RICE UNIVERSITY

PREDICTION OF BINARY CRITICAL LOCI
BY CUBIC EQUATIONS OF STATE

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A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

MASTER OF SCIENCE

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May, 1985

3 1272 00289 0653

ABSTRACT

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The equations of state by Redlich Kwong, Soave, Peng and Robinson, Adachi, and Teja generated the critical loci of four class 1 and four class 2 binary mixtures. Two unlike pair parameters were used to fit the equations to a single experimental critical point in the mixture. The Teja equation was the most accurate for class 1 mixtures with a 0.9% deviation in predicting critical temperatures and a 2.6% deviation in predicting critical pressures. The Peng and Robinson equation was least accurate with errors of 1.9% and 4.5% respectively. For class 2 systems, none of the equations were quantitatively correct in generating the critical curves. The Soave equation was the only one to at least qualitatively predict the critical lines for all the mixtures. All of the equations were incapable of accurately predicting the critical volumes of the mixtures.

ACKNOWLEDGEMENTS

I would like to thank Dr. Thomas W. Leland for serving as my research advisor. He gave me many ideas while I was working on my thesis.

I would also like to thank Dr. Clarence Miller and Dr. Mark Robert for serving on my committee and for providing helpful comments after reading my thesis.

I wish to acknowledge the financial support of the Gas Research Institute (GRI) which made this study possible.

This thesis is dedicated to my parents.

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LIST OF SYMBOLS

a_{12}	Unlike pair parameter for equation of state
b_{12}	Unlike pair parameter for equation of state
C_1	Critical point of component 1
C_2	Critical point of component 2
C_m	Critical point at infinite pressure
f	fugacity
P	Pressure
P_C	Critical pressure
R	Gas constant
T	Temperature
T_C	Critical temperature
T_r	Reduced temperature
V	Volume
V_C	Critical volume
x_1	Mole fraction of component 1
x_2	Mole fraction of component 2

z_c	Critical compressibility factor for Teja equation
ζ_{12}	Fitted binary interaction parameter
λ_{12}	Fitted binary interaction parameter
ω	Pitzer acentric factor

Chapter I

INTRODUCTION

The critical state of multicomponent mixtures is important from both a theoretical and practical point of view. The critical point is a key point in the construction of phase diagrams since at this point liquid and vapor phases have identical properties. Critical properties of mixtures are required in petroleum and gas engineering and for the accurate design of separation equipment and reactors at high pressure. Many interesting physical phenomena occur in the critical region. The isothermal compressibility of a pure fluid, which is usually finite, becomes infinite at the critical point. The heat capacity at constant pressure, C_p , also diverges at the critical point. Retrograde condensation, the phenomenon of condensation progressing on increase of temperature or decrease in pressure, has its boundaries at the critical locus of the mixture. Recently it has been shown (Chang, Sengers) that scaled equations of state diverge when used to predict the critical point of mixtures. These as well as other reasons make it essential to have available methods for estimating the critical points of mixtures. This thesis examines the ability of five cubic equa-

tions of state in predicting the critical locus of binary hydrocarbon and non-hydrocarbon mixtures. Much of the data cited below is drawn from van Konynenburg (1968).

In the last twenty years considerable work has been done in the study and prediction of binary critical loci (Joffe, Spear, Hissong, Peng, Teja). Using the Van Der Waals equation, van Konynenburg has qualitatively predicted nine different types of binary critical loci. He distinguished these different types of critical behavior by the shapes of their critical locus projections on a pressure - temperature diagram.

In general, the critical curve of a binary mixture begins or ends at the critical point of one of the components in the mixture, C_1 or C_2 , or at a critical endpoint. A critical endpoint is the thermodynamic state of a system which is at a critical point of phase separation and, simultaneously, is in equilibrium with a noncritical phase (Robert). There are two types of critical endpoints. An upper critical endpoint (UCEP) occurs when two of the phases in a heterogeneous (usually two liquid phases and a gas phase) system become homogeneous when the temperature is raised. In a lower critical endpoint (LCEP) this occurs when the temperature is decreased.

An azeotropic point, where vapor and liquid composition are identical, is another distinguishing characteristic on

the critical curve. Systems exhibiting negative azeotropy show a maximum temperature point on the critical curve. A minimum temperature point on the critical line is characteristic of systems with positive azeotropy.

The nine different binary critical loci behavior categorized by van Konynenburg are:

Class 1

- I. One gas - liquid critical line connecting the two pure component critical points ($C_1 - C_2$).
- I-A. The same as I, with the addition of a negative azeotrope.
- II. Two critical lines: $C_1 - C_2$ and a liquid - liquid critical line originating from the critical point at infinite pressure (C_m) to an UCEP.
- II-A. The same as II, with the addition of a positive azeotrope.

Class 2

- III-HA. Two critical lines: C_1 to UCEP, C_m to C_2 . A three phase line runs from the UCEP to $P = 0$, $T = 0$ at lower temperatures than the one component vapor-pressure curves, producing 'heteroazeotropic' behavior.

- III. The same as III-HA except that the three phase line lies between the two one-component vapor-pressure curves.
- IV. Three critical lines: C_1 to UCEP, LCEP to C_2 , and C_m to UCEP.
- V. Two critical lines: C_1 to UCEP, LCEP to C_2 .
- V-A. The same as V, with the addition of a negative azeotrope.

In addition, there are class 3 binary systems which have very complex critical behavior. The phase behavior of these mixtures results from strong specific interactions between the two components which lead to a high degree of order in the liquid mixture. Such systems cannot be represented by cubic equations of state such as the van der Waals equation and therefore van Konynenburg did not study them.

Eight mixtures were studied which correspond to six of the nine types of critical loci discovered by Van Konynenburg. These mixtures are:

1. propane - hexane (type I)
2. methane - carbon dioxide (type I)
3. butane - carbon dioxide (type I)
4. decane - carbon dioxide (type II)
5. benzene - water (type III-HAm)

6. water - carbon dioxide (type III)
7. methane - hexane (type V)
8. methane - heptane (type V)

The five cubic equations of state which were used to predict the critical curves of the above mixtures are:

1. Redlich Kwong Equation of State
2. Soave Equation of State
3. Peng and Robinson Equation of State
4. Adachi Equation of State
5. Teja Equation of State

These equations were first checked to see if they qualitatively generated the correct shapes of the critical curve. Then further analysis was performed to determine the quantitative accuracy of the prediction.

Chapter II

THERMODYNAMICS OF THE CRITICAL POINT

The critical state of a mixture may be defined as the point where the differences in properties between two coexisting phases vanish. The thermodynamic condition for the existence of a critical point was first derived by Gibbs more than a hundred years ago. For a pure component, the gas-liquid critical point must obey the following equation:

$$\left(\frac{\partial P}{\partial V} \right)_t = 0 \quad (2.1)$$

$$\left(\frac{\partial^2 P}{\partial V^2} \right)_t = 0 \quad (2.2)$$

For the case of a binary mixture, the defining equations are most easily written in terms of the molar Gibbs free energy as:

$$\left(\frac{\partial^2 G}{\partial X_1^2} \right)_{p,t} = 0 \quad (2.3)$$

$$\left(\frac{\partial^3 G}{\partial X_1^3} \right)_{p,t} = 0 \quad (2.4)$$

When working with pressure explicit equations of state, such as the cubic equations of state studied in this report, it is more convenient to express the above equations in terms of the measured variables P , V , T , and X . Using straightforward thermodynamic relationships (see appendix A), the critical point equations become (Redlich and Kister):

$$\begin{aligned} \left(\frac{\partial^2 G}{\partial X_1^2} \right)_{p,t} &= \frac{RT}{X_1 X_2} + \int_v^\infty \left(\frac{\partial^2 P}{\partial X_1^2} \right)_{v,t} dv \\ &- \left(\frac{\partial P}{\partial X_1} \right)_{v,t} \left(\frac{\partial V}{\partial X_1} \right)_{p,t} = 0 \end{aligned} \quad (2.5)$$

$$\begin{aligned}
\left(\frac{\partial^3 G}{\partial X_1^3}\right)_{p,t} &= \frac{RT(X_1 - X_2)}{X_1^2 X_2^2} + \int_v^\infty \left(\frac{\partial^3 P}{\partial X_1^3}\right)_{v,t} dv \\
&- \left(\frac{\partial P}{\partial X_1}\right)_{v,t} \left(\frac{\partial^2 V}{\partial X_1^2}\right)_{p,t} - \left(\frac{\partial V}{\partial X_1}\right)_{p,t}^2 \left(\frac{\partial^2 P}{\partial V \partial X_1}\right)_t \\
&- 2 \left(\frac{\partial V}{\partial X_1}\right)_{p,t} \left(\frac{\partial^2 P}{\partial X_1^2}\right)_{v,t} = 0
\end{aligned} \tag{2.6}$$

The above equations contain partial derivatives of volume with respect to mole fraction. To calculate these derivatives with pressure explicit equations of state some mathematical identities must be used. Appendix A lists these identities and the final form of the critical loci equations.

Equations 2.1 and 2.2 define a single critical point in the two-dimensional T, V , space appropriate for a one-component system. On the other hand, the binary mixture equations, equations 2.3 and 2.4, define a critical line in the three dimensional space T, P, X , appropriate for a binary mixture. Thus there is a critical temperature T_c for each fixed pressure, or a critical pressure P_c for each fixed temperature (Scott).

Chapter III

EQUATIONS OF STATE

The thermodynamic properties of liquid mixtures can be described by many alternative theoretical approaches. Corresponding states theory is the oldest method and seems to show the greatest promise for the quantitative interpretation of the properties of dense fluids. Van der Waals was first to apply the principles of corresponding states by assuming that mixtures can be represented by a 'single-fluid' equation if the appropriate reduced variables and mixture rules are chosen. In particular he tied all his predictions and theories to his famous equation:

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad (3.1)$$

The parameter a is a measure of the attractive forces between the molecules and thus lowers the overall pressure. The parameter b is a measure of the size (intrinsic volume) of the molecules and increases the total pressure in the equation. If the conditions for the pure-fluid critical

point, equations 2.1 and 2.2, are applied to the van der Waals equation then the parameters a and b can be obtained as a function of the critical temperature and critical pressure:

$$a = 27 \cdot R^2 \cdot T_C^2 / (64 \cdot P_C) \quad (3.2)$$

$$b = R \cdot T_C / (8 \cdot P_C) \quad (3.3)$$

The attraction term in the van der Waals equation is rather simple in form with no temperature dependence. Because of this, more complex two and three parameter cubic equations of state have been suggested as a model for the phase behavior of fluids and fluid mixtures.

3.1 REDLICH KWONG EQUATION OF STATE

The Redlich-Kwong equation is an improvement over the van de Waals equation and is one of the most widely used equations for engineering calculations. It has the form:

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)} \quad (3.4)$$

$$a = 0.4278 \cdot R^2 \cdot T_C^{2.5} / P_C \quad (3.5)$$

$$b = 0.0867 \cdot R \cdot T_C / P_C \quad (3.6)$$

Unlike the van der Waals equation, equation 3.4 contains the temperature dependent term $T^{-1/2}$ in the attraction term. According to the authors the form of this equation was "by no means rigorous and its justification rests mainly on the degree of approximation obtained by comparatively simple means". At the time it was published, the Redlich-Kwong equation was the best two parameter equation available.

3.2 SOAVE EQUATION OF STATE

Although the Redlich-Kwong equation predicts P-V-T with relatively good accuracy, its application to pure and multi-component vapor-liquid equilibrium does not produce satisfactory results (Wilkinson). The Soave equation of state is an attempt to improve the equation by assuming a more general temperature dependence for the a parameter:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \quad (3.7)$$

$$a(T) = 0.42747 \cdot \alpha(T) \cdot R^2 \cdot T_C^2 / P_C \quad (3.8)$$

$$b = 0.08664 \cdot R \cdot T_C / P_C \quad (3.9)$$

$$\alpha(T) = \{1 + m(1 - T_r^{0.5})\}^2 \quad (3.10)$$

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \quad (3.11)$$

As can be seen above, the Soave equation includes the fugacity of the pure component as one of the correlation parameters. Soave found that his equation worked well for mixtures of hydrocarbons. Greater deviations were obtained, however, for mixtures containing hydrogen, carbon dioxide, hydrogen sulfide, and polar compounds.

3.3 PENG AND ROBINSON EQUATION OF STATE

The last of the two parameter cubic equation of state tested in this work is that proposed by Peng and Robinson. It has the same repulsion form as the Soave equation but a more complex attraction term:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \quad (3.12)$$

$$a(T) = 0.45724 \cdot \alpha(T) \cdot R^2 \cdot T_C^2 / P_C \quad (3.13)$$

$$b = 0.07780 \cdot R \cdot T_C / P_C \quad (3.14)$$

$$\alpha(T) = \{1 + \kappa(1 - T_r^{0.5})\}^2 \quad (3.15)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (3.16)$$

The Peng and Robinson equation also contains the pure component fugacity as a correlation parameter. However, the

authors found that equation 3.12 predicts thermodynamic properties of substances more accurately than the Soave equation.

3.4 ADACHI EQUATION OF STATE

When an equation of state is applied to represent saturation properties for pure components, it is desirable to satisfy the following three equations at equilibrium:

$$v^v_{\text{calc}} = v^v_{\text{exp}} \quad (3.17)$$

$$v^l_{\text{calc}} = v^l_{\text{exp}} \quad (3.18)$$

$$f^v_{\text{calc}} = f^l_{\text{calc}} \quad (3.19)$$

With this in mind, Adachi proposed an equation of state that contained a third parameter c , in addition to the parameters a and b . The equation of state by Adachi has the following form:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+c)} \quad (3.20)$$

$$a(T) = A_0 \cdot Z_C \{1 + \alpha(1 - Tr^{0.5})\}^2 R^2 \cdot T_C^2 / P_C \quad (3.21)$$

$$b = B \cdot Z_C \cdot R \cdot T_C / P_C \quad (3.22)$$

$$c = C \cdot Z_C \cdot R \cdot T_C / P_C \quad (3.23)$$

$$\alpha = 0.479817 + 1.55553\omega - 0.287787\omega^2 \quad (3.24)$$

$$A_O = B \cdot (1+C)^3 / (1-B)^3 \quad (3.25)$$

$$B = 0.260796 - 0.0682692\omega - 0.367338\omega^2 \quad (3.26)$$

$$C = \{(4/B-3)^{0.5}-3\}/2 \quad (3.27)$$

$$Z_C = \{1/(1-B)-A_O/(1+C)\} \quad (3.28)$$

In his paper, Adachi compared four different forms for the repulsion term and four different forms for the attraction term before deciding on equation 3.20 as the best equation. Equation 3.20 is rather simple compared to the supporting equations for calculating the constants a , b , and c which are relatively complex functions of the pure component critical temperature and pressure and the fugacity coefficient.

3.5 TEJA EQUATION OF STATE

The last equation of state studied in this thesis is the Teja equation of state. Like the Adachi equation, it contains three parameters a , b , and c . However, the attraction term is more complex than the corresponding term in the Adachi equation. The Teja equation of state is:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+c(V-b)} \quad (3.29)$$

$$a(T) = \Omega_a \cdot \alpha(T) \cdot R^2 \cdot T_C^2 / P_C \quad (3.30)$$

$$b = \Omega_b \cdot R \cdot T_C / P_C \quad (3.31)$$

$$c = \Omega_C \cdot R \cdot T_C / P_C \quad (3.32)$$

$$\Omega_a = 3Z_C^2 + 3(1-2Z_C)\Omega_b + \Omega_b^2 + 1-3Z_C \quad (3.33)$$

Ω_b equals the smallest positive root of:

$$\Omega_b^3 + (2-3Z_C)\Omega_b^2 + 3Z_C^2\Omega_b - Z_C^3 = 0 \quad (3.34)$$

$$\Omega_C = 1 - 3Z_C \quad (3.35)$$

$$Z_C = 0.329032 - 0.076799\omega + 0.0211947\omega^2 \quad (3.36)$$

$$\alpha(T) = \{1 + F(1 - Tr^{0.5})\}^2 \quad (3.37)$$

$$F = 0.452413 + 1.30982\omega - 0.295937\omega^2 \quad (3.38)$$

This equation, unlike the other four state equations which predict a fixed value for the critical compressibility, contains a variable critical compressibility factor Z_C . Teja fitted Z_C for a number of substances and then correlated the values against the acentric factor to produce equation 3.36.

3.6 MIXTURE RULES FOR EQUATIONS OF STATE

In applying equations of state to the prediction of thermodynamic properties of mixtures, it is necessary to relate the mixture parameters a_m , b_m , and c_m , to the properties of the individual components. In this study, the mixture constants a_m , b_m , and c_m for the equations of state were calculated with the following mixture rules:

$$a_m = a_{11}X_1^2 + 2a_{12}X_1X_2 + a_{22}X_2^2 \quad (3.39)$$

$$b_m = b_{11}X_1^2 + 2b_{12}X_1X_2 + b_{22}X_2^2 \quad (3.40)$$

$$c_m = c_{11}X_1 + c_{22}X_2 \quad (3.41)$$

The parameters a_{11} and a_{22} are measures of the attractive forces between pairs of molecules of the pure components 1 and 2, respectively. The interaction parameter, a_{12} is a measure of the force that exist between unlike pairs of molecules. b_{11} , b_{22} , and b_{12} are size parameters (proportional to volume) for the pure components and for the mixed pairs. For their evaluation, the interaction parameters, a_{12} and b_{12} , were calculated from pure component data according to the following equations:

$$a_{12} = \zeta_{12} \cdot (a_{11}a_{22})^{0.5} \quad (3.42)$$

$$b_{12} = \lambda_{12} \cdot (b_{11} + b_{22})/2 \quad (3.43)$$

Where ζ_{12} and λ_{12} are adjustable parameters which are fit to experimental data. Equations 3.39 and 3.40 implies random mixing of the two components when ζ_{12} and λ_{12} are set equal to one (van Konynenburg). This approximation has been shown to be approximately true in the case of non-polar, non-

reacting components. These approximations will be poorest when there are large differences between critical temperatures and between the molecular sizes of the pure components and when there is significant molecular orientation in the mixture or in one of the pure components. Thus ζ_{12} and λ_{12} can be viewed as a measure of the 'randomness' of the system.

3.7 CALCULATION OF THE CRITICAL POINT

Equations 2.5 and 2.6, together with an equation of state make up a system of three non-linear equations in three unknowns: T_C , P_C , and V_C . Initially, the interaction parameters ζ_{12} and λ_{12} were set equal to one. Then, for a given composition, the free energy equations were solved for the critical temperature and critical volume of the system. A program package solved the equations using a modification of the Powell hybrid method. The critical pressure was then determined from the equation of state using the critical volume and critical temperature obtained from the free energy equations. To calculate the optimum values for λ_{12} and ζ_{12} , the following functions were calculated at $X_1 = 0.50$:

$$F_1 = |T_{Cexp} - T_{Ccalc}| \quad (3.44)$$

$$F_2 = |P_{Cexp} - P_{Ccalc}| \quad (3.45)$$

If the experimental data at $X_1 = 0.50$ was unavailable, then the closest experimental value to $X_1 = 0.50$ was used. New values of λ_{12} and ζ_{12} were selected, using a damped Newton Rapson method, until the absolute values of the functions F_1 and F_2 were less than 0.0005. Once the optimum values of ζ_{12} and λ_{12} were calculated in this manner, they were used to calculate the entire critical locus from $X_1 = 0.0$ to $X_1 = 1.0$. All of the calculations were carried out on a VAX - 11/750 digital computer.

Chapter IV

RESULTS AND DISCUSSION

The critical loci of eight binary systems have been calculated with the five cubic equations of state mentioned in chapter 3. The predicted critical curves of these systems, which represent six of the nine different types of critical behavior discussed by Van Konynenberg, are compared to experimental data. No single equation of state was clearly the best in predicting the critical values of the systems studied. Table 1 summarizes the average deviation from experimental data of the five equations in predicting the critical constants of the binary systems tested. Table 2 lists the optimum values for the fitted parameters λ_{12} and ζ_{12} for each equation of state.

4.1 CLASS 1 CRITICAL LOCI

The different types of critical loci are grouped into different classes according to their projections on a pressure - temperature diagram. The simplest types of critical behavior that have been observed experimentally belong to class 1. Class 1 type binary mixtures are characterized by a continuous critical line connecting the critical points of

Table 1

Average Percent Error in Predicting Binary
Critical Loci by Cubic Equations of State

system		Redlich Kwong	Soave	Adachi	Peng and Robinson	Teja
propane/ hexane	(1)	0.37	0.08	0.14	0.80	0.05
	(2)	1.09	0.49	0.73	2.52	0.33
	(3)	18.31	19.51	16.78	7.70	16.78
methane/ CO ₂		2.53 6.32	2.18 5.86	2.88 7.99	3.64 8.58	2.16 5.82
butane/ CO ₂		0.77 2.62 17.00	0.54 1.77 20.96	1.18 2.96 28.06	1.28 2.47 7.99	0.51 1.56 13.38
decane/ CO ₂		- -	1.67 9.61	- -	- -	- -
benzene/ water		1.61 18.94	2.69 30.89	- -	- -	- -
water/ CO ₂		1.38 21.66	1.14 16.62	- -	- -	2.02 27.70
methane/ hexane		- -	4.91 19.42	- -	- -	6.14 22.67
methane/ heptane		- - -	2.43 3.39 18.89	- - -	- - -	4.90 8.30 22.23

- (1) percent error critical temperature prediction
 (2) percent error critical pressure prediction
 (3) percent error critical volume prediction (if available)
 - equation failed to generate critical loci

Table 2

Values of fitted parameters λ_{12} and
 ζ_{12} for each Cubic Equation of State

system		Redlich Kwong	Soave	Adachi	Peng and Robinson	Teja
propane/ hexane	(1)	0.9244	1.0097	0.9094	0.8320	0.9897
	(2)	0.9111	0.9734	0.8846	0.8245	0.9771
methane/ CO ₂		0.9558	1.0524	1.0990	0.7476	1.0465
		0.8765	0.9222	0.8871	0.7893	0.9250
butane/ CO ₂		0.9182	0.9990	1.2607	0.6600	0.9578
		0.7567	0.8390	0.9713	0.7475	0.8294
decane/ CO ₂		-	1.3268	-	-	-
		-	0.9352	-	-	-
benzene/ water		0.8015	0.8019	-	-	-
		0.6556	0.5980	-	-	-
water/ CO ₂		1.0546	1.0446	-	-	1.2307
		0.8828	1.0407	-	-	1.2927
methane/ hexane		-	1.1310	-	-	1.0682
		-	1.1441	-	-	0.9661
methane/ heptane		-	1.0237	-	-	0.8861
		-	0.9661	-	-	0.7446

(1) Calculated value for λ_{12}

(2) Calculated value for ζ_{12}

- equation failed to generate critical loci

the pure components. The critical lines are loci of critical points which are most easily viewed as gas-liquid ones, although the distinction is one of convenience only. Mixtures of two components with similar gas-liquid critical temperatures (usually $T_{c1}/T_{c2} \leq 2$) display this type of behavior (van Konynenburg). The four class 1 binary mixtures studied in this investigation are:

- (1) propane - hexane (Kay)
- (2) methane - carbon dioxide (Donnelly)
- (3) butane - carbon dioxide (Olds)
- (4) decane - carbon dioxide (Reamer)

4.1.1 Propane - Hexane System

Figures 1 - 20 compare the calculated critical curves of the propane - hexane system with experimental data. This system is a type I mixture because there is a single critical line connecting the pure critical points. The agreement between calculated and experimental values is very good for the critical temperature and pressure. This is to be expected because propane and hexane have relatively similar

critical temperatures, 666.1°R and 914.2°R respectively, and are similar in molecular size. The critical temperature curve decreases monotonically while the critical pressure curve has a local maximum. This experimentally verified behavior is a characteristic of hydrocarbon systems as well as other systems. The Teja equation of state was the best overall with a 0.05% deviation in predicting the critical temperatures and a 0.33% deviation for the critical pressures. These values are well within the experimental error of the data points as reported by Kay. The Peng and Robinson equation was the least accurate of the five. It predicted critical temperatures with a 0.80% accuracy and critical pressures with an accuracy of 2.52%. However even these values may be within the experimental accuracy of the data used.

Table 3 compares the predicted critical loci of the propane - hexane system when the optimum values of ζ_{12} and λ_{12} are used and when they are set equal to one. The need for using the fitted parameters is evident because the accuracy of the prediction improves dramatically when the optimum values are used. Figures 3,7,11,15, and 19 also show this comparison graphically.

Unlike the critical pressures and temperatures, the critical volume curve of the propane - hexane system was predicted with much less accuracy. The Peng and Robinson

equation was the best with an average deviation of 7.7% and the Soave equation was poorest with a 19.5% deviation from experimental data. These values are definitely greater than the experimental error and represent a problem with predicting critical volumes with cubic equations of state. The reasons for this will be discussed later in this chapter.

FIGURE 1

CRITICAL TEMPERATURE OF PROPANE - HEXANE SYSTEM

FIGURE 2

CRITICAL PRESSURE OF PROPANE - HEXANE SYSTEM

FIGURE 3

FIGURE 4

FIGURE 5

CRITICAL TEMPERATURE OF PROPANE - HEXANE SYSTEM

FIGURE 6

CRITICAL PRESSURE OF PROPANE - HEXANE SYSTEM

FIGURE 9

CRITICAL TEMPERATURE OF PROPANE - HEXANE SYSTEM

FIGURE 10

CRITICAL PRESSURE OF PROPANE - HEXANE SYSTEM

FIGURE 11

FIGURE 12

FIGURE 13

FIGURE 14

FIGURE 15

FIGURE 16

FIGURE 17

CRITICAL TEMPERATURE OF PROPANE - HEXANE SYSTEM

FIGURE 18

CRITICAL PRESSURE OF PROPANE - HEXANE SYSTEM

FIGURE 19

FIGURE 20

Table 3

Comparison of Calculating the Critical Loci of the
Propane - Hexane System with and without Fitted Parameters

percent error		Redlich Kwong	Soave	Adachi	Peng and Robinson	Teja
critical pressure	(1)	1.09	0.49	2.52	2.52	0.33
	(2)	3.59	0.72	2.63	10.17	0.43
critical temperature		0.37	0.08	0.14	0.80	0.05
		0.20	0.51	0.22	1.25	0.20
critical volume		18.31	19.51	16.78	7.7	11.61
		21.75	19.63	20.88	14.51	12.18

percent error critical loci prediction:

(1) with optimum values of ζ_{12} and λ_{12} .

(2) with ζ_{12} and λ_{12} set equal to one.

4.1.2 Methane - Carbon Dioxide System

Figures 21 - 35 compare the predicted versus experimental critical curves for the methane - carbon dioxide system. This is an important system because carbon dioxide occurs in varying quantities in most natural gases and gas condensate well effluents. The critical temperatures and pressures were predicted with good accuracy considering that mixtures containing carbon dioxide are difficult to model. This may be due to carbon dioxide's relatively high fugacity coefficient of 0.255 and relatively low critical temperature of 547.5°R. Again the Teja equation was the best in predicting the critical temperatures and pressures with 2.16% and 5.82% deviation respectively. The Peng and Robinson equation was the least accurate with a 3.64% deviation for the critical temperatures and an 8.58% deviation for the pressures. The critical volume data for this system were not available so no volume comparison could be made.

FIGURE 21

FIGURE 22

FIGURE 23

FIGURE 24

FIGURE 25

FIGURE 26

FIGURE 27

FIGURE 28

FIGURE 29

FIGURE 30

FIGURE 31

FIGURE 32

FIGURE 33

FIGURE 34

FIGURE 35

4.1.3 The Butane - Carbon dioxide System

Figures 36 - 56 compare the predicted versus experimental critical curves for the butane - carbon dioxide system. The predicted critical pressures and temperatures are considerably better for this system compared to the methane - hexane system. However, all of the equations predicted a critical pressure curve with a local minimum that is unsubstantiated by experimental data. This error lies in the values of ζ_{12} and λ_{12} chosen. Figure 56 compares the predicted critical pressure curve obtained when the fitted parameters are set equal to one, with that obtained when the optimum values are used. While the former curve does not contain the erroneous local minimum, the critical pressure prediction suffers considerably. Overall greater accuracy is obtained with the latter curve.

As with the previous systems, the Teja equation was the most accurate with a 0.51% deviation in predicting the critical temperatures and a 1.56% deviation in predicting the critical pressures. The Peng and Robinson equation was the poorest in predicting the critical temperatures with a 1.28% deviation. The Adachi equation was the least accurate in predicting the critical pressures with a 2.96% overall deviation.

All the equations generated critical volume curves which were greater than experimental data. The Peng and

Robinson equation was best with a 7.99% deviation while the Adachi equation of state had a 28.06% error.

FIGURE 36

CRITICAL TEMPERATURE OF BUTANE - CO₂ SYSTEM

FIGURE 37

CRITICAL PRESSURE OF BUTANE - CO₂ SYSTEM

FIGURE 38

CRITICAL LOCI OF BUTANE - CO₂ SYSTEM

FIGURE 39

CRITICAL VOLUME OF BUTANE - CO₂ SYSTEM

FIGURE 42

CRITICAL LOCI OF BUTANE - CO₂ SYSTEM

FIGURE 43

CRITICAL VOLUME OF BUTANE - CO₂ SYSTEM

FIGURE 44

CRITICAL TEMPERATURE OF BUTANE - CO₂ SYSTEM

FIGURE 45

CRITICAL PRESSURE OF BUTANE - CO₂ SYSTEM

FIGURE 46

CRITICAL LOCI OF BUTANE - CO₂ SYSTEM

FIGURE 47

CRITICAL VOLUME OF BUTANE - CO₂ SYSTEM

FIGURE 48

CRITICAL TEMPERATURE OF BUTANE - CO₂ SYSTEM

FIGURE 49

CRITICAL PRESSURE OF BUTANE - CO₂ SYSTEM

FIGURE 52

CRITICAL TEMPERATURE OF BUTANE - CO₂ SYSTEM

FIGURE 53

CRITICAL PRESSURE OF BUTANE - CO₂ SYSTEM

FIGURE 54
CRITICAL LOCI OF BUTANE - CO₂ SYSTEM

FIGURE 55
CRITICAL VOLUME OF BUTANE - CO₂ SYSTEM

FIGURE 56
CRITICAL PRESSURE OF BUTANE - CO₂ SYSTEM

4.1.4 The Decane - Carbon dioxide System

Figure 57 compares the predicted versus experimental critical curves for the decane - carbon dioxide system. Unlike the previous type I systems, this mixture displays type II behavior because its pressure - temperature diagram shows two distinct critical lines. The gas-liquid critical curve is parabolic in shape and connects the two pure component critical points. The second critical line is a liquid-liquid type and originates at a three - phase LCEP and continues at a steep slope to infinite pressures.

Unlike the type I binary mixtures, none of the equations tested were able to predict the two critical lines characteristic of the type II system, decane and carbon dioxide. Only the Soave equation was able to predict the gas - liquid critical locus with any reasonable accuracy. The critical values were predicted with an average error of 1.67% for the critical temperatures and 9.61% for the critical pressures. The Soave equation also failed, however to generate the second liquid - liquid critical curve.

4.2 CLASS 2 BINARY CRITICAL LOCI

If the gas-liquid critical temperature of one of the components is of the order of two or more times that of the other component, there is often no continuous critical line joining the two critical points of the pure components. The four class 2 binary mixtures studied are:

- (1) benzene - water (Rebert, Schnieder)
- (2) carbon dioxide - water (Takenouchi)
- (3) methane - hexane (Kohn)
- (4) methane - heptane (Chang, Kohn, Reamer)

4.2.1 The Benzene - Water System

Figures 58 and 59 compare the predicted versus experimental critical curves for the benzene - water system. This mixture is type III- HA_m and exhibits two critical curves on its pressure-temperature graph. The lower branch of the curve, originating at the critical point of benzene, has a negative slope, which is characteristic of type III- HA_m systems, and terminates at an UCEP. The coordinates of this point are $974.6^{\circ}R$ and 1364 psia. The upper branch of the

locus, beginning at the critical point of water, passes through a minimum temperature point, which is represented by the subscript "m" in type III-HA_m, before diverging to infinite pressures. The coordinates of the minimum point are 1154.1°R and 2300 psia.

Of the five equations tested, only the Redlich-Kwong and Soave equation generated both critical curves with the correct qualitative shape. Neither equation, however, was quantitatively correct. The Redlich-Kwong equation was 'best' with a 1.61% average deviation in the critical temperatures and an 18.94% error in the pressures. It predicted an UCEP at 966.4°R and 1522 psia and a minimum point for the upper critical curve at 1054.4°R and 3727 psia. The Soave equation had errors of 2.69% for the critical temperatures and 30.89% for the critical pressures. The UCEP was placed at 967.8°R and 1440.1 psia while the minimum point had coordinates of 1112.4°R and 4157.8 psia.

FIGURE 58
CRITICAL LOCI OF BENZENE - WATER SYSTEM

FIGURE 59
CRITICAL LOCI OF BENZENE - WATER SYSTEM

4.2.2 The Carbon dioxide - Water System

Figures 60 - 62 compare the predicted versus experimental critical curves for the carbon dioxide - water system. This is a type III_m system. Its two critical curves are similar to those of the benzene - water system except that the lower critical curve, which originates at the critical point of carbon dioxide and terminates at an UCEP, has a positive slope. The coordinates of the UCEP are not available but it is believed to be near the carbon dioxide critical point (Takenouchi). The upper critical line begins at the critical point of water and passes through a minimum temperature point at 968.7°R and 30775 psia, before diverging to infinite pressures.

As with the benzene - water system, all of the critical loci predictions were qualitative at best. The Soave equation was most accurate with a 1.41% deviation in predicting the critical temperatures and a 16.62% deviation in predicting the critical pressures. This equation generated an UCEP at 586.7°R and 1415.8 psia and a minimum temperature point at 967.4°R and 19827 psia. The Peng and Robinson equation and the Adachi equation failed to predict even qualitatively acceptable critical curves for this system.

FIGURE 60

FIGURE 62
CRITICAL LOCI OF WATER - CO₂ SYSTEM

4.2.3 The Methane - Hexane System

Figures 63 and 64 compare the predicted versus experimental critical curves for the Methane - Hexane system. This system is classified as a type V mixture. The upper critical curve begins at the critical point of hexane and passes through a maximum pressure point instead of diverging to infinite pressures as with the previous class 2 systems. It then terminates at a LCEP where three phases are present. The coordinates of the maximum point are 536.7°R and 2845 psia while the LCEP lies at 327°R and 495 psia. The lower critical curve is a gas-liquid type and begins at the critical point of methane and ends at an UCEP. The latter point is at 352°R and 760 psia.

None of the five equations tested were able to correctly predict the two critical curves of this system. However, two of the equations, Soave and Teja predicted a single critical curve which originated at the critical point of hexane. But instead of terminating at a LCEP, the curve ended at the critical point of methane. The equations were not accurate enough to predict the two critical endpoints. This may be due to the proximity of the LCEP and UCEP with the critical point of methane (only 25 degrees Rankine separate the three points).

4.2.4 The Methane - Heptane System

Figures 65 - 68 compare the predicted versus experimental critical curves for the methane - heptane system. Like the methane - hexane system, this mixture is also type V. The lower critical curve begins at the methane critical point and ends at an UCEP with coordinates 345°R and 694 psia. The upper critical curve originates from the heptane critical point and passes through a maximum pressure point. Instead of ending at a LCEP, as with methane and hexane, a solid heptane phase appears and terminates the critical curve. Presumably the UCEP would have appeared if not for the relatively high freezing point of heptane (Scott).

For this system, only the Soave and Teja equation, generated both critical curves. The Soave equation had a 2.43% average deviation in predicting the critical temperatures and a 3.39% error for the critical pressures. It placed the UCEP at 348°R and 715 psia. The corresponding errors for the Teja equation were 4.9% and 8.3%. It predicted the UCEP at 350.9°R and 733 psia.

For this equation critical volume data were also available so a comparison could be made. Both the Soave and the Teja equation did poorly however, with average deviations of 18.89% and 22.23% respectively.

FIGURE 65
CRITICAL LOCI OF METHANE - HEPTANE SYSTEM

FIGURE 66
CRITICAL LOCI OF METHANE - HEPTANE SYSTEM

FIGURE 67. CRITICAL LOCI OF METHANE - HEPTANE
SYSTEM NEAR METHANE CRITICAL POINT

FIGURE 68. CRITICAL LOCI OF METHANE - HEPTANE
SYSTEM NEAR METHANE CRITICAL POINT

4.3 CRITICAL VOLUME PREDICTION

As mentioned earlier, none of the equations was able to satisfactorily predict the critical volumes of the mixtures tested. Most of the deviations were greater than 10%.

Figure 69 shows that the critical volumes of the propane - hexane system could be predicted much more accurately by using the following equation:

$$V_{Cm} = V_{C1} \cdot X_1 + V_{C2} \cdot X_2 \quad (44)$$

The above equation simply uses a mole fraction average of the pure component critical volumes to calculate the critical volume for the mixture. This conclusion was also obtained with two other systems for which critical volume data was available (1) methane - carbon dioxide and (2) methane - heptane. Table 4 summarizes the results.

The reason for the poor critical volume prediction by the equations of state is due to the relatively high pure component critical compressibility generated by these equations. The Redlich Kwong equation predicts the highest value of 0.333. The corresponding value for the Peng and Robinson equation is 0.307. The equation by Teja is unique in that it contains a variable compressibility. Its average value of 0.31 however, was still higher than the experimental values which lie between 0.25 and 0.30.

FIGURE 69
COMPARISON OF CRITICAL VOLUME
PREDICTION IN PROPANE - HEXANE SYSTEM

Table 4

Comparison of Methods for Predicting
Critical Volumes

system		Redlich Kwong	Soave	Adachi	Peng and Robinson	Teja
propane/ hexane	(1)	18.31	19.51	16.78	7.70	11.61
	(2)	3.56	3.56	3.56	3.56	3.56
butane/ CO ₂		17.00	20.95	28.06	7.99	13.38
		6.50	6.50	6.50	6.50	6.50
methane/ heptane		-	18.89	-	-	22.23
		-	21.75	-	-	21.75

percent error critical volume prediction by:

(1) equation of state

(2) equation 44

Chapter V

CONCLUSION

The critical loci of eight binary hydrocarbon and non-hydrocarbon mixtures have been predicted with five cubic equations of state. These mixtures correspond to four class 1 and four class 2 critical loci as categorized by van Konynenburg. The predictions have been compared with experimental data to determine the most accurate equation.

No single equation was the most accurate for all types of mixtures tested. For calculating the critical pressures and temperatures of hydrocarbon mixtures the Teja equation of state was the best. The average deviation from experimental results was well within the experimental error for this equation. For more complex binary mixtures, such as benzene and water, the predictions were qualitative at best. The Soave equation was the only equation able to generate the critical curves of all the mixtures tested. However, its predictions for the class 2 systems were also only qualitatively accurate.

It appears that the common cubic equations of state are incapable of modeling the critical loci of class 2 mixtures, due to the complex molecular interactions that occur in

these systems. Because these types of mixtures are encountered in supercritical extraction (Paulaitis, Schneider), future work should concentrate on improving the critical loci prediction of these systems.

Unlike the critical temperatures and pressures, the critical volume predictions were inaccurate even in the case of simple class 1 binary systems. Most of the predictions had errors of at least ten percent.

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Appendix A

DERIVATION OF FREE ENERGY EQUATIONS IN TERMS OF P, V, AND X

Note: The equations derived below are analogous to the Helmholtz free energy equations as stated in Rowlinson.

At the critical point of a binary mixture:

$$\left(\frac{\partial^2 G}{\partial X_1^2} \right)_{p,t} = 0 \quad (\text{A.1})$$

$$\left(\frac{\partial^3 G}{\partial X_1^3} \right)_{p,t} = 0 \quad (\text{A.2})$$

On a molar basis at constant temperature and pressure, the chemical potential can be written as:

$$\mu_1 = \left(\frac{\partial G}{\partial X_1} \right)_{p,t} \quad (\text{A.3})$$

Written in terms of the chemical potential, equations A.1 and A.2 become:

$$\left(\frac{\partial \mu_1}{\partial X_1} \right)_{p,t} = 0 \quad (\text{A.4})$$

$$\left(\frac{\partial^2 \mu_1}{\partial X_1^2} \right)_{p,t} = 0 \quad (\text{A.5})$$

Using the definition of the fugacity at constant t and p :

$$\partial \mu_1 = RT \partial \ln(f_1) \quad (\text{A.6})$$

The critical point equations become (for constant t and p :

$$\frac{\partial}{\partial X_1} \ln(f_1) = 0 \quad (\text{A.7})$$

$$\frac{\partial^2}{\partial X_1^2} \ln(f_1) = 0 \quad (\text{A.8})$$

Substituting the definition of the fugacity coefficient:

$$\phi_1 X_1 P = f_1 \quad (\text{A.9})$$

gives:

$$\frac{\partial}{\partial X_1} \ln(\phi_1 X_1 P) = 0 \quad (\text{A.10})$$

$$\frac{\partial^2}{\partial X_1^2} \ln(\phi_1 X_1 P) = 0 \quad (\text{A.11})$$

The above equations are at constant t and p . Because $\partial X_1 = -\partial X_2$ equations A.10 and A.11 can also be written in terms of component 2 as:

$$\frac{\partial}{\partial X_1} \ln (\Phi_2 X_2 P) = 0 \quad (\text{A.12})$$

$$\frac{\partial^2}{\partial X_1^2} \ln (\Phi_2 X_2 P) = 0 \quad (\text{A.13})$$

Subtracting equation A.12 from A.10 and A.13 from A.11 gives:

$$\frac{\partial}{\partial X_1} \ln \left(\frac{\Phi_1 X_1}{\Phi_2 X_2} \right) = 0 \quad (\text{A.14})$$

$$\frac{\partial^2}{\partial X_1^2} \ln \left(\frac{\Phi_1 X_1}{\Phi_2 X_2} \right) = 0 \quad (\text{A.15})$$

Performing the indicated differentiation (at constant t and p) gives:

$$\frac{\partial}{\partial X_1} \ln \left(\frac{\Phi_1}{\Phi_2} \right) = \frac{-1}{X_1 X_2} \quad (\text{A.16})$$

$$\frac{\partial^2}{\partial X_1^2} \ln \left(\frac{\Phi_1}{\Phi_2} \right) = \frac{X_2 - X_1}{X_1^2 X_2^2} \quad (\text{A.17})$$

Thermodynamics gives the following equations:

$$\ln(\Phi_1) = \int_0^P [V_1/RT - 1/P] dp \quad (\text{A.18})$$

$$\left(\frac{\partial V}{\partial X_1}\right)_{p,t} = \left(\frac{\partial P}{\partial X_1}\right)_{v,t} \left(\frac{\partial V}{\partial P}\right)_{x,t} \quad (\text{A.19})$$

Using equations A.17 and A.18, the ratio of the fugacity coefficients can be calculated as:

$$\ln\left(\frac{\phi_1}{\phi_2}\right) = - \int_{\infty}^V \left(\frac{\partial P}{\partial X_1}\right)_{v,t} dV/RT \quad (\text{A.20})$$

Substituting A.20 into equations A.16 and A.17, performing the indicated differentiation (the integral can be differentiated with Leibnitz' formula), and using the following relations:

$$\left(\frac{\partial V}{\partial X_1}\right)_{p,t} = - \left(\frac{\partial V}{\partial P}\right)_{x,t} \left(\frac{\partial P}{\partial X_1}\right)_{v,t} \quad (\text{A.21})$$

$$\begin{aligned} \left(\frac{\partial^2 V}{\partial X_1^2}\right)_{p,t} &= - \left(\frac{\partial^2 V}{\partial P \partial X_1}\right)_t \left(\frac{\partial P}{\partial X_1}\right)_{v,t} \\ &\quad - \left(\frac{\partial V}{\partial P}\right)_{x,t} \left(\frac{\partial^2 P}{\partial X_1^2}\right)_{v,t} \\ &\quad - \left(\frac{\partial V}{\partial P}\right)_{x,t} \left(\frac{\partial V}{\partial X_1}\right)_{p,t} \left(\frac{\partial^2 P}{\partial V \partial X_1}\right)_t \end{aligned} \quad (\text{A.22})$$

Gives the final form of the equations for calculating the critical loci of binary mixtures using an equation of state:

$$\int_{\infty}^v \left(\frac{\partial^2 P}{\partial X_1^2} \right)_{v,t} dv - \left(\frac{\partial P}{\partial X_1} \right)_{v,t}^2 \left(\frac{\partial V}{\partial P} \right)_{x,t}$$

$$= \frac{RT}{X_1 X_2} \quad (A.23)$$

$$\int_{\infty}^v \left(\frac{\partial^3 P}{\partial X_1^3} \right)_{v,t} dv - 2 \left(\frac{\partial^2 P}{\partial X_1^2} \right)_{v,t} \left(\frac{\partial P}{\partial X_1} \right)_{v,t} \left(\frac{\partial V}{\partial P} \right)_{x,t}$$

$$+ \left(\frac{\partial^2 P}{\partial X_1 \partial V} \right)_T \left(\frac{\partial V}{\partial P} \right)_{x,t}^2 \left(\frac{\partial P}{\partial X_1} \right)_{v,t}^2$$

$$- \left(\frac{\partial V}{\partial P} \right)_{x,t} \left[\frac{\partial}{\partial X_1} \left(\frac{\partial P}{\partial X_1} \right)_{v,t} \right]_{p,t} \left(\frac{\partial P}{\partial X_1} \right)_{v,t}$$

$$+ \left(\frac{\partial V}{\partial P} \right)_{x,t}^2 \left(\frac{\partial P}{\partial X_1} \right)_{v,t}^2 \left[\frac{\partial}{\partial X_1} \left(\frac{\partial P}{\partial V} \right)_{x,t} \right]_{p,t}$$

$$= \frac{RT(X_1 - X_2)}{X_1^2 X_2^2} \quad (A.24)$$