & + (mDr^3/Tr^2)(2nDr)\exp(-nDr^2) + (mDr^3/Tr^2)(1. + nDr^2) \\ & (-2nDr)\exp(-nDr^2)]Dr' \end{aligned}$$

Let

$$U = Pr' - [fDr + gDr^2 + 2iDr^2/Tr^3 + jDr^3 - 2mDr^3(1. + nDr^2) \exp(-nDr^2)/Tr^3]Tr' \quad (1)$$

$$V = fTr + 2gTrDr - 2hDr - 2iDr/Tr^2 + 3jTrDr^2 - 3kDr^2 + 6(1)Dr^5 + (m/Tr^2)\exp(-nDr^2)(3Dr^2 + 3nDr^4 - 2n^2Dr^6) \quad (2)$$

therefore,

$$Dr' = U/V \quad (3)$$

also,

$$Dr'' = U'/V - UV'/V^2 = (U' - Dr'V')/V \quad (4)$$

$$\begin{aligned} Dr''' = & (U'' - Dr'V'' - Dr''V')/V - (U' - Dr'V')V'/V^2 \\ = & (U'' - Dr'V'' - Dr''V')/V - Dr''V'/V \\ = & (U'' - V''Dr' - 2V'Dr'')/V \end{aligned} \quad (5)$$

Let

$$T_t = Tr'/Tr^3 = Tr'T_n \quad (6)$$

$$T_t' = Tr''T_n + Tr'T_n' \quad (7)$$

$$\begin{aligned} T_t'' = & Tr'''T_n + Tr''T_n' + Tr'T_n'' + Tr'T_n'' \\ = & Tr'''T_n + Tr'T_n'' + 2Tr''T_n' \end{aligned} \quad (8)$$

Therefore

$$U = Pr' - fDrTr' - gDr^2Tr' - 2iDr^2T_nTr' - jDr^3Tr' + 2mDr^3(1. + nDr^2) \exp(-nDr^2)T_nTr'$$

$$U' = Pr'' - fDrTr'' - fDr'Tr' - gDr^2Tr'' - 2gDrDr'Tr' - 2iDr^2T_nTr'' - 2iDr^2T_n'Tr' - 4iDrDr'T_t - jDr^3Tr'' - 3jDr^2Dr'Tr' + 2mDr^3(1. + nDr^2)\exp(-nDr^2)T_t' + 2mDr^3(2nDrDr')\exp(-nDr^2)T_t + 6mDr^2Dr'(1. + nDr^2)\exp(-nDr^2)T_t$$

or

$$U' = Pr'' - fDrTr'' - fDr'Tr' - gDr^2Tr'' - 2gDrDr'Tr' - 2iDr^2T_t' - 4iDrDr'T_t - jDr^3Tr'' - 3jDr^2Dr'Tr' + 2mDr^3(1. + nDr^2)\exp(-nDr^2) \cdot T_t' + 2m \cdot \exp(-nDr^2)T_t(3 + 3nDr^2 - 2n^2Dr^4)Dr^2Dr' \quad (9)$$

$$V' = fTr' + 2gDr'Tr + 2gDrTr' - 2hDr' - 2iDr'/Tr^2 + 4iDrT_t + 6jTrDr'Dr + 3jTr'Dr^2 - 6kDrDr' + 30(1)Dr^4Dr' + m \cdot \exp(-nDr^2)(6DrDr'/Tr^2 + 6nDr^3Dr'/Tr^2 - 18n^2Dr^5Dr'/Tr^2 + 4n^3Dr^7Dr'/Tr^2 - 6Dr^2T_t - 6nDr^4T_t + 4n^2Dr^6T_t) \quad (10)$$

$$U'' = Pr''' - fDrTr''' - 2fDr'Tr'' - fDr''Tr' - gDr^2Tr''' - 4gDrDr'Tr'' - 2gDrDr''Tr' - 2g(Dr')^2Tr' - 2iDr^2T_t'' - 8iDrDr'T_t' - 4iDrDr''T_t - 4i(Dr')^2T_t - jDr^3Tr''' - 6jDr^2Dr'Tr'' - 3jDr^2Dr''Tr' - 6jDr(Dr')^2Tr' + [2m \cdot \exp(-nDr^2)(Dr^3T_t'' + nDr^5T_t'' + 6Dr^2Dr'T_t' + 6Dr^4nDr'T_t' - 4n^2Dr^6Dr'T_t' + 3Dr^2Dr''T_t + 3nDr^4Dr''T_t - 2n^2Dr^6Dr''T_t + 6nDr^3(Dr')^2T_t + 6Dr(Dr')^2T_t - 18n^2Dr^5(Dr')^2T_t + 4n^3Dr^7(Dr')^2T_t)] \quad (11)$$

$$\begin{aligned}
V'' = & f\text{Tr}'' + 2g\text{Dr}''\text{Tr} + 4g\text{Dr}'\text{Tr}' + 2g\text{DrTr}'' - 2h\text{Dr}'' - 2i\text{Dr}''/\text{Tr}^2 \\
& + 8i\text{Dr}'\text{T}_t + 4i\text{DrT}_t' + 12j\text{Tr}'\text{DrDr}' + 6j\text{Tr}(\text{Dr}')^2 + 6j\text{DrDr}''\text{Tr} \\
& + 3j\text{Tr}''\text{Dr}^2 - 6k(\text{Dr}')^2 - 6k\text{DrDr}'' + 30(1)\text{Dr}^4\text{Dr}'' \\
& + 120(1)\text{Dr}^3 \cdot (\text{Dr}')^2 + 2m \cdot \exp(-n\text{Dr}^2)(3\text{DrDr}''/\text{Tr}^2 + 3n\text{Dr}^3\text{Dr}''/\text{Tr}^2 \\
& - 9n^2\text{Dr}^5\text{Dr}''/\text{Tr}^2 + 2n^3\text{Dr}^7\text{Dr}''/\text{Tr}^2 + 3(\text{Dr}')^2/\text{Tr}^2 \\
& + 3n\text{Dr}^2(\text{Dr}')^2/\text{Tr}^2 - 51n^2\text{Dr}^4(\text{Dr}')^2/\text{Tr}^2 + 32n^3\text{Dr}^6(\text{Dr}')^2/\text{Tr}^2 \\
& - 4n^4\text{Dr}^8(\text{Dr}')^2/\text{Tr}^2 - 3\text{Dr}^2\text{T}_t' - 3n\text{Dr}^4\text{T}_t' + 2n^2\text{Dr}^6\text{T}_t' \\
& - 12\text{DrDr}'\text{T}_t - 12n\text{Dr}^3\text{Dr}'\text{T}_t + 36n^2\text{Dr}^5\text{Dr}'\text{T}_t - 8n^3\text{Dr}^7\text{Dr}'\text{T}_t)
\end{aligned}$$

(12)

APPENDIX V

Derivation of Equations for Z, Z', Z'', and Z'''

$$Z = P/RTD = PrPc/RTrTcDrDc = (Pr/TrDr)(Pc/RTcDc) = Pr/fTrDr$$

Let

$$Y = Pr/fTr \quad (1)$$

$$Y' = (Pr' - fYTr')/(fTr) \quad (2)$$

$$Y'' = (Pr'' - fYTr'' - 2fY'Tr')/(fTr) \quad (3)$$

$$Y''' = (Pr''' - fYTr''' - 3fY'Tr'' - 3fY''Tr')/(fTr) \quad (4)$$

Then

$$Z = Y/Dr \quad (5)$$

$$Z' = (Y' - ZDr')/Dr \quad (6)$$

$$Z'' = (Y'' - ZDr'' - 2Z'Dr')/Dr \quad (7)$$

$$Z''' = (Y''' - ZDr''' - 3Z'Dr'' - 3Z''Dr')/Dr \quad (8)$$

## APPENDIX VI

### Program LINEAR

The objective of program LINEAR is to vary simultaneously the value of reduced temperature ( $Tr$ ) and reduced density ( $Dr$ ) at successive values of composition ( $x$ ) until the second and third derivatives of the free energy,  $G''$  and  $G'''$ , become equal to zero. This program follows the flow diagram in Figure 5, page 37.

Starting at one end of the composition range ( $x_1 = 0$ ), the boundary conditions  $Tr = 1$  and  $Pr = 1$  are used. The value of composition is incremented twice and guesses are made for  $Tr$  and  $Dr$  at these compositions ( $x_2, x_3$ ). Then by simple linear interpolation the value of  $Dr_3$  ( $Dr_2$ ,  $Tr_2$ , or  $Tr_3$  could also have been chosen) is changed until  $G_2''$  is equal to zero.

Guesses for  $Tr$  and  $Dr$  are then made for the next composition ( $x_4$ ). These guesses ( $Dr_4, Tr_4$ ) are changed simultaneously by a linear convergence method until  $G_3''$  and  $G_3'''$  become equal to zero. This process is repeated until the entire composition range has been covered.

The only restriction on the values of  $Tr$  and  $Dr$  which are selected is that they be positive since negative values have no physical significance.

The main divisions of program LINEAR are:

1. Program LINEAR-Main Body
2. Subroutine CONVERG
3. Subroutine POLY
4. Subroutine WBKAY
5. Subroutine PRCALC
6. Subroutine G2CALC
7. Subroutine G3CALC
8. Data

```

PROGRAM LINEAR
  DIMENSION X(25), W(25), PC(25), TC(25), PK(25), TK(25), PR(25),
1  TR(25), DR(25), ZR(25), Z(5), FUNC(5), DELTAD(4), DELTAT(4), G(6)
2  ,PZRWRPR(25)
  COMMON I,DCB,TCB,AC,BC,CC,DC,EC,C,C1,C2,C3,C4,C5,C6,C7,C8,C9,DR,
1  DR1DER,DR2DER,TR,TR1DER,TR2DER,TR3DER,PR,PR1DER,PR2DER,PR3DER,
2  PC,PK,TC,TK,QQ,TO,TO1DER,TO2DER,TN,TN1DER,TN2DER,TT,TT1DER,V,
3  V1DER,Y,Y1DER,Y2DER,ZK,ZK1DER,ZK2DER,ZR,Z,X,W,G2DER,G3DER,FUNC
4  ,PZRWRPR
1  FORMAT (E18.11)
2  FORMAT (25X,25HDOUBLE LINEAR CONVERGENCE,4(/))
3  FORMAT (I2)
16  FORMAT (6X,5E21.10)
40  FORMAT(20H NO OF ITERATIONS = ,I2,/)
41  FORMAT(1H1)
42  FORMAT (2/,15X,8HFUNCTION,13X,9HFIRST DER,11X,10HSECOND DER,12X,
1  9HTHIRD DER,/,3H TC,3X,4E21.10,/,3H PC,3X,4E21.10,/,3H TR,3X,
2  4E21.10,/,3H PR,3X,4E21.10)
43  FORMAT (/,11X,1HX,18X,2HTR,18X,2HPR,18X,2HDR,18X,2HZR,15X,
1  7HPZRWRPR,/,6E20.10,/,6E20.10)
44  FORMAT (9H G2DER = ,E18.10,3X,8HG3DER = ,E18.10)
45  FORMAT (25H DOES NOT CONVERGE AFTER ,I2,11H ITERATIONS)
46  FORMAT(/20H CALCULATION AT X = ,F5.3,//17X,2HTR,19X,2HDR,17X,
1  5HG2DER,16X,5HG3DER)
50  FORMAT (4H PK(,I2,4H) = ,E18.10,4X,3HTK(,I2,4H) = ,E18.10,,4X,
1  4H PC(,I2,4H) = ,E18.10,4X,3HTC(,I2,4H) = ,E18.10)
51  FORMAT (11H INPUT DATA,/,9H TR(2) = ,E18.10,5X,8HTR(3) = ,E18.10,
1  5X,8HTR(4) = ,E18.10,/,9H DR(2) = ,E18.10,5X,8HDR(3) = ,E18.10,
2  5X,8HDR(4) = ,E18.10,/)
  PRINT 2
  READ 1, DCB,TCB,PCB,R,B0,A0,C0,B,A,C,ALPHA,GAMMA,AC,BC,CC,DC,EC
C  PRELIMINARY CALCULATIONS
  C1 = (DCB*TCB*R)/PCB
  C2 = C1*B0*DCB
  C3 = (A0*DCB**2)/PCB
  C5 = C1*DCB**2*B
  C6 = (DCB**3/PCB)*A
  C7 = C6*DCB**3*ALPHA
  C8 = (C6/(A*TCB**2))*C
  C9 = DCB**2*GAMMA
C  C1=F, C2=G, C3=H, C4=I, C5=J, C6=K, C7=L, C8=M, C9=N
  TOL = 1.E-12
  X(1) = 0
  X(2) = 0.025
  X(3) = 0.05
  TR(1) = 1.0
  DR(1) = 1.0
  PR(1) = 1.0
  ZR(1) = 1.0
  DELTAX = 0.05
  NUM = (1. - X(3))/DELTAX + 3.
  DO 6 I=4,NUM
6  X(I) = X(I-1) + DELTAX
  DO 5 I=1,NUM

```

```

5 CALL WBKAY
  I = 1
  PC(I) = PK(I)/PR(I)
  TC(I) = TK(I)/TR(I)
  READ 3, NUMDATA
  DO 25 NN=1,NUMDATA
4 READ 1, (TR(I),I = 2,4), (DR(I), I = 2,4)
  PRINT 51, (TR(I),I=2,4),(DR(I),I=2,4)
  PRINT 50, I, PK(I), I, TK(I), I, PC(I), I, TC(I)
104 I = 2
  CALL PRCALC
  TC(I) = TK(I)/TR(I)
  PC(I) = PK(I)/PR(I)
C THIS PROGRAM USES DR(3) TO CONVERGE G2DER(2)
  DELTADR = 0.02
  G2DER1 = 0
  DO 8 L=1,40
  I = I + 1
  DR(I) = DR(I) + DELTADR
  CALL PRCALC
  TC(I) = TK(I)/TR(I)
  PC(I) = PK(I)/PR(I)
  I = I-1
  DELTAX = X(I+1) - X(I)
  TC1DER = (TC(I+1) - TC(I-1))/(2.*DELTAX)
  TC2DER = (TC(I+1) - 2.*TC(I) + TC(I-1))/DELTAX**2
  TR1DER = -TR(I)*TC1DER/TC(I)
  TR2DER = -2.*TR1DER*TC1DER/TC(I) - TR(I)*TC2DER/TC(I)
  PC1DER = (PC(I+1)-PC(I-1))/(2.*DELTAX)
  PC2DER = (PC(I+1) - 2.*PC(I) + PC(I-1))/DELTAX**2
  PR1DER = -PR(I)*PC1DER/PC(I)
  PR2DER = -2.*PR1DER*PC1DER/PC(I) - PR(I)*PC2DER/PC(I)
  CALL G2CALC
  IF (ABSF(DELTADR) - TOL)9,9,7
7 DELTADR = -G2DER*DELTADR/(G2DER - G2DER1)
8 G2DER1 = G2DER
  STOP 0007
9 PRINT 42, TC(I), TC1DER, TC2DER, X(I),PC(I), PC1DER,PC2DER, X(I),
  1 TR(I), TR1DER, TR2DER, X(I), PR(I), PR1DER, PR2DER, X(I)
  PRINT 43,X(I),TR(I),PR(I),DR(I),ZR(I),PZRWRPR(I),X(I+1),TR(I+1),
  1 PR(I+1),DR(I+1),ZR(I+1),PZRWRPR(I+1)
  I = I + 1
29 NUMBER = 0
  PRINT 46, X(I)
C TO STATEMENT 31-12 SETS UP 3 SETS OF GUESSES (TR,DR) AND
C CALCULATES G2DER AND G3DER
  DELTAT(1) = 0.1
  DELTAT(2) = 0
  DELTAD(1) = 0
  DELTAD(2) = 0.1
  M = 1
  GO TO 10
28 M = M + 1
  TR(I+1) = TR(I+1) + DELTAT(M-1)

```

```

DR(I+1) = DR(I+1) + DELTAD(M-1)
10 I = I + 1
CALL PRCALC
PC(I) = PK(I)/PR(I)
TC(I) = TK(I)/TR(I)
DO 30 K=1,4
Z(K) = X(I-4+K)
30 FUNC(K) = TC(I-4+K)
CALL POLY (TC1DER,TC2DER,TC3DER)
DO 31 K =1,4
31 FUNC(K) = PC(I-4+K)
CALL POLY (PC1DER,PC2DER,PC3DER)
I = I - 1
TR1DER = -TR(I)*TC1DER/TC(I)
TR2DER = -2.*TR1DER*TC1DER/TC(I) - TR(I)*TC2DER/TC(I)
TR3DER = 6.*TK(I)*TC1DER*TC2DER/TC(I)**3-6.*TK(I)*TC1DER**3/TC(I)
1 **4 - TK(I)*TC3DER/TC(I)**2
PR1DER = -PR(I)*PC1DER/PC(I)
PR2DER = -2.*PR1DER*PC1DER/PC(I) - PR(I)*PC2DER/PC(I)
PR3DER = 6.*PK(I)*PC1DER*PC2DER/PC(I)**3-6.*PK(I)*PC1DER**3/PC(I)
1 **4 - PK(I)*PC3DER/PC(I)**2
CALL G3CALC
G(M) = G2DER
G(M+3) = G3DER
IF (M-3)28,32,35
32 IF (G(3)**2 + G(6)**2 - TOL)15,15,14
C THIS CONVERGENCE PROCEDURE USES A LINEAR INTERPOLATION
14 CALL CONVERG (DELTAT(1), DELTAT(2), DELTAT(3), DELTAD(1), DELTAD
1 (2), DELTAD(3), G(1), G(2), G(3), G(4), G(5), G(6))
17 IF(DR(I+1) + DELTAD(3))18,18,750
750 IF(DR(I+1)+DELTAD(3)-2.)19,18,18
18 DELTAD(3) = DELTAD(3)/2.
GO TO 17
19 IF(TR(I+1) + DELTAT(3))20,20,751
751 IF(TR(I+1)+DELTAT(3)-4.)21,20,20
20 DELTAT(3) = DELTAT(3)/2.
GO TO 19
21 DO 23 L=1,2
DELTAT(L) = DELTAT(L+1)
DELTAD(L) = DELTAD(L+1)
G(L) = G(L+1)
23 G(L+3) = G(L+4)
PRINT 16, TR(I+1), DR(I+1), G2DER, G3DER
TR(I+1) = TR(I+1) + DELTAT(3)
DR(I+1) = DR(I+1) + DELTAD(3)
NUMBER = NUMBER + 1
IF (NUMBER-30)10,10,24
15 PRINT 42,TC(I), TC1DER, TC2DER, TC3DER,PC(I), PC1DER,PC2DER,
1 PC3DER, TR(I), TR1DER, TR2DER, TR3DER, PR(I), PR1DER, PR2DER,
2 PR3DER
NNN = I+1
PRINT 43, (X(J),TR(J),PR(J),DR(J),ZR(J),PZRWRPR(J), J=I,NNN)
PRINT 44, G2DER, G3DER
PRINT 40, NUMBER

```

```
I = I+1
DR(I+1) = 1.1*DR(I)
TR(I+1) = 1.1*TR(I)
IF(I-NUM)29,35,35
24 PRINT *5, NUMBER
25 PRINT *1
35 STOP 5555
END
```

Program LINEAR-Main Body

**Purpose:** To generate values of  $Tr$  and  $Dr$  at  $x_{i+1}$  ( $i$  equal to or greater than 2) such that  $G_i''$  and  $G_i'''$  equals zero.

**Input:** P-V-T data on a reference compound (in this case, propane). This data includes the critical properties, the gas constant  $R$ , eight Benedict-Webb-Rubin constants, and five constants for computing  $C_0$  as a function of temperature. Also input are the first guesses of  $Tr$  and  $Dr$  at  $x_2$  and  $x_3$ .

**Details:** Using the values of  $Tr$  and  $Dr$  at  $x_1$ ,  $x_2$ , and  $x_3$  ( $Tr = 1$  and  $Dr = 1$  at  $x_1 = 0$ ), this program changes  $Dr_3$  until the second derivative of free energy,  $G_2''$ , is equal to zero at  $x_2$ . For  $x_{i+1}$  ( $i$  equal to or greater than 3) the guesses of  $Tr_{i+1}$  and  $Dr_{i+1}$  are adjusted until  $G_i''$  and  $G_i'''$  equal zero. This latter process is repeated until the entire composition range has been covered.

A linear convergence scheme is employed to adjust  $Dr_3$  until  $G_2''$  equals zero. Two guesses are made for  $Dr_3$ , and then a new guess is calculated from:

$$\frac{(\text{new } Dr_3 - \text{present } Dr_3)}{(\text{present } Dr_3 - \text{previous } Dr_3)} = \frac{(\text{desired } G_2'' - \text{present } G_2'')}{(\text{present } G_2'' - \text{previous } G_2'')}$$

Since desired  $G_2'' = 0$ ,

$$\text{new } Dr_3 = \text{pres } Dr_3 + \left[ \frac{-\text{pres } G_2''}{(\text{pres } G_2'' - \text{prev } G_2'')} \right] (\text{pres } Dr_3 - \text{prev } Dr_3). \quad (1)$$

Calculation of  $G_2''$  requires first and second derivatives of  $Tr$  and  $Pr$  at  $x_2$ . These derivatives are computed by fitting a quadratic equation through the values of  $Tc$  and  $Pc$  at  $x_1$ ,  $x_2$ , and  $x_3$ , and then computing  $Tc_2'$  and  $Tc_2''$  from:

$$Tc_2' = (Tc_3 - Tc_1)/(2\Delta x) \quad (2)$$

$$Tc_2'' = (Tc_3 - 2Tc_2 + Tc_1)/(\Delta x)^2 \quad (3)$$

Similar equations may be written for  $Pc_2'$  and  $Pc_2''$ .

First and second derivatives of Tr and Pr are computed from:

$$Tr' = [\partial(T/Tc)/\partial x]_{T,P} = -T \cdot Tc' / Tc^2 = -Tr \cdot Tc' / Tc \quad (4)$$

$$Tr'' = [\partial^2(T/Tc)/\partial x^2]_{T,P} = -2Tr' \cdot Tc' / Tc - Tr \cdot Tc'' / Tc \quad (5)$$

Values of Tr and Dr at  $x_{i+1}$  (i equal to or greater than 3) are computed using a convergence process which assumes  $G''$  and  $G'''$  to be linear functions of Tr and Dr. The values of Tr and Dr at  $x_i$ ,  $x_{i-1}$ , and  $x_{i-2}$  must be known because third derivatives are needed to calculate  $G_1''''$ . Three sets of guesses for  $(Tr_{i+1}, Dr_{i+1})$  are needed before the linear interpolation method can be applied. Subroutine CONVERG is called to compute the next increment of  $Tr_{i+1}$  and  $Dr_{i+1}$  from the previous three sets of guesses for  $Tr_{i+1}$  and  $Dr_{i+1}$ , and the values of  $G_1''$  and  $G_1'''$  calculated from those sets of guesses.

Whenever the double linear convergence process is used, all derivatives of Tc and Pc are computed using subroutine POLY. This subroutine fits a third degree polynomial to the values of Tc and Pc at  $x_{i+1}$ ,  $x_i$ ,  $x_{i-1}$ , and  $x_{i-2}$ . Subscript i is necessarily at least 3. The value of  $Tr_1''''$  is calculated from:

$$Tr'''' = [\partial^3(T/Tc)/\partial x^3]_{T,P} = 6T \cdot Tc' \cdot Tc'' / Tc^3 - 6T(Tc')^3 / Tc^4 - T \cdot Tc'''' / Tc^2 \quad (6)$$

and similarly for  $Pr''''$ .

The only restrictions imposed on the calculated values of Tr and Dr are that they must remain positive since negative values do not have physical significance. This program also

limits the number of iterations to thirty before the convergence process is interrupted because of lack of convergence.

#### Method of

Checking: Since the primary function of the main body of this program is to provide convergence, the program must work properly if such convergence is obtained.

#### Fortran

##### Nomen-

clature: AC, BC, CC, DC, EC = five constants to compute  $C_0$  as a function of temperature  
 AO, BO, CO, A, B, C, ALPHA, GAMMA = the eight Benedict-Webb-Rubin constants  $B_0, A_0, C_0, a, b, c, \alpha, \gamma$

C1 = f  
 C2 = g  
 C3 = h  
 C5 = j  
 C6 = k  
 C7 = l  
 C8 = m  
 C9 = n

DCB, TCB, PCB, = critical density, temperature and pressure of propane

DELTAD = variable used to represent differences in Dr  
 DELTADR = difference between the most recent value of  $Dr_3$   
 DELTAT = variable used to represent differences in Tr  
 DELTAX = increment of x after  $x_3$   
 DR = reduced density (Dr)  
 NUM = highest value of the subscript on x  
 NUMBER = a variable used to count iterations  
 NUMDATA = a variable used to represent the total number of sets of data

PC = pseudocritical pressure ( $P_c$ )  
 PC1DER =  $P_c'$   
 PC2DER =  $P_c''$   
 PC3DER =  $P_c'''$

PK = critical pressure of mixture ( $P_k$ )  
 PR = reduced pressure (Pr)  
 PR1DER =  $Pr'$   
 PR2DER =  $Pr''$   
 PR3DER =  $Pr'''$

R = gas constant (liter·atm.)/(g-mole·°K)  
 TC = pseudocritical temperature ( $T_c$ )  
 TC1DER =  $T_c'$   
 TC2DER =  $T_c''$   
 TC3DER =  $T_c'''$

TK = critical temperature of mixture ( $T_k$ )  
 TR = reduced temperature (Tr)

TR1DER = Tr<sup>0</sup>

TR2DER = Tr<sup>0 0</sup>

TR3DER = Tr<sup>0 0 0</sup>

X = mole fraction ethane

ZR = reduced compressibility factor (Zr)

```
SUBROUTINE CONVERG (DELTAX1, DELTAX2, DELTAX, DELTAY1, DELTAY2,  
1 DELTAY, F1, F2, F3, G1, G2, G3)  
DENOM1 = DELTAX1*DELTAY2 - DELTAX2*DELTAY1  
COEFF1 = ((F2-F1)*DELTAY2 - (F3-F2)*DELTAY1)/DENOM1  
COEFF2 = ((F3-F2)*DELTAX1 - (F2-F1)*DELTAX2)/DENOM1  
COEFF3 = ((G2-G1)*DELTAY2 - (G3-G2)*DELTAY1)/DENOM1  
COEFF4 = ((G3-G2)*DELTAX1 - (G2-G1)*DELTAX2)/DENOM1  
DENOM2 = COEFF1*COEFF4 - COEFF2*COEFF3  
DELTAX = (G3*COEFF2 - F3*COEFF4)/DENOM2  
DELTAY = (F3*COEFF3 - G3*COEFF1)/DENOM2  
END
```

Subroutine CONVERG

**Purpose:** To compute the estimated increment for each of two variables which will make two functions of those two variables equal zero.

**Input:** The differences between the previous three guesses of both variables and the previous three values of both functions computed from those variables.

**Details:** The equations for a double linear convergence process are developed for two general functions,  $F(X,Y)$  and  $G(X,Y)$ . This procedure is called a double linear convergence process because two functions,  $F(X,Y)$  and  $G(X,Y)$  are assumed to be linear functions of the two variables,  $X$  and  $Y$ .

Required initially are three different sets of guesses for  $X$  and  $Y$   $[(X_1, Y_1), (X_2, Y_2), (X_3, Y_3)]$  and the values of  $F$  and  $G$  for each set of  $X$  and  $Y$ . Values of  $X_4$  and  $Y_4$  are desired such that  $F_4 = 0, G_4 = 0$ .

Letting  $\Delta X_1 = X_2 - X_1, \Delta X_2 = X_3 - X_2$ , etc., six equations and six unknowns ( $a, b, c, d, X_4, Y_4$ ) can be written:

$$a\Delta X_1 + b\Delta Y_1 = \Delta F_1 \quad (1)$$

$$a\Delta X_2 + b\Delta Y_2 = \Delta F_2 \quad (2)$$

$$a\Delta X_3 + b\Delta Y_3 = \Delta F_3 = -F_3 \quad (3)$$

$$c\Delta X_1 + d\Delta Y_1 = \Delta G_1 \quad (4)$$

$$c\Delta X_2 + d\Delta Y_2 = \Delta G_2 \quad (5)$$

$$c\Delta X_3 + d\Delta Y_3 = \Delta G_3 = -G_3 \quad (6)$$

Equations (1) and (2) are solved for  $a$  and  $b$ , equations (4) and (5) for  $c$  and  $d$ , and equations (3) and (6) for  $\Delta X_3$  and  $\Delta Y_3$ .

The expressions for  $\Delta X_3$  and  $\Delta Y_3$  are:

$$\Delta X_3 = X_4 - X_3 = (G_3 b - F_3 d)/(ad - bc) \quad (7)$$

$$\Delta Y_3 = Y_4 - Y_3 = (F_3 c - G_3 a)/(ad - bc) \quad (8)$$

The last two mathematical statements of the subroutine are equivalent to equations (7) and (8).

#### Method of

**Checking:** This subroutine was checked by using it on a system of two linear functions of two unknowns. Three sets of guesses were made for the two unknowns, and the subroutine was employed to compute the increments necessary to make the functions equal to zero. Only one step was needed which indicated that the subroutine was extrapolating properly.

#### Fortran

##### Nomen-

##### clature:

COEFF1 = coefficient a in equations (1) to (3)  
 COEFF2 = coefficient b in equations (1) to (3)  
 COEFF3 = coefficient c in equations (4) to (6)  
 COEFF4 = coefficient d in equations (4) to (6)

$$\text{DELTA}X1 = X_2 - X_1$$

$$\text{DELTA}X2 = X_3 - X_2$$

$\text{DELTA}X = X_4 - X_3 =$  difference between the next value of X and  
 the most recent value of X

$$\text{DELTA}Y1 = Y_2 - Y_1$$

$$\text{DELTA}Y2 = Y_3 - Y_2$$

$\text{DELTA}Y = Y_4 - Y_3 =$  difference between the next value of Y and  
 the most recent value of Y

$$\text{DENOM1} = (Y_3 - Y_2)(X_2 - X_1) - (Y_2 - Y_1)(X_3 - X_2)$$

$$\text{DENOM2} = ad - bc$$

```

SUBROUTINE POLY (FSTDER,SECDER,THRDER)
DIMENSION X(25), W(25), PC(25), TC(25), PK(25), TK(25), PR(25),
1 TR(25), DR(25), ZR(25), Z(5), FUNC(5), DEN(5), PZRWRPR(25)
COMMON I,DCB,TCB,AC,BC,CC,DC,EC,C,C1,C2,C3,C4,C5,C6,C7,C8,C9,DR,
1 DR1DER,DR2DER,TR,TR1DER,TR2DER,TR3DER,PR,PR1DER,PR2DER,PR3DER,
2 PC,PK,TC,TK,QQ,TO,TO1DER,TO2DER,TN,TN1DER,TN2DER,TT,TT1DER,V,
3 V1DER,Y,Y1DER,Y2DER,ZK,ZK1DER,ZK2DER,ZR,Z,X,W,G2DER,G3DER,FUNC
4 ,PZRWRPR
DEN(1) = (Z(1)-Z(2))*(Z(1)-Z(3))*(Z(1)-Z(4))
DEN(2) = (Z(2)-Z(1))*(Z(2)-Z(3))*(Z(2)-Z(4))
DEN(3) = (Z(3)-Z(1))*(Z(3)-Z(2))*(Z(3)-Z(4))
DEN(4) = (Z(4)-Z(1))*(Z(4)-Z(2))*(Z(4)-Z(3))
S = Z(3)
FSTDER = ((3.*S**2-2.*S*(Z(2)+Z(3)+Z(4))+Z(3)*(Z(2)+Z(4))+Z(2)*
1 Z(4))*FUNC(1))/DEN(1)+((3.*S**2-2.*S*(Z(1)+Z(3)+Z(4))+Z(1)*
2 (Z(3)+Z(4))+Z(3)*Z(4))*FUNC(2))/DEN(2)+((3.*S**2-2.*S*(Z(1)+
3 Z(2)+Z(4))+Z(1)*(Z(2)+Z(4))+Z(2)*Z(4))*FUNC(3))/DEN(3)+((3.*S**2
4 -2.*S*(Z(1)+Z(2)+Z(3))+Z(1)*(Z(2)+Z(3))+Z(2)*Z(3))*FUNC(4))
5 /DEN(4)
SECDER = (6.0*S -2.*(Z(4) + Z(2) + Z(3)))*FUNC(1)/DEN(1)
1 + (6.0*S -2.*(Z(1) + Z(3) + Z(4)))*FUNC(2)/DEN(2)
2 + (6.0*S -2.*(Z(1) + Z(2) + Z(4)))*FUNC(3)/DEN(3)
3 + (6.0*S -2.*(Z(1) + Z(2) + Z(3)))*FUNC(4)/DEN(4)
THRDER = 6.*(FUNC(1)/DEN(1)) + 6.*(FUNC(2)/DEN(2))
1 + 6.*(FUNC(3)/DEN(3)) + 6.*(FUNC(4)/DEN(4))
END

```

Subroutine POLY

**Purpose:** To calculate numerically first, second and third derivatives of a function at a given value of the independent variable.

**Input:** Four values of the function,  $f(Z_1)$ ,  $f(Z_2)$ ,  $f(Z_3)$ , and  $f(Z_4)$ , and four values of the independent variable,  $Z_1$ ,  $Z_2$ ,  $Z_3$ , and  $Z_4$  are placed in memory prior to the calling of the subroutine.

**Details:** A third degree polynomial (four points) may be written<sup>41</sup>:

$$f(Z) = aZ^3 + bZ^2 + cZ + d \quad (1)$$

or

$$f(Z) = \frac{(Z-Z_2)(Z-Z_3)(Z-Z_4)}{(Z_1-Z_2)(Z_1-Z_3)(Z_1-Z_4)} f(Z_1) + \frac{(Z-Z_1)(Z-Z_3)(Z-Z_4)}{(Z_2-Z_1)(Z_2-Z_3)(Z_2-Z_4)} f(Z_2) \\ + \frac{(Z-Z_1)(Z-Z_2)(Z-Z_4)}{(Z_3-Z_1)(Z_3-Z_2)(Z_3-Z_4)} f(Z_3) + \frac{(Z-Z_1)(Z-Z_2)(Z-Z_3)}{(Z_4-Z_1)(Z_4-Z_2)(Z_4-Z_3)} f(Z_4) \quad (2)$$

$$f'(Z) = \frac{3Z^2 - 2(Z_2+Z_3+Z_4)Z + Z_2Z_3 + Z_2Z_4 + Z_3Z_4}{(Z_1-Z_2)(Z_1-Z_3)(Z_1-Z_4)} f(Z_1) \\ + \dots \quad (3)$$

$$f''(Z) = \frac{6Z - 2(Z_2+Z_3+Z_4)}{(Z_1-Z_2)(Z_1-Z_3)(Z_1-Z_4)} f(Z_1) + \dots \quad (4)$$

$$f'''(Z) = \frac{6}{(Z_1-Z_2)(Z_1-Z_3)(Z_1-Z_4)} f(Z_1) + \dots \quad (5)$$

Equations (3), (4), and (5) can be used to calculate numerically first, second, and third derivatives, respectively, at any value  $Z$ . The value of  $Z$  is called  $S$  in the Fortran program. In this particular program, the derivatives are computed at  $Z_3$ .

**Method of**

**Checking:** A third degree polynomial was constructed and values of  $f(Z)$  calculated at four arbitrary values of  $Z$ . These results were then

input into the subroutine to see if the generated values agreed with the original polynomial and its derivatives, for specific values of Z.

**Fortran****Nomen-**

**clature:** DEN = the denominators of the terms in equations (2), (3), (4), and (5). DEN(1) represents the denominator of the first term, etc.

FSTDER = calculated value of the first derivative

FUNC = value of the function

S = the value of Z at which the derivatives are being calculated

SECDER = calculated value of the second derivative

THRDER = calculated value of the third derivative

Z = specific values of the independent variable (Z) for which the values of the function are known

```
SUBROUTINE WBKAY
DIMENSION X(25), W(25), PC(25), TC(25), PK(25), TK(25), PR(25),
1 TR(25), DR(25), ZR(25), Z(5), FUNC(5), PZRWRPR(25)
COMMON I, DCB, TCB, AC, BC, CC, DC, EC, C, C1, C2, C3, C4, C5, C6, C7, C8, C9, DR,
1 DR1DER, DR2DER, TR, TR1DER, TR2DER, TR3DER, PR, PR1DER, PR2DER, PR3DER,
2 PC, PK, TC, TK, QQ, TO, TO1DER, TO2DER, TN, TN1DER, TN2DER, TT, TT1DER, V,
3 V1DER, Y, Y1DER, Y2DER, ZK, ZK1DER, ZK2DER, ZR, Z, X, W, G2DER, G3DER, FUNC
4 , PZRWRPR
W(I) = 30.06*X(I)/(30.06*X(I)+(1.-X(I))*100.17)
TK(I) = (513.3-186.4392126*X(I)+20.413825*X(I)**2-558.3704113*
1 X(I)**3+121.1957936*X(I)**4+459.67)/1.8
PK(I) = (396.+3051.927387*W(I)-1199.746006*W(I)**2-4263.827785*
1 W(I)**3+2727.646362*W(I)**4)/14.696
END
```

Subroutine WBKAY

**Purpose:** To calculate  $T_k$  and  $P_k$  at a given composition.

**Input:** The value of composition ( $x_1$ ) and the value of subscript  $i$  must be placed in memory before this subroutine is called.

**Details:** The experimental  $T_k$  and  $P_k$  values for the ethane-n-heptane system, as published by W. B. Kay,<sup>23</sup> were fitted to a fourth degree polynomial by a modification of the method of least squares. This modification was necessary in order to obtain an exact fit for pure ethane and pure n-heptane.

The critical temperature envelope curve is expressed as a function of mole fraction ethane. However, the critical pressure envelope curve is expressed as a function of weight fraction ethane because a better fit of the pressure data was obtained using this variable.

**Method of**

**Checking:** The compositions as recorded in the published article were input, and the results were compared with the published values at these compositions.

**Fortran****Nomen-**

**clature:** I = subscript  $i$  on composition ( $x$ )  
 PK = true critical pressure of mixture ( $P_k$ ), atm.  
 TK = true critical temperature of mixture ( $T_k$ ), °K  
 W = weight fraction ethane  
 X = mole fraction ethane ( $x$ )

```

SUBROUTINE PRCALC
DIMENSION X(25), W(25), PC(25), TC(25), PK(25), TK(25), PR(25),
1 TR(25), DR(25), ZR(25), Z(5), FUNC(5), PZRWRPR(25), SAVE(4)
COMMON I, DCB, TCB, AC, BC, CC, DC, EC, C, C1, C2, C3, C4, C5, C6, C7, C8, C9, DR,
1 DR1DER, DR2DER, TR, TR1DER, TR2DER, TR3DER, PR, PR1DER, PR2DER, PR3DER,
2 PC, PK, TC, TK, QQ, TO, TO1DER, TO2DER, TN, TN1DER, TN2DER, TT, TT1DER, V,
3 V1DER, Y, Y1DER, Y2DER, ZK, ZK1DER, ZK2DER, ZR, Z, X, W, G2DER, G3DER, FUNC
4 , PZRWRPR
Q = (TR(I)*TCB)/100.
Q1 = (10.*Q**6)**4
CO = (EC/(Q**2*Q1) + DC/Q/Q1 + BC/Q1 + AC)/(CC/Q1 + 1.)
C4 = ((C8/C)*CO)/DCB
DO 5 K=1,2
DR(I) = 1.E-05*(-1.)**K + DR(I)
QQ = EXPF(-C9*DR(I)**2)
PR(I) = C1*DR(I)*TR(I)+C2*TR(I)*DR(I)**2-C3*DR(I)**2-C4*DR(I)**2
1 /TR(I)**2+C5*TR(I)*DR(I)**3-C6*DR(I)**3+C7*DR(I)**6+(1.+C9*DR(I)
2 **2)*QQ*C8*DR(I)**3/TR(I)**2
ZR(I) = PR(I)/TR(I)/DR(I)
SAVE(K) = PR(I)
5 SAVE(K+2) = ZR(I)
PZRWRPR(I) = (SAVE(4)-SAVE(3))/(SAVE(2)-SAVE(1))
END

```

Subroutine PRCALC

**Purpose:** To calculate Pr and Zr at a given composition.

**Input:** Values for constants f, g, h, j, k, l, m, n, c,  $aC_0$ ,  $bC_0$ ,  $cC_0$ ,  $dC_0$ ,  $eC_0$ , critical temperature (TCB), critical density (DCB),  $Tr_1$ ,  $Dr_1$ , and the value of the subscript i must be placed in memory before this subroutine is called.

**Details:** The expression for the Benedict-Webb-Rubin constant  $C_0$  as a function of temperature is:

$$C_0 = [eC_0/Q^2 \cdot Q1 + dC_0/(Q \cdot Q1) + bC_0/Q1 + aC_0] / (cC_0/Q1 + 1) \quad (1)$$

where

$$Q = Tr \cdot TCB / 100$$

$$Q1 = (10 \cdot Q^6)^4$$

From the value of  $C_0$  the constant i is computed from:

$$i = m \cdot C_0 / c / DCB \quad (2)$$

For use in the subroutine and subroutines G2CALC and G3CALC, a quantity called QQ is defined:

$$QQ = \exp(-n \cdot Dr_1^2) \quad (3)$$

$Pr_1$  is calculated according to equation (3), Appendix III.

$Zr_1$  is computed from:

$$Zr_1 = Pr_1 / (Tr_1 \cdot Dr_1) \quad (4)$$

As added information, the slope of the reduced compressibility factor curve as a function of reduced pressure at constant temperature is computed numerically. This quantity is called PZRWRPR.

**Method of**

**Checking:** This expression for reduced pressure was used to calculate fugacities. These calculated fugacities checked very well

with known fugacities.

Fortran

Nomen-

clature:

$$AC = aC_0$$

$$BC = bC_0$$

$$C = c$$

$$CC = cC_0$$

$$CO = C_0$$

C4 = Benedict-Webb-Rubin reduced equation of state constant i

$$DC = dC_0$$

$$EC = eC_0$$

I = subscript i

$$PZRWRPR = (\partial Zr / \partial Pr)_{Tr}$$

```

SUBROUTINE G2CALC
DIMENSION X(25), W(25), PC(25), TC(25), PK(25), TK(25), PR(25),
1 TR(25), DR(25), ZR(25), Z(5), FUNC(5), PZRWRPR(25)
COMMON I, DCB, TCB, AC, BC, CC, DC, EC, C, C1, C2, C3, C4, C5, C6, C7, C8, C9, DR,
1 DR1DER, DR2DER, TR, TR1DER, TR2DER, TR3DER, PR, PR1DER, PR2DER, PR3DER,
2 PC, PK, TC, TK, QQ, TO, TO1DER, TO2DER, TN, TN1DER, TN2DER, TT, TT1DER, V,
3 V1DER, Y, Y1DER, Y2DER, ZK, ZK1DER, ZK2DER, ZR, Z, X, W, G2DER, G3DER, FUNC
4 , PZRWRPR
CALL PRCALC
TO = 1./TR(I)
TO1DER = -TO**2*TR1DER
TO2DER = (2.*TR1DER**2/TR(I) - TR2DER)/TR(I)**2
TN = TO**3
TN1DER = 3.*TO**2*TO1DER
TN2DER = 6.*TO1DER**2*TO + 3.*TO**2*TO2DER
TT = TR1DER*TN
TT1DER = TR2DER*TN + TR1DER*TN1DER
U = PR1DER-(C1*DR(I)+C2*DR(I)**2+2.*C4*DR(I)**2/TR(I)**3)*TR1DER
1 + (-C5*DR(I)**3+2.*C8*DR(I)**3*(1.+C9*DR(I)**2)*QQ/TR(I)**3)*
2 TR1DER
V = C1*TR(I)+2.*C2*DR(I)*TR(I)-2.*C3*DR(I)-2.*C4*DR(I)/TR(I)**2
1 + 3.*C5*TR(I)*DR(I)**2-3.*C6*DR(I)**2+6.*C7*DR(I)**5+(C8/TR(I)**2)
2 *QQ*(3.*DR(I)**2+3.*C9*DR(I)**4-2.*C9**2*DR(I)**6)
DR1DER = U/V
U1DER = PR2DER-C1*DR(I)*TR2DER-C1*DR1DER*TR1DER-C2*DR(I)**2*TR2DER
1 -2.*C2*DR(I)*DR1DER*TR1DER-2.*C4*DR(I)**2*TT1DER-4.*C4*DR(I)*
2 DR1DER*TT-C5*DR(I)**3*TR2DER-3.*C5*DR(I)**2*DR1DER*TR1DER
3 +2.*C8*DR(I)**3*(1.+C9*DR(I)**2)*QQ*TT1DER+2.*C8*TT*QQ*
4 (3.+3.*C9*DR(I)**2-2.*C9**2*DR(I)**4)*DR(I)**2*DR1DER
V1DER = C1*TR1DER+2.*C2*DR1DER*TR(I)+2.*C2*DR(I)*TR1DER-2.*C3*
1 DR1DER-2.*C4*DR1DER/TR(I)**2+4.*C4*DR(I)*TT+6.*C5*TR(I)*DR(I)*
2 DR1DER+3.*C5*TR1DER*DR(I)**2-6.*C6*DR(I)*DR1DER+30.*C7*DR(I)**4*
3 DR1DER+C8*QQ*(6.*DR(I)*DR1DER/TR(I)**2+6.*C9*DR(I)**3*DR1DER/TR(I)
4 **2-18.0*C9**2*DR(I)**5*DR1DER/TR(I)**2+4.*C9**3*DR(I)**7*DR1DER
5 /TR(I)**2-6.*DR(I)**2*TT-6.*C9*DR(I)**4*TT+4.*C9**2*DR(I)**6*TT)
DR2DER = (U1DER - V1DER*DR1DER)/V
Y = PR(I)/(C1*TR(I))
ZK = Y/DR(I)
Y1DER = (PR1DER - Y*C1*TR1DER)/(C1*TR(I))
Y2DER = (PR2DER - Y*C1*TR2DER - 2.*Y1DER*C1*TR1DER)/(C1*TR(I))
ZK1DER = (Y1DER - ZK*DR1DER)/DR(I)
ZK2DER = (Y2DER-ZK*DR2DER-2.*ZK1DER*DR1DER)/DR(I)
G2DER = 1.0/(X(I)-X(I)**2)+ZK2DER-ZK2DER/ZK+(ZK1DER/ZK)**2 +
1 (C2*DR2DER-C3*(TO*DR2DER+TO2DER*DR(I)+2.*TO1DER*DR1DER)-C4*
2 (TN*DR2DER+TN2DER*DR(I)+2.*TN1DER*DR1DER)+(2.*C5/2.)*(DR(I)*
3 DR2DER+DR1DER**2)-(C6/2.)*(2.*TO*DR(I)*DR2DER+TO2DER*DR(I)**2+
4 4.*TO1DER*DR(I)*DR1DER+2.*TO*DR1DER**2)+C7*(2.*TO1DER*DR(I)**4*
5 DR1DER+TO2DER*DR(I)**5/5.+4.*TO*DR(I)**3*DR1DER**2+TO*DR(I)**4*
6 DR2DER)+C8/(2.*C9)*(2.*TN2DER+QQ*(-2.*TN2DER-C9*DR(I)**2*TN2DER+
7 4.*C9*DR(I)*DR1DER*TN1DER+2.*C9*DR(I)*DR2DER*TN+2.*C9*DR1DER**2*
8 TN+4.*C9**2*DR(I)**3*DR1DER*TN1DER+2.*C9**2*DR(I)**3*DR2DER*TN+2.
9 *C9**2*DR(I)**2*DR1DER**2*TN-4.*C9**3*DR(I)**4*DR1DER**2*TN))/C1
END

```

Subroutine G2CALC

**Purpose:** To calculate  $G''$ .

**Input:** Derivatives  $Tr'$ ,  $Tr''$ ,  $Pr'$ , and  $Pr''$  at  $x_1$  must be in memory when G2CALC is called. In addition, the input requirements for subroutine PRCALC must be satisfied because PRCALC is called in this subroutine.

**Details:** Subroutine PRCALC is called to compute the constant  $i$  and the quantity  $QQ$ .

The derivations of all equations used in this subroutine are in Appendices III, IV, and V. The equations in the order used are:

III - 9, 10, 11  
 III - 12, 13, 14  
 IV - 6, 7  
 IV - 1, 2, 3  
 IV - 9, 10  
 IV - 4  
 V - 1  
 V - 5  
 V - 2,3  
 V - 6,7  
 III - 18

**Method of**

**Checking:** Program CHECK was used to check the equations used in this subroutine.

**Fortran**

**Nomen-**

**clature:** DR = reduced density ( $Dr$ )  
 DR1DER =  $Dr'$   
 DR2DER =  $Dr''$   
 G2DER =  $G''$   
 PR = reduced pressure ( $Pr$ )  
 PR1DER =  $Pr'$   
 PR2DER =  $Pr''$   
 TN =  $T_n$   
 TN1DER =  $T_n'$   
 TN2DER =  $T_n''$

TO = T<sub>o</sub>  
TO1DER = T<sub>o</sub>'  
TO2DER = T<sub>o</sub>''  
TR = reduced temperature (Tr)  
TR1DER = Tr'  
TR2DER = Tr''  
TT = T<sub>t</sub>  
TT1DER = T<sub>t</sub>'  
U = U  
U1DER = U'  
V = V  
V1DER = V'  
X = mole fraction ethane (x)  
Y = Y  
Y1DER = Y'  
Y2DER = Y''  
ZK = compressibility factor (Z)  
ZK1DER = Z'  
ZK2DER = Z''

```

SUBROUTINE G3CALC
DIMENSION X(25), W(25), PC(25), TC(25), PK(25), TK(25), PR(25),
1 TR(25), DR(25), ZR(25), Z(5), FUNC(5),PZRWRPR(25)
COMMON I,DCB,TCB,AC,BC,CC,DC,EC,C,C1,C2,C3,C4,C5,C6,C7,C8,C9,DR,
1 DR1DER,DR2DER,TR,TR1DER,TR2DER,TR3DER,PR,PR1DER,PR2DER,PR3DER,
2 PC,PK,TC,TK,QQ,TO,TO1DER,TO2DER,TN,TN1DER,TN2DER,TT,TT1DER,V,
3 V1DER,Y,Y1DER,Y2DER,ZK,ZK1DER,ZK2DER,ZR,Z,X,W,G2DER,G3DER,FUNC
4 ,PZRWRPR
CALL G2CALC
TO3DER = -TO*(3.*(TO1DER*TR2DER+TO2DER*TR1DER)+TO*TR3DER)
TN3DER = 3.*(2.*TO1DER**3+6.*TO*TO1DER*TO2DER+TO3DER*TO**2)
TT2DER = TR3DER*TN+TR1DER*TN2DER+2.*TR2DER*TN1DER
U2DER = PR3DER-C1*(DR(I)*TR3DER+2.*DR1DER*TR2DER+DR2DER*TR1DER)
1 -C2*(DR(I)**2*TR3DER+4.*DR(I)*DR1DER*TR2DER+2.*DR(I)*DR2DER*
2 TR1DER+2.*DR1DER**2*TR1DER)-C4*(2.*DR(I)**2*TT2DER+8.*DR(I)*
3 DR1DER*TT1DER+4.*DR(I)*DR2DER*TT+4.*DR1DER**2*TT)-C5*(DR(I)**3
4 *TR3DER+6.*DR(I)**2*DR1DER*TR2DER 3.*DR(I)**2*DR2DER*TR1DER+
5 6.*DR(I)*DR1DER**2*TR1DER)+2.*C8*QQ*(DR(I)**3*TT2DER+C9*DR(I)**5
6 *TT2DER+6.*DR(I)**2*DR1DER*TT1DER 6.*DR(I)**4*C9*DR1DER*TT1DER
7-4.*C9**2*DR(I)**6*DR1DER*TT1DER+3.*DR(I)**2*DR2DER*TT+3.*C9*DR(I)
8 **4*DR2DER*TT-2.*C9**2*DR(I)**6*DR2DER*TT+6.*C9*DR(I)**3*DR1DER**
9 2*TT+6.*DR(I)*DR1DER**2*TT-18.*C9**2*DR(I)**5*DR1DER**2*TT)
U2DER = U2DER+2.*C8*QQ*4.*C9**3*DR(I)**7*DR1DER**2*TT
V2DER = C1*TR2DER+C2*2.*DR2DER*TR(I)+4.*C2*DR1DER*TR1DER +
1 2.*C2*DR(I)*TR2DER-2.*C3*DR2DER+C4*(-2.*DR2DER/TR(I)**2+8.*DR1DER
2 *TT+4.*DR(I)*TT1DER)+C5*(12.*TR1DER*DR(I)*DR1DER+6.*TR(I)*DR1DER
3 **2+6.*DR(I)*DR2DER*TR(I)+3.*TR2DER*DR(I)**2)-6.*C6*(DR1DER**2+
4 DR(I)*DR2DER)+30.*C7*(DR(I)**4*DR2DER+4.*DR(I)**3*DR1DER**2)
5 +2.*C8*QQ*(3.*DR(I)*DR2DER+3.*C9*DR(I)**3*DR2DER-9.*C9**2*DR(I)
6 **5*DR2DER+2.*C9**3*DR(I)**7*DR2DER)/TR(I)**2+(3.*DR1DER**2+
7 3.*C9*DR(I)**2*DR1DER**2-51.*C9**2*DR(I)**4*DR1DER**2+32.*C9**3*
8 DR(I)**6*DR1DER**2-4.*C9**4*DR(I)**8*DR1DER**2)/TR(I)**2-3.*DR(I)
9 **2*TT1DER-3.*C9*DR(I)**4*TT1DER+2.*C9**2*DR(I)**6*TT1DER)
V2DER = V2DER + 2.*C8*QQ*(-12.*DR(I)*DR1DER*TT-12.*C9*DR(I)**3*
1 DR1DER*TT+36.*C9**2*DR(I)**5*DR1DER*TT-8.*C9**3*DR(I)**7*DR1DER
2 *TT)
DR3DER = (U2DER-(2.*V1DER*DR2DER+V2DER*DR1DER))/V
Y3DER = (PR3DER-Y*C1*TR3DER-3.*Y1DER*C1*TR2DER-3.*Y2DER*C1*TR1DER)
1 /(C1*TR(I))
ZK3DER = (Y3DER-ZK*DR3DER-3.*ZK1DER*DR2DER-3.*ZK2DER*DR1DER)/DR(I)
11 G3DER = (2.*X(I)-1.)/((X(I)-X(I)**2)**2)+ZK3DER-ZK3DER/ZK+3.*
1 ZK2DER*ZK1DER/ZK**2-2.*(ZK1DER/ZK)**3+(C2*DR3DER-C3*(TO*DR3DER+
2 TO3DER*DR(I)+3.*DR1DER*TO2DER+3.*DR2DER*TO1DER)-C4*(TN*DR3DER+
3 TN3DER*DR(I)+3.*DR1DER*TN2DER+3.*DR2DER*TN1DER)+C5*(DR(I)*DR3DER
4 +3.*DR1DER*DR2DER)-(C6/2.)*(2.*TO*DR(I)*DR3DER+TO3DER*DR(I)**2)
5 -(C6/2.)*(6.*TO*DR1DER*DR2DER+6.*TO1DER*DR(I)*DR2DER+6.*TO2DER*
6 DR(I)*DR1DER+6.*TO1DER*DR1DER**2) C7*(3.*TO2DER*DR(I)**4*DR1DER+
7 12.*TO1DER*DR(I)**3*DR1DER**2+3.*TO1DER*DR(I)**4*DR2DER+12.*TO
8 *DR(I)**2*DR1DER**3+12.*TO*DR(I)**3*DR1DER*DR2DER+TO*DR(I)**4*
9 DR3DER+TO3DER*DR(I)**5/5.)+C8/C9*TN3DER)/C1
G3DER = G3DER+((C8/(2.*C9))*QQ*(-2.*TN3DER-C9*DR(I)**2*TN3DER+6.*
1 C9*DR(I)*DR1DER*TN2DER+6.*C9*DR(I)*DR2DER*TN1DER+6.*C9*DR1DER**2*
2 TN1DER+2.*C9*DR(I)*DR3DER*TN+6.*C9*DR1DER*DR2DER*TN+6.*C9**2*
3 DR(I)**3*DR1DER*TN2DER+6.*C9**2*DR(I)**3*DR2DER*TN1DER+6.*C9**2*

```

```
4 DR(I)**2*DR1DER**2*TN1DER+2.*C9**2*DR(I)**3*DR3DER*TN+6.*C9**2*
5 DR(I)**2*DR1DER*DR2DER*TN-12.*C9**3*DR(I)**4*DR1DER**2*TN1DER-12.
6 *C9**3*DR(I)**4*DR1DER*DR2DER*TN-20.*C9**3*DR(I)**3*DR1DER**3*TN+
7 8.*C9**4*DR(I)**5*DR1DER**3*TN)/C1
END
```

Subroutine G3CALC

**Purpose:** To calculate  $G'''$ .

**Input:**  $Tr'''$  and  $Pr'''$  at  $x_1$ . Also, the input requirements of subroutine G2CALC must be satisfied because G2CALC is called in this subroutine.

**Details:** Subroutine G2CALC is called to make preliminary calculations.

The derivations of the equations used in this subroutine are found in Appendices III, IV, and V. The equations in the order used are:

III - 11  
 III - 15  
 IV - 8  
 IV - 11, 12  
 IV - 5  
 V - 4  
 V - 8  
 III - 19

**Method of**

**Checking:** Program CHECK was used to check the equations used in this subroutine.

**Fortran****Nomen-**

**clature:** DR3DER =  $Dr'''$   
 G3DER =  $G'''$   
 PR3DER =  $Pr'''$   
 TN3DER =  $T_n'''$   
 TO3DER =  $T_o'''$   
 TR3DER =  $Tr'''$   
 TT2DER =  $T_t''$   
 U2DER =  $U''$   
 V2DER =  $V''$   
 ZK3DER =  $Z'''$

DATA  
5.153462298  
370.0505321  
42.38841074  
  .08207  
  .097313  
6.87225  
508256.  
  .0225  
  .9477  
129000.  
  .000607175  
  .022  
508256.1345  
  1.388457033E-06  
  2.844569141E-12  
  .0  
  .0  
1  
1.005  
1.010  
1.017  
1.002  
1.004  
1.007

Data

The data represents the following:

- 5.153462298 = the critical density of propane as computed from the Benedict-Webb-Rubin equation of state, g-moles/liter
- 370.0505321 = the critical temperature of propane as computed from the Benedict-Webb-Rubin equation of state, °K
- 42.38841074 = the critical pressure of propane as computed from the Benedict-Webb-Rubin equation of state, atm.
- 0.08207 = gas constant R, (liter-atm.)/(g-mole-K°)
- 0.097313 = Benedict-Webb-Rubin constant B
- 6.87225 = Benedict-Webb-Rubin constant A<sup>o</sup>
- 508256. = Benedict-Webb-Rubin constant C<sup>o</sup>
- 0.0225 = Benedict-Webb-Rubin constant b<sup>o</sup>
- 0.9477 = Benedict-Webb-Rubin constant a
- 129000. = Benedict Webb-Rubin constant c
- 0.000607175 = Benedict-Webb-Rubin constant α
- 0.022 = Benedict-Webb-Rubin constant γ
- 508256.1345 = aC
- $1.388457033 \times 10^{-6} = bC_0$
- $2.844569141 \times 10^{-12} = cC_0$
- 0 = dC<sub>0</sub>
- 0 = eC<sub>0</sub>
- 1 = number of sets of guesses of Tr<sub>2</sub>, Tr<sub>3</sub>, Tr<sub>4</sub>, Dr<sub>2</sub>, Dr<sub>3</sub>, Dr<sub>4</sub>
- 1.005 = first guess of Tr<sub>2</sub>
- 1.010 = first guess of Tr<sub>3</sub>
- 1.017 = first guess of Tr<sub>4</sub>
- 1.002 = first guess of Dr<sub>2</sub>
- 1.004 = first guess of Dr<sub>3</sub>
- 1.007 = first guess of Dr<sub>4</sub>

va:

un'

ra

x<sub>2</sub>

fo:

pu:

si:

co:

The

sy:

no:

ab:

li:

## APPENDIX VII

### Program TOTRANGE

The objective of program TOTRANGE is to vary simultaneously the values of reduced temperature (Tr) and reduced density (Dr) at  $x_2$  and  $x_3$  until  $G_2''$ ,  $G_3''$ ,  $G_2'''$ , and  $G_3'''$  become equal to zero. The composition range is split into only three intervals. Therefore, possible values of  $x_2$ ,  $x_3$ , and  $x_4$  could be 0.33, 0.67, and 1.0, respectively. This program follows the flow diagram in Figure 6, page 38.

Program TOTRANGE makes use of the known values of Tr and Pr for both pure components. Because four variables ( $Tr_2$ ,  $Tr_3$ ,  $Dr_2$ ,  $Dr_3$ ) are changed simultaneously to satisfy four known conditions, it should be possible to converge to a solution. Negative values of Tr and Dr are not permitted. The convergence method used is similar to Newton's convergence method for systems of equations.<sup>42</sup>

The main body and subroutine PHICALC are listed for reference. The nomenclature is identical to that listed on page 104 except for the variable PHI which is defined as the sum of the squares of the four above listed G quantities.

The main divisions of program TOTRANGE are:

1. Program TOTRANGE-Main Body
2. Subroutine PHICALC
3. Subroutine WBKAY
4. Subroutine POLY
5. Subroutine PRCALC
6. Subroutine G2CALC
7. Subroutine G3CALC
8. Data



```

PROGRAM TOTRANGE
DIMENSION X(25), W(25), PC(25), TC(25), PK(25), TK(25), PR(25),
1 TR(25), DR(25), ZR(25), Z(5), FUNC(5), G(4), XX(7), TINC1(4),
2 DINC1(4), TINC(4), DINC(4), PHIN(7), DELXX(7), PX(10), D(7,4),
3 PPD(7), DELTAXX(6), DA(5,4), PDX(7), BB(5,4), PZRWRPR(25)
COMMON I, DCB, TCB, C, AC, BC, CC, DC, EC, C1, C2, C3, C4, C5, C6, C7, C8, C9, X, W,
1 DR, DR1DER, DR2DER, TR, TR1DER, TR2DER, TR3DER, PR, PR1DER, PR2DER, PR3DER
2 , TC, PC, TK, PK, QQ, TO, TO1DER, TO2DER, TN, TN1DER, TN2DER, TT, TT1DER
3 , V, V1DER, Y, Y1DER, Y2DER, ZK, ZK1DER, ZK2DER, ZR, Z, S, FUNC, G2DER, G3DER,
4 G, PHI, PZRWRPR
1 FORMAT (E18.11)
2 FORMAT (/ , 13H CALCULATION , I2, /)
3 FORMAT (/ , 3H X, 4E21.10, / , 3H TR, 4E21.10, / , 3H DR, 4E21.10, / , 3H PR,
1 4E21.10, / , 3H ZR, 4E21.10, / , 8H PZRWRPR, 16X, 2E21.10)
4 FORMAT (1H1)
6 FORMAT (I2)
7 FORMAT (8H RESULTS, 8X, 6HPHI = , E18.10)
8 FORMAT (10H G2DER2 = , E18.10, 3X, 9HG3DER2 = , E18.10, 3X, 9HG2DER3 = ,
1 E18.10, 3X, 9HG3DER3 = , E18.10, /)
9 FORMAT (9H TR(2) = , E18.10, 4X, 8HTR(3) = , E18.10, 4X, 8HTR(4) = ,
1 E18.10, / , 9H DR(2) = , E18.10, 4X, 8HDR(3) = , E18.10, 4X, 8HDR(4) = ,
2 E18.10)
11 FORMAT (25X, 34HFOUR VARIABLES AND FOUR CONDITIONS, 4(/))
PRINT 11
READ 1, DCB, TCB, PCB, R, BO, AO, CO, B, A, C, ALPHA, GAMMA, AC, BC, CC, DC, EC
C PRELIMINARY CALCULATIONS
C1 = (DCB*TCB*R)/PCB
C2 = C1*BO*DCB
C3 = (AO*DCB**2)/PCB
C5 = C1*DCB**2*B
C6 = (DCB**3/PCB)*A
C7 = C6*DCB**3*ALPHA
C8 = (C6/(A*TCB**2))*C
C9 = DCB**2*GAMMA
C C1=F, C2=G, C3=H, C4=I, C5=J, C6=K, C7=L, C8=M, C9=N
READ 6, NUMDATA
DO 39 NN=1, NUMDATA
200 READ 1, (TR(I), I=2,3), (DR(I), I=2,3)
DELTA = 1.E-05
X(1) = 0.0
X(2) = 0.6215
X(3) = 0.8723
X(4) = 1.0
TR(1) = 1.0
DR(1) = 1.0
PR(1) = 1.0
ZR(1) = 1.0
TR(4) = 1.0
DR(4) = 1.0
PR(4) = 1.0
ZR(4) = 1.0
DO 201 I = 1,4
201 CALL WBKAY
PC(1) = PK(1)/PR(1)

```

```

TC(1) = TK(1)/TR(1)
PC(4) = PK(4)/PR(4)
TC(4) = TK(4)/TR(4)
CALL PHICALC
PHIN(1) = PHI
PRINT 7, PHI
PRINT 9, (TR(I), I=2,4), (DR(I), I=2,4)
PRINT 8, (G(I), I=1,4)
DO 37 M = 1,50
PRINT 2, M
DO 18 L=1,4
18 D(5,L) = -G(L)
5 DO 10 I=1,2
XX(I) = TR(I+1)
10 XX(I+2) = DR(I+1)
DO 20 J=1,4
XX(J) = XX(J) + DELTA
DO 15 I=1,2
TR(I+1) = XX(I)
15 DR(I+1) = XX(I+2)
CALL PHICALC
XX(J) = XX(J) - DELTA
DO 20 I=1,4
20 D(J,I) = (G(I) + D(5,I))/DELTA
DO 66 I=1,5
DO 66 J=1,4
66 DA(I,J) = D(I,J)
DO 74 I=1,4
DO 71 J=1,4
DIVISOR = DA(1,J)
IF (DA(I,J))69,71,69
69 DO 70 K = 1,5
DA(K,J) = DA(K,J)/DIVISOR
70 BB(K,I) = DA(K,J)
71 CONTINUE
77 DO 74 J=1,4
IF (DA(I,J))72,74,72
72 DO 73 K=1,5
73 DA(K,J) = DA(K,J) - BB(K,I)
74 CONTINUE
PDX(5) = -1.
DO 75 MA = 1,4
I = 5 - MA
PDX(I) = 0.
L = I + 1
DO 75 K=L,5
75 PDX(I) = PDX(I) - BB(K,I)*PDX(K)
DO 41 N=1,4
DELTAXX(N) = PDX(N)
41 XX(N) = XX(N) + DELTAXX(N)
DO 88 KK=1,15
43 DO 42 I=1,2
TR(I+1) = XX(I)
42 DR(I+1) = XX(I+2)

```

```
CALL PHICALC
PRINT 7, PHI
PRINT 9, (TR(I),I=2,4),(DR(I),I=2,4)
IF (PHIN(1)-PHI)87,87,79
87 DO 88 N = 1,4
   DELTAXX(N) = DELTAXX(N)/2.
88 XX(N) = XX(N) - DELTAXX(N)
   GO TO 38
79 PHIN(1) = PHI
34 PRINT 8, (G(I),I=1,4)
   IF (PHI - 1.E-10)38,38,37
37 CONTINUE
38 PRINT 3, (X(I),I=1,4), (TR(I),I=1,4), (DR(I),I=1,4),(PR(I),I=1,4),
1 (ZR(I),I=1,4), (PZRWRPR(I),I=2,3)
39 PRINT 4
END
```

```

SUBROUTINE PHICALC
DIMENSION X(25), W(25), PC(25), TC(25), PK(25), TK(25), PR(25),
1 TR(25), DR(25), ZR(25), Z(5), FUNC(5), G(4), PZRWRPR(25)
COMMON I,DCB,TCB,C,AC,BC,CC,DC,EC,E1,C2,C3,G4,C5,C6,C7,C8,C9,X,W,
1 DR,DR1DER,DR2DER,TR,TR1DER,TR2DER,TR3DER,PR,PR1DER,PR2DER,PR3DER
2 ,TC,PC,TK,PK,QQ,TO,TO1DER,TO2DER,TN,TN1DER,TN2DER,TT,TT1DER
3 ,V,V1DER,Y,Y1DER,Y2DER,ZK,ZK1DER,ZK2DER,ZR,Z,S,FUNC,G2DER,G3DER,
4 G,PHI,PZRWRPR
DO 10 I=2,3
CALL PRCALC
TC(I) = TK(I)/TR(I)
10 PC(I) = PK(I)/PR(I)
DO 14 I=2,3
DO 11 K=1,4
Z(K) = X(K)
11 FUNC(K) = TC(K)
S = Z(I)
CALL POLY (TC1DER,TC2DER,TC3DER)
DO 12 K=1,4
12 FUNC(K) = PC(K)
CALL POLY (PC1DER,PC2DER,PC3DER)
TR1DER = -TR(I)*TC1DER/TC(I)
TR2DER = -2.*TR1DER*TC1DER/TC(I) - TR(I)*TC2DER/TC(I)
TR3DER = 6.*TK(I)*TC1DER*TC2DER/TC(I)**3-6.*TK(I)*TC1DER**3/TC(I)
1 **4 - TK(I)*TC3DER/TC(I)**2
PR1DER = -PR(I)*PC1DER/PC(I)
PR2DER = -2.*PR1DER*PC1DER/PC(I) - PR(I)*PC2DER/PC(I)
PR3DER = 6.*PK(I)*PC1DER*PC2DER/PC(I)**3-6.*PK(I)*PC1DER**3/PC(I)
1 **4 - PK(I)*PC3DER/PC(I)**2
CALL G2CALC
CALL G3CALC
G(2*I-3) = G2DER
14 G(2*I-2) = G3DER
PHI = G(1)**2 + G(2)**2 + G(3)**2 G(4)**2
END

```

```

SUBROUTINE PHICALC
DIMENSION X(25), W(25), PC(25), TC(25), PK(25), TK(25), PR(25),
1 TR(25), DR(25), ZR(25), Z(5), FUNC(5), G(4), PZRWRPR(25)
COMMON I,DCB,TCB,C,AC,BC,CC,DC,EC,E1,C2,C3,C4,C5,C6,C7,C8,C9,X,W,
1 DR,DR1DER,DR2DER,TR,TR1DER,TR2DER,TR3DER,PR,PR1DER,PR2DER,PR3DER
2 ,TC,PC,TK,PK,QQ,TO,TO1DER,TO2DER,TN,TN1DER,TN2DER,TT,TT1DER
3 ,V,V1DER,Y,Y1DER,Y2DER,ZK,ZK1DER,ZK2DER,ZR,Z,S,FUNC,G2DER,G3DER,
4 G,PHI,PZRWRPR
DO 10 I=2,3
CALL PRCALC
TC(I) = TK(I)/TR(I)
10 PC(I) = PK(I)/PR(I)
DO 14 I=2,3
DO 11 K=1,4
Z(K) = X(K)
11 FUNC(K) = TC(K)
S = Z(1)
CALL POLY (TC1DER,TC2DER,TC3DER)
DO 12 K=1,4
12 FUNC(K) = PC(K)
CALL POLY (PC1DER,PC2DER,PC3DER)
TR1DER = -TR(I)*TC1DER/TC(I)
TR2DER = -2.*TR1DER*TC1DER/TC(I) - TR(I)*TC2DER/TC(I)
TR3DER = 6.*TK(I)*TC1DER*TC2DER/TC(I)**3-6.*TK(I)*TC1DER**3/TC(I)
1 **4 - TK(I)*TC3DER/TC(I)**2
PR1DER = -PR(I)*PC1DER/PC(I)
PR2DER = -2.*PR1DER*PC1DER/PC(I) - PR(I)*PC2DER/PC(I)
PR3DER = 6.*PK(I)*PC1DER*PC2DER/PC(I)**3-6.*PK(I)*PC1DER**3/PC(I)
1 **4 - PK(I)*PC3DER/PC(I)**2
CALL G2CALC
CALL G3CALC
G(2*I-3) = G2DER
14 G(2*I-2) = G3DER
PHI = G(1)**2 + G(2)**2 + G(3)**2 + G(4)**2
END

```

G'

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## APPENDIX VIII

### Program CHECK

The purpose of program CHECK was to check the equations for  $G''$  and  $G'''$  and their supporting equations in subroutine G2CALC and G3CALC. Beginning with the expression for  $G$ , the derivatives were calculated by numerical differentiation and from the mathematical expressions for the derivatives. These two answers were then compared, and if they were nearly identical, the mathematical equations for the  $G$  quantity were assumed to be correct. This program follows the flow diagram in Figure 7, page 39.

The main division of program CHECK are:

1. Program CHECK-Main Body
2. Subroutine PRCALC
3. Subroutine G2CALC
4. Subroutine G3CALC
5. Data

## PROGRAM CHECK

```

DIMENSION X(25), W(25), PC(25), TC(25), PK(25), TK(25), PR(25),
1 TR(25), DR(25), ZR(25), Z(5), FUNC(5), G(4), XX(7), TINC1(4),
2 DINC1(4), TINC(4), DINC(4), PHIN(7), DELXX(7), PX(10), D(7,3),
3 PPD(7), DELTAXX(6), DA(4,3), PDX(7), BB(4,3)
4 ,DCC(20), DK(20)

```

```

COMMON I,DCB,TCB,PCB,R,B0,A0,CO,B,A,C,ALPHA,GAMMA,AC,BC,CC,DC,EC,
1 C1,C2,C3,C4,C5,C6,C7,C8,C9,X,W,DR,DR1DER,DR2DER,TR,TR1DER,TR2DER,
2 TR3DER,PR,PR1DER,PR2DER,PR3DER,TC,PC,TK,PK,QQ,TO,TO1DER,TO2DER,
3 TN,TN1DER,TN2DER,TT,TT1DER,V,V1DER,Y,Y1DER,Y2DER,ZK,ZK1DER,
4 ZK2DER,ZR,Z,S,FUNC,FSTDER,SECDER,THRDER,G2DER,G3DER,G,PHI
5 ,GG,G1DER

```

```
1 FORMAT (E18.11)
```

```
2 FORMAT (I2)
```

```
3 FORMAT(25X,13HCHECK PROGRAM,4(/))
```

```
10 FORMAT (3E20.10)
```

```
11 FORMAT (/ ,6H CHECK,3E20.10,/,6X,3E20.10,3(/))
```

```
PRINT 3
```

```
READ 1, DCB,TCB,PCB,R,B0,A0,CO,B,A,C,ALPHA,GAMMA,AC,BC,CC,DC,EC
```

## C PRELIMINARY CALCULATIONS

```
C1 = (DCB*TCB*R)/PCB
```

```
C2 = C1*B0*DCB
```

```
C3 = (A0*DCB**2)/PCB
```

```
C5 = C1*DCB**2*B
```

```
C6 = (DCB**3/PCB)*A
```

```
C7 = C6*DCB**3*ALPHA
```

```
C8 = (C6/(A*TCB**2))*C
```

```
C9 = DCB**2*GAMMA
```

## C C1=F, C2=G, C3=H, C4=I, C5=J, C6=K, C7=L, C8=M, C9=N

```
DELTA = 0.00001
```

```
READ 2, NUMDATA
```

```
DO 64 NN=1,NUMDATA
```

```
READ 1, X(1)
```

```
ASSIGN 60 TO JOHN
```

```
I = 1
```

```
TK(I) = (513.3-186.4392126*X(I)+20.413825*X(I)**2-558.3704113*
1 X(I)**3+121.1957936*X(I)**4+459.67)/1.8
```

```
DK(I) = 2.3 + 2.*X(I) + 3.*X(I)**2
```

```
59 TC(I) = 530. + 200.*X(I) - 400.*X(I)**3
```

```
TC1DER = +200. -1200.*X(I)**2
```

```
TC2DER = -2400.*X(I)
```

```
TC3DER = -2400.
```

```
PC(I) = 25. + 140.*X(I) - 120.*X(I)**3
```

```
PC1DER = 140. - 360.*X(I)**2
```

```
PC2DER = -720.*X(I)
```

```
PC3DER = -720.
```

```
DCC(I) = C1*PC(I)/TC(I)/R
```

```
58 TR(I) = TK(I)/TC(I)
```

```
DR(I) = DK(I)/DCC(I)
```

```
CALL PRCALC
```

```
PK(I) = PC(I)*PR(I)
```

```
PRINT 10, TC(I),TK(I),TR(I),DCC(I),DK(I),DR(I),PC(I),PK(I),PR(I),
```

```
1 X(I)
```

```
TR1DER = -TR(I)*TC1DER/TC(I)
```

```

TR2DER = -2.*TR1DER*TC1DER/TC(I) - TR(I)*TC2DER/TC(I)
TR3DER = 6.*TK(I)*TC1DER*TC2DER/TC(I)**3-6.*TK(I)*TC1DER**3/TC(I)
1 **4 - TK(I)*TC3DER/TC(I)**2
PR1DER = -PR(I)*PC1DER/PC(I)
PR2DER = -2.*PR1DER*PC1DER/PC(I) - PR(I)*PC2DER/PC(I)
PR3DER = 6.*PK(I)*PC1DER*PC2DER/PC(I)**3-6.*PK(I)*PC1DER**3/PC(I)
1 **4 - PK(I)*PC3DER/PC(I)**2
CALL G2CALC
CALL G3CALC
GO TO JOHN
60 X(I) = X(I) + DELTA
PRINT 10, GG, G1DER, G2DER, G3DER
PK1 = PK(I)
GG1 = GG
G11 = G1DER
G21 = G2DER
G31 = G3DER
ASSIGN 61 TO JOHN
GO TO 59
61 X(I) = X(I) - DELTA
PGWRXDT = (GG - GG1)/DELTA
P1WRXDT = (G1DER - G11)/DELTA
PFWRXDT = (G2DER - G21)/DELTA
PPWRXDT = (PK(I) - PK1)/DELTA
PRINT 10, PGWRXDT, P1WRXDT, PFWRXDT, PPWRXDT
ASSIGN 62 TO JOHN
GO TO 59
62 DK(I) = DK(I) + DELTA
ASSIGN 63 TO JOHN
GO TO 58
63 PFWRPXT = (G2DER - G21)/(PK(I) - PK1)
PGWRPXT = (GG - GG1)/(PK(I) - PK1)
P1WRPXT = (G1DER - G11)/(PK(I) - PK1)
PRINT 10, PGWRPXT, P1WRPXT, PFWRPXT
G1DERN = PGWRXDT - PGWRPXT*PPWRXDT
G2DERN = P1WRXDT - P1WRPXT*PPWRXDT
G3DERN = PFWRXDT - PFWRPXT*PPWRXDT
64 PRINT 11, G11, G21, G31, G1DERN, G2DERN, G3DERN
END

```

Program CHECK-Main Body

**Purpose:** To check the equations for  $G'$  and  $G'''$  and all of the supporting equations in subroutine G2CALC and G3CALC.

**Input:** P-V-T data on a reference compound (in this case propane). This data includes the critical properties, the gas constant R, eight Benedict-Webb-Rubin constants, and five constants for computing  $C_0$  as a function of temperature. Also, the value of composition ( $x_1$ ) at which the derivatives are to be calculated.

**Details:** This program computes derivatives  $G'$ ,  $G''$ , and  $G'''$  from the mathematical expressions for these derivatives, and also by numerical differentiation. If each pair of results are nearly identical, the equations are assumed to be correct.

The expression for the derivative of a function  $F(T,D,P,x)$  with respect to  $x$  at constant  $T$  and  $P$  was shown on page 39 to be:

$$\left(\frac{\partial F}{\partial x}\right)_{T,P} = \left(\frac{\partial F}{\partial x}\right)_{T,D} - \left(\frac{\partial F}{\partial P}\right)_{T,x} \left(\frac{\partial P}{\partial x}\right)_{T,D} \quad (1)$$

where  $F$  can equal  $G$ ,  $G'$ , or  $G''$ .

Up to third derivatives are needed for  $T_c$  and  $P_c$ . For this program it is sufficient to use simple, arbitrary functions for these variables. The functions were selected such that they approximated the  $T_c$  and  $P_c$  values for pure ethane and pure n-heptane. The expressions used were:

$$T_c = 530 + 200x - 400x^3 \quad (2)$$

$$P_c = 25 + 140x - 120x^3 \quad (3)$$

Equations (2) and (3) are readily differentiable with respect to  $x$ . This differentiation was done by hand and the resulting formulas put into the program.

For the sake of accuracy, an expression was devised for  $D_k$  which approximated the experimental data of Kay<sup>23</sup>. For purposes of this check program, a constant value of  $D_k$  could also have been used. The expression for  $D_k$  is:

$$D_k = 2.3 + 2x + 3x^2 \quad (4)$$

The expression used for  $T_k$  is the same one which is used in subroutine WBKAY.

Extensive use is made of subscripted variables in this program, although this is unnecessary. This is done for two reasons. First, program CHECK was prepared from other programs which were already written, and these had subscripted variables in them. Second, since the equations in this project actually use subscripted variables it is better to check those specific equations. The specific subscript used throughout this program is 1.

#### Method of

Checking: A second person checked over this program.

#### Fortran Nomen-

clature: DCC = pseudocritical density, moles/liter  
 GG = G  
 G1DER = G'  
 G2DER = G''  
 G3DER = G'''  
 G1DERN = numerical value of  $G' = (\partial G / \partial x)_{T,P}$   
 G2DERN = numerical value of  $G'' = (\partial G' / \partial x)_{T,P}$   
 G3DERN = numerical value of  $G''' = (\partial G'' / \partial x)_{T,P}$   
 G11 = name of variable which is used to save the first value of G'  
 G21 = name of variable which is used to save the first value of G''  
 G31 = name of variable which is used to save the first value of G'''  
 PK1 = name of variable which is used to save the first value of Pk  
 PGWRXDT =  $(\partial G / \partial x)_{T,D}$   
 P1WRXDT =  $(\partial G' / \partial x)_{T,D}$

$$PFWRXDT = (\partial G'' / \partial x)_{T,D}$$

$$PFWRXDT = (\partial P / \partial x)_{T,D}$$

$$PGWRPXT = (\partial G / \partial P)_{T,x}$$

$$PLWRPXT = (\partial G' / \partial P)_{T,x}$$

$$PFWRPXT = (\partial G'' / \partial P)_{T,x}$$

Subroutine PRCALC - Same as for program LINEAR

Subroutine G2CALC - Same as for program LINEAR except that  $G$  and  $G'$  are also computed.  $G$  is calculated from equation III-18 and  $G'$  is calculated from equation III-19.

Subroutine G3CALC - Same as for program LINEAR.

Data - Same as for program LINEAR except that no values for  $D_r$  and  $T_r$  are put in the data. Instead, after the data card for  $eC_0$ , values are read for NUMDATA and the compositions at which a check is to be made. The number of values of  $x$  must be equal to the value of NUMDATA.

## APPENDIX IX

### Generated Pseudocritical Curve Results - Approaches I and II

#### Approach I

Using as known conditions, experimental critical temperatures, pressures, and compressibility factors and the fact that  $G''$  equals zero at the critical point, an attempt was made to generate pseudocritical temperature and pressure curves. Representative data points are listed in Tables 11 and 12. Table 11 contains the generated values of pseudocritical temperature as a function of composition, while Table 12 contains the generated values of pseudocritical pressure as a function of composition. Figure 20 is a plot of the pseudocritical temperature data.

The temperature data in Figure 20 show a large amount of instability. The stability of each curve was directly dependent on the original guess made for  $T_{c,0.05}^*$  (shown as  $Tr_{,05}$  in Figure 20). In general, Figure 20 contains two shapes of curves. The S-shaped curves ( $Tr_{,05} = 1.02, 1.0202$ ) exhibit the greatest irregularity. Reference to a typical diagram<sup>20</sup> of compressibility factor as a function of reduced pressure and temperature indicates that there are two values of reduced pressure which give the same compressibility factor at the same reduced temperature. Because reduced pressure is a function of reduced density and temperature, there must also be two values of reduced density for a given compressibility factor. If the computer used the high and low values of reduced density in an irregular manner, as the composition range was crossed, erratic results such as the S-shaped curves in Figure 20 could occur.

\* $T_{c,0.05}$  represents  $T_c$  at  $x = 0.05$ .

TABLE 11. Generated values of pseudocritical temperature ( $^{\circ}\text{K}$ ) in Approach I

| $T_{r.05}$ | $T_{c.05}$ | $T_{c.10}$ | $T_{c.15}$ | $T_{c.20}$ | $T_{c.25}$ | $T_{c.30}$ |
|------------|------------|------------|------------|------------|------------|------------|
| 1.035      | *          |            |            |            |            |            |
| 1.032      | 518.99     | 508.52*    |            |            |            |            |
| 1.031875   | 519.06     | 508.65*    |            |            |            |            |
| 1.03175    | 519.12     | 508.78     | 499.82     | 491.53     | 484.64     | 485.55*    |
| 1.0315     | 519.24     | 509.06     | 500.40     | 493.10     | 490.92*    |            |
| 1.031      | 519.50     | 509.69     | 502.05**   |            |            |            |
| 1.0305     | 519.75     | 510.42     | 504.46     | 512.17**   |            |            |
| 1.03       | 520.00     | 511.24     | 507.76     | 540.67**   |            |            |
| 1.0298125  | 520.10     | 511.56     | 509.25*    |            |            |            |
| 1.02925    | 520.38     | 512.62     | 514.63*    |            |            |            |
| 1.0285     | 520.78     | 514.19     | 524.11*    |            |            |            |
| 1.025      | 522.54     | 523.56*    |            |            |            |            |
| 1.0202     | 525.00     | 540.11     | 514.42*    |            |            |            |
| 1.02       | 525.10     | 540.86     | 516.83*    |            |            |            |
| 0.99       | 541.01     | 532.57*    |            |            |            |            |

Note:  $T_c$  for pure n-heptane = 540.54  $^{\circ}\text{K}$

\*Indicates that  $G''$  did not converge to zero at that value of  $x$ .

\*\*Indicates that  $G''$  did not converge to a single value, but that it was near zero.

TABLE 12. Generated values of pseudocritical pressure (atm.) in Approach I

| Tr <sub>.05</sub> | Pc <sub>.05</sub> | Pc <sub>.10</sub> | Pc <sub>.15</sub> | Pc <sub>.20</sub> | Pc <sub>.25</sub> | Pc <sub>.30</sub> |
|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| 1.035             | *                 |                   |                   |                   |                   |                   |
| 1.032             | 23.28             | 23.35*            |                   |                   |                   |                   |
| 1.031875          | 23.32             | 23.45*            |                   |                   |                   |                   |
| 1.03175           | 23.35             | 23.56             | 24.45             | 26.03             | 28.95             | 36.58*            |
| 1.0315            | 23.42             | 23.77             | 24.96             | 27.26             | 32.72*            |                   |
| 1.031             | 23.56             | 24.10*            |                   |                   |                   |                   |
| 1.0305            | 23.69             | 24.65             | 27.45             | 36.88**           |                   |                   |
| 1.03              | 23.82             | 25.12             | 29.16             | 49.37**           |                   |                   |
| 1.0298125         | 23.86             | 25.30             | 29.84*            |                   |                   |                   |
| 1.02925           | 24.01             | 25.85             | 32.21*            |                   |                   |                   |
| 1.0285            | 24.19             | 26.62             | 32.24*            |                   |                   |                   |
| 1.025             | 25.02             | 30.62*            |                   |                   |                   |                   |
| 1.0202            | 26.07             | 37.06             | 32.25*            |                   |                   |                   |
| 1.02              | 26.12             | 37.34             | 33.31*            |                   |                   |                   |
| 0.99              | 32.12             | 34.15*            |                   |                   |                   |                   |

Note: Pc for pure n-heptane = 26.946 atm.

\*Indicates that G' did not converge to zero at that value of x.

\*\*Indicates that G' did not converge to a single value, but that it was near zero.





The second type of curve in Figure 20 is parabolic. The reason for this shaped curve is not as obvious as that for the S-shaped curves. Although a thorough mathematical analysis is not possible, it could be speculated that errors in the numerical differentiation eventually became magnified enough to cause unreasonable results. Each of the curves in Figure 20 was terminated before the entire composition range had been traversed because no further convergence could be obtained. All values of  $Tr_{.05}$  which showed any promise of yielding satisfactory results were thoroughly investigated. This was especially true of the transition area between the parabolic and S-shaped curves shown in Figure 20.

The programs which began at the pure ethane end of the composition range instead of at the pure n-heptane end, showed no improvement in behavior. The same instability was still indicated. Likewise, the changing of the increment size of  $x$  was not an improvement. When butane was used as a reference compound instead of propane, the curves were similar in shape to those of Figure 20, but the butane curves were offset slightly from the propane curves.

This approach was eventually abandoned because the condition that  $G'''$  also equals zero at the critical point was not being satisfied by the results.

#### Approach II

The approach used here was to generate pseudocritical temperature and pressure curves using as known conditions, experimental critical temperatures and pressures and the fact that  $G''$  and  $G'''$  equal zero at the critical point. A mathematical convergence method was required for the calculations.

The first convergence method used, the double linear process, was not

completely satisfactory. This method sometimes diverged if the quantities  $(\Delta X_1 \cdot \Delta Y_2)$  and  $(\Delta X_2 \cdot \Delta Y_1)$  [See page 107 for definitions of these quantities.] became nearly equal. These quantities being nearly equal meant that the process was near an unstable region and thus, behaved inconsistently.

The usefulness of this convergence method was limited by its tendency to diverge in certain cases. If only one or some small number of convergences are required, then this procedure may be of some use. However, the percentage of failures is too high to use this method without some discretion. Of course, the more linear the equations, the better the method will work.

The success achieved in this project from using the double linear convergence process appeared highly dependent on the starting values for the variables Tr and Dr at  $x_2$  and  $x_3$ . This pointed up again the possibility of an error becoming magnified in the system.

At its best, the program using linear convergence did not proceed higher than  $x = 0.35$  before lack of convergence caused termination of the program. Program LINEAR is listed in Appendix VI in lieu of specific results which are meaningful.

Another convergence method which was used to solve systems of two equations and two unknowns was Newton's method for systems of equations (also known as the Newton-Raphson method).<sup>42</sup> This procedure extrapolated using the partial derivatives at a single point. In cases where both the linear method and Newton's method worked, Newton's method always required less iterations. However, the linear method often gave convergence when Newton's method did not. For this reason the linear method was considered the better method for use in this research.

For solving systems with more variables than conditions, the method

of steepest descent as defined in this thesis, was not a good convergence method. There appeared to be two reasons for the difficulties with this method. First, the assumption that  $d\phi/dz = \Delta\phi/\Delta x$  was not always a good one to make. Even for the simplest of the linear cases,  $d\phi/dx$  is twice as large as  $\Delta\phi/\Delta x$ . This means that the value calculated for  $\rho$  was not always as good as it could have been. Second, the amount of interplay between the quantities  $(G'')^2$ ,  $(G_3'')^2$ , and  $(G_3''')^2$  in the expression for  $\phi$ , required the method to make many more iterations than would have been necessary if the method did not use a function such as  $\phi$ .

The convergence method which used an approach similar to the Newton-Raphson method<sup>42</sup> to simultaneously vary the variables ( $Tr_2, Tr_3, Tr_4, Dr_2, Dr_3, Dr_4$ ) until  $G''$  and  $G'''$  were zero at  $x_2, x_3$ , and  $x_4$  gave good convergence. The program using this convergence method gave results for almost all sets of input tried. The objective was to obtain what appeared to be a good set of starting values (i.e.  $Tr$  and  $Dr$  at  $x_2, x_3$ , and  $x_4$ ) and then use these values as starting values in program LINEAR.

Table 13 lists a typical set of results from this procedure. The generated values are reasonable until  $x = 0.35$ . At this point large changes take place in  $T_c$  and  $P_c$ . Using double linear convergence, no set of values was found for  $T_{c,0.40}$  and  $P_{c,0.40}$  which made  $G''$  and  $G'''$  equal to zero at  $x = 0.35$ . These large changes in  $T_c$  and  $P_c$  at  $x = 0.35$  could once again have been caused by the magnification of an error. The values of  $(\partial Z_r/\partial Pr)_{Tr}$  are quite regular which indicates that the computer did not use the low and high values of reduced pressure in an arbitrary manner.

Table 13. Generated  $T_{c_m}$  and  $P_{c_m}$  values from program LINEAR using a set of starting values from program DECLINE

| x     | $P_c$      | $T_c$     | $(\partial Z_r / \partial P_r)_{Tr}$ |
|-------|------------|-----------|--------------------------------------|
| 0     | 26.95 atm. | 540.54 °K | ..                                   |
| 0.025 | 26.77      | 533.06    | -10.73                               |
| 0.050 | 26.64      | 525.80    | -5.12                                |
| 0.100 | 26.40      | 511.55    | -2.27                                |
| 0.150 | 25.91      | 496.34    | -1.27                                |
| 0.200 | 24.60      | 477.33    | -0.70                                |
| 0.250 | 21.79      | 451.15    | -0.29                                |
| 0.300 | 16.97      | 414.64    | +0.03                                |
| 0.350 | 41.63      | 338.62    | +0.26                                |

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