A Rigorous Method for Predicting the Critical Properties of Multicomponent Systems from an Equation of State

This paper shows how the rigorous critical state criterion enunciated by Willard Gibbs can be used with a recently formulated two-parameter equation of state to obtain an analytical solution to the problem of predicting the critical properties of defined multicomponent mixtures. Comparisons are made between predicted and experimental values for several systems containing paraffin hydrocarbons and related materials.

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SCOPE

The critical state of multicomponent mixtures is important from both a theoretical and practical point of view, and an ability to predict this condition is highly desirable. Even though the rigorous thermodynamic criterion for the critical state was enunciated by J. Willard Gibbs (1928) one hundred years ago, no satisfactory analytical method for predicting the critical condition in multicomponent systems based on this criterion has ever been formulated. The object of the work undertaken in this study was to develop a solution to the problem of predicting the critical properties of defined multicomponent mixtures from the rigorous thermodynamic method together with a recently developed two-parameter equation of state.

The significance of the work is that it has the potential of replacing the more cumbersome, often unreliable, and sometimes inapplicable methods based on semiempirical or empirical procedures or on conformal solution theory with a method that is thermodynamically rigorous, generally applicable, and simple to use. Furthermore, the proposed method for handling critical property calculations is internally consistent with calculations of all other thermodynamic properties using the same equation of state.

Although the majority of the comparisons reported in this work are limited to systems containing three or more components, the method works equally well for binary systems. Only one detailed comparison for a binary system is included, because several previous workers have used the thermodynamic criteria for binary cases (Joffe and Zudkevitch, 1967; Spear et al., 1969; Hissong and Kay, 1970).

CONCLUSIONS AND SIGNIFICANCE

Although previous workers (Spencer et al., 1973) have stated recently that it is not practical to extend the methods for predicting the critical state using the minimum Gibbs free energy criterion to multicomponent systems, it has been concluded from the work undertaken in this study that this is not the case. Use of the thermodynamic criterion together with a simple two-parameter equation of state has yielded results which are remarkably reliable and relatively easy to obtain. One of the key factors in the success of the method has been the use of an equation of state (Peng and Robinson, 1976) that predicts the critical density of pure materials better than any earlier models.

Extensive testing of the program on ternary and all available multicomponent mixtures has shown that the method predicts critical temperatures with an absolute error of about 1.31% and an arithmetic average error of +1.14%. It predicts critical pressures with an absolute error of 2.33% and an arithmetic average error of +0.13%. The thirty-two systems studied included those containing from three to twelve components consisting of paraffin hydrocarbons from methane through *n*-decane, nitrogen, carbon dioxide, and/or hydrogen sulfide. The range of critical pressures varied by a factor of 4.43 and the range of critical temperatures by a factor of 2.88.

The principal significance of this work is that it provides a thermodynamically rigorous method for predicting the critical properties of defined mixtures which is more reliable, easier to use, and more generally applicable than any of the existing methods which are based on semiempirical or empirical correlations, or on conformal solution theory. It provides a method for the prediction of the critical state for multicomponent hydrocarbon and related mixtures that is internally consistent with the calculation of all other thermodynamic properties of the sys-

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tem using the same equation of state. This feature has many attractive advantages for the generalized computer calculation of fluid properties required for process design work.

The prediction of the true critical properties of a multicomponent system is an important aspect of the general problem of predicting the overall phase behavior of the system. The critical state is the unique condition about which the liquid and vapor phases are defined, and hence it has theoretical as well as practical significance. In hydrocarbon processing and producing operations, a knowledge of the critical condition is of particular significance because many of these operations take place under conditions which are at or near the bubble point or upper dew point regions and are frequently accompanied by isobaric or isothermal retrograde phenomena. Fluid property predictions and design calculations in this region are often the most difficult to make, and a knowledge of the precise location of the critical point for the system under study is of the utmost assistance.

From a theoretical point of view, the derivatives of many of the thermodynamic and transport properties take on a special significance as the critical state is approached. In an empirical way the critical state has formed an integral part of many useful generalized correlations such as those based on the theorem of corresponding states or the convergence pressure concept in vapor-liquid equilibrium calculations.

In many ways the characteristics of the critical state that make it theoretically and practically significant are also the characteristics that make it one of the more difficult conditions to measure experimentally. The very fact that density differences between phases vanish, that the rate of volume change with respect to pressure approaches infinity, or that infinitesimal temperature gradients can be responsible for a transition from 100% liquid to 100% vapor all make the critical condition one of the more difficult to measure or observe accurately. For obvious economic reasons, it is a condition that cannot be obtained by experiment in any practical way for the many systems for which it is required. Consequently, many attempts have been made to develop methods for predicting the critical properties based on generalized empirical or semiempirical procedures.

Many of the earlier methods were essentially empirical in nature and were aimed at predicting the critical properties of naturally occurring hydrocarbon systems. Among the better known of these was the method of Kurata and Katz (1942) for the critical properties of volatile hydrocarbon mixtures and of Organick (1953) for complex hydrocarbon systems. Somewhat later, Davis et al. (1954) modified the original Kurata-Katz procedure to make it applicable to lighter natural gas systems. All of these procedures made use of graphical correlations with parameters such as pseudo critical temperature and pressure, molal average boiling point, weight average equivalent molecular weight, or weight average critical temperature. The procedure of Davis et al. (1954) represented one of the first attempts to make use of a fitted binary interaction parameter to predict multicomponent fluid properties.

More recently, attempts to predict the critical properties of mixtures have relied primarily on one of three approaches, namely, empirical procedures involving the use of excess properties or fitted correction factors, the use of conformal solution theory based on the concept that all thermodynamic properties of mixtures can be evaluated from pure component properties if the components conform to certain postulates of statistical mechanics, or a rigorous thermodynamic condition based on the second and third partial derivatives of the molar Gibbs free energy with respect to composition.

Spencer et al. (1973) have presented a comprehensive review of the first two of these three approaches. They did not consider the classical thermodynamic approach because generalization to multicomponent systems was not thought to be practical. Although the empirical correlation method and the conformal solution theory method are relatively simple and easy to apply, they are not without significant limitations.

To illustrate some of these, the consequences of using the empirical correlation method of Chueh and Prausnitz (1967), for example, might be analyzed. This method uses an empirical correlation to calculate V_c and T_c and then the Redlich-Kwong equation of state to calculate P_c. If one then uses the Prausnitz and Chueh (1968) method or any other method to carry out vapor-liquid phase behavior calculations, there is no assurance whatsoever that the predicted critical point will be consistent with the predicted phase envelope. This follows because the two predictions are basically independent of each other. On occasion these methods may also lead to completely erroneous results. For example, some systems containing high concentrations of nonhydrocarbons, like hydrogen sulfide, may not have a vapor-liquid critical point. However, generalized or empirical correlations, even if they will handle this type of system at all, would never be able to detect the fact that the upper dew point locus was terminated by the appearance of another liquid rather than by a critical point.

These examples simply serve to emphasize the fact that there are always advantages, both in terms of reliability and economics, in being able to carry out all fluid property calculations based on a single thermodynamic relationship between P, V, and T. For these reasons, it was felt worthwhile to reassess the practicability of the method based on the rigorous thermodynamic approach and a suitable equation of state for determining the critical state of multicomponent systems.

The theory relating to the critical state of mixtures was formulated by Willard Gibbs (1928) exactly one century ago; however, since that time only a few limited attempts have been made to utilize the defining equations in conjunction with equations of state to obtain quantitative results. It is probably because of the apparent complexity of the defining equations that previous attempts were limited to applications to binary systems (Joffe and Zudkevich, 1967; Spear et al., 1969; and Hissong and Kay, 1970) and more recently by Spear et al. (1971) to ternary mixtures. Another key reason is that until recently no simple equation of state that satisfactorily predicts the critical condition for most pure substances of interest to the hydrocarbon processing or producing industry has been formulated.

In the one paper dealing with the application of the rigorous method to ternary mixtures, Spear et al. (1971) specified temperature and pressure and searched for the critical composition of the ternary mixture in an iterative manner. It is evident that their procedure cannot be applied to mixtures having more than three components be-

cause then the number of independent unknown variables would exceed the number of independent equations available. Furthermore, their method was based on the Redlich-Kwong equation of state model which predicts a critical compressibility factor of 0.333 for pure materials. This is considerably higher than the true value for most substances of interest to the petroleum industry, and therefore the method can not be expected to yield quantitatively acceptable results for hydrocarbon mixtures.

In this study, the rigorous critical state criterion enunciated by Gibbs (1928) was used in conjunction with a recently developed equation of state to find the critical properties of multicomponent mixtures.

EQUATION OF STATE

The equation of state (Peng and Robinson, 1976), used for this work has the form

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \tag{1}$$

For pure components, the parameters a and b are expressed in terms of the critical properties and the acentric factor:

$$a(T) = a_c\alpha$$

$$a_c = 0.45724\frac{R^2T_c^2}{P_c}$$

$$\alpha^{1/2} = 1 + \kappa\,(1 - T_r^{1/2})$$
$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

$$b = 0.07780\frac{RT_c}{P_c}$$

Equation (1) generates a universal critical compressibility factor of 0.307 for pure substances, while most of the compounds encountered by the hydrocarbon industry have critical compressibility factors between about 0.25 and 0.30.

For mixtures, the parameters a and b are defined by the mixing rules

$$a = \sum_i \sum_j x_i x_j (1-\delta_{ij}) a_i^{1/2} a_j^{1/2}$$

$$b = \sum_i x_i b_i$$

where δ_{ij} is an empirically determined interaction coefficient characterizing the binary formed by component i and component j.

From Equation (1) the molar Helmholtz free energy can be constructed as

$$A = RT\sum_i x_i \ln\frac{x_i RT}{V-b} - \frac{a}{2.828b}\ln\left(\frac{V+2.414b}{V-0.414b}\right)$$

$$+ \int_{T_o}^{T}\sum_i x_i C_{pi}^{\circ}\,dT - T\int_{T_o}^{T}\sum_i x_i\frac{Cp_i^{\circ}}{T}\,dT - RT \tag{2}$$

It can readily be seen that Equations (1) and (2) satisfy the thermodynamic equation of state

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,x} \tag{3}$$

CRITICAL STATE CRITERION

The rigorous thermodynamic definition of the critical state of an n-component mixture as given by Gibbs (1928) involves two simple mathematical expressions. These are in the form of the following two determinants:

$$U = \begin{vmatrix} \frac{\partial^2 G}{\partial x_1^2} & \frac{\partial^2 G}{\partial x_1\partial x_2} & \cdots & \frac{\partial^2 G}{\partial x_1\partial x_{n-1}} \\ \frac{\partial^2 G}{\partial x^2\partial x_1} & \frac{\partial^2 G}{\partial x_2^2} & \cdots & \frac{\partial^2 G}{\partial x_2\partial x_{n-1}} \\ \vdots & \vdots & & \vdots \\ \frac{\partial^2 G}{\partial x_{n-1}\partial x_1} & \frac{\partial^2 G}{\partial x_{n-1}\partial x_2} & \cdots & \frac{\partial^2 G}{\partial x_{n-1}^2} \end{vmatrix} \tag{4}$$

and

$$M = \begin{vmatrix} \frac{\partial U}{\partial x_1} & \frac{\partial U}{\partial x_2} & \cdots & \frac{\partial U}{\partial x_{n-1}} \\ \frac{\partial^2 G}{\partial x^2\partial x_1} & \frac{\partial^2 G}{\partial x_2^2} & \cdots & \frac{\partial^2 G}{\partial x_2\partial x_{n-1}} \\ \vdots & \vdots & & \vdots \\ \frac{\partial^2 G}{\partial x_{n-1}\partial x_1} & \frac{\partial^2 G}{\partial x_{n-1}\partial x_2} & \cdots & \frac{\partial^2 G}{\partial x_{n-1}^2} \end{vmatrix} \tag{5}$$

where the partial derivatives with respect to x_i are obtained at constant values of P, T, and $x_{k,k\neq i,n}$. Both of these must equal zero at the critical point.

It is understood in the above equations that $G = G(T, P, x_1, x_2, \ldots, x_{n-1})$. To make Equations (4) and (5) suitable for use with a pressure explicit equation of state, it was necessary to express the partial derivatives of the molar Gibbs free energy in terms of partial derivatives of the molar Helmholtz free energy and partial derivatives of pressure through transformation of the independent variables.

From the fundamental thermodynamic relation

$$G = A + PV \tag{6}$$

one can readily obtain

$$\left(\frac{\partial^2 G}{\partial x_i\partial x_j}\right) = \left(\frac{\partial^2 A}{\partial x_i\partial x_j}\right) + \frac{\left(\frac{\partial P}{\partial x_i}\right)\left(\frac{\partial P}{\partial x_j}\right)}{\left(\frac{\partial P}{\partial V}\right)} \tag{7}$$

and

$$\left(\frac{\partial^3 G}{\partial x_i\partial x_j\partial x_k}\right) = \left(\frac{\partial^3 A}{\partial x_i\partial x_j\partial x_k}\right) + \frac{1}{\left(\frac{\partial P}{\partial V}\right)}$$

$$\left[\left(\frac{\partial P}{\partial x_i}\right)\left(\frac{\partial^2 P}{\partial x_j\partial x_k}\right) + \left(\frac{\partial P}{\partial x_j}\right) + \left(\frac{\partial^2 P}{\partial x_k\partial x_i}\right) + \left(\frac{\partial P}{\partial x_k}\right)\left(\frac{\partial^2 P}{\partial x_i\partial x_j}\right)\right] - \frac{1}{\left(\frac{\partial P}{\partial V}\right)^2}$$

$$\left[\left(\frac{\partial P}{\partial x_i}\right)\left(\frac{\partial P}{\partial x_j}\right)\left(\frac{\partial^2 P}{\partial x_k\partial V}\right) + \left(\frac{\partial P}{\partial x_j}\right)\left(\frac{\partial P}{\partial x_k}\right)\left(\frac{\partial^2 P}{\partial x_i\partial V}\right) + \left(\frac{\partial P}{\partial x_k}\right)\left(\frac{\partial P}{\partial x_i}\right)\left(\frac{\partial^2 P}{\partial x_j\partial V}\right)\right]$$

$$+ \frac{1}{\left(\frac{\partial P}{\partial V}\right)^3}\left(\frac{\partial P}{\partial x_i}\right)\left(\frac{\partial P}{\partial x_j}\right)\left(\frac{\partial P}{\partial x_k}\right)\left(\frac{\partial^2 P}{\partial^2 V}\right) \tag{8}$$

Table 1. Multicomponent Systems Studied

Mixture No.	Mixture composition, mole fraction														
	C_1	C_2	C_3	iC_4	nC_4	iC_5	nC_5	nC_6	nC_7	nC_8	nC_9	nC_{10}	N_2	CO_2	H_2S
1		0.429			0.373				0.198						
2		0.726			0.171				0.103						
3		0.514			0.412				0.074						
4		0.801					0.064		0.135						
5		0.612					0.271		0.117						
6		0.615					0.296		0.089						
7	0.415		0.542										0.043		
8	0.360		0.545										0.095		
9	0.4530		0.5005										0.0465		
10	0.4115		0.5030										0.0855		
11		0.3414	0.3421				0.3165								
12			0.3276		0.3398		0.3326								
13					0.6449		0.2359	0.1192							
14	0.070													0.616	0.314
15		0.6168			0.1376		0.0726		0.1730						
16		0.2542	0.2547		0.2554		0.2357								
17			0.4858		0.3316		0.1213	0.0613							
18	0.4345	0.0835	0.4330										0.0490		
19	0.9100	0 0560	0.0012										0.0330		
20	0.9590	0.0260	0.0001										0.0150		
21	0.9500	0.0260	0 0078										0.0160		
22	0.9450	0.0260	0.0081		0.0052								0.0160		
23							0.2465	0.2176	0.1925	0.1779	0.1656				
24	0.6626	0.1093	0.1057				0.0616	0.0608							
25	0.7057	0 0669	0 0413		0.0508		0.1353								
26	0.2019	0.2029	0.2033		0.2038		0.1881								
27		0.3977	0.2926		0.1997		0.0713	0.0369							
28	0.1015	0.3573	0.2629		0.1794		0.0657	0.0332							
29	0 316	0.388	0.223		0.043		0.008						0.022		
30	0.9430	0.0270	0.0074		0.0049		0.0010	0.0027					0.0140		
31						0.1989	0.1963	0.1483	0.1344	0.1213	0.1137	0.1142			
32	0.6870	0.0333	0.0144	0.0030	0.0040	0.0016	0.0010	0 0011	0.0006[a]	0.0008[a]			0.2441	0.0091	

[a] Reported value was 0.0014 mole fraction heptanes-plus.

TABLE 1. (Continued)

Critical states of multicomponent systems

Mixture No.	Critical pressure Exp. kPa	Calc. kPa	Abs. error 1 kPa	Percent error	Critical temperature Expt. K	Calc. K	Abs. error K	Percent error	Reference
1	6 612	6 291	−321	−4.85	438.15	440.24	2.09	0.47	Ekiner & Thodos
2	7 605	7 486	−118	−1.55	385.92	389.81	3.88	1.00	Ekiner & Thodos
3	6 405	6 231	−174	−2.72	400.37	404.46	4.09	1.02	Ekiner & Thodos
4	8 101	8 310	209	2.57	391.48	395.96	4.47	1.14	Ekiner & Thodos
5	7 156	7 055	−101	−1.41	421.48	426.05	4.56	1.08	Ekiner & Thodos
6	7 060	6 953	−107	−1.51	415.92	420.79	4.86	1.17	Ekiner & Thodos
7	8 674	8 630	−44	−0.50	322.03	327.98	5.94	1.84	Yarborough & Smith
8	9 204	9 182	−22	−0.23	322.03	328.61	6.57	2.04	Yarborough & Smith
9	9 232	9 101	−131	−1.41	313.70	321.88	8.18	2.60	Yarborough & Smith
10	9 797	9 541	−256	−2.61	313.70	322.33	8.62	2.75	Yarborough & Smith
11	5 602	5 552	−49	−0.88	397.15	404.43	7.28	1.83	Etter & Kay
12	4 188	4 174	−14	−0 33	428.81	430.72	1.91	0.44	Etter & Kay
13	3 880	3 797	−83	−2.14	450.20	450.77	0.57	0.12	Etter & Kay
14	8 274	8 420	146	1.76	310 92	311.87	0 94	0.30	Robinson & Bailey
15	7 412	7 373	−39	−0.52	423.15	425.52	2.37	0.56	Ekiner
16	5 113	5 063	−50	−0.98	405.87	410.74	4.87	1.20	Etter & Kay
17	4 506	4 429	−77	−1.70	417.92	419.80	1.87	0 44	Etter & Kay
18	8 963	8 993	30	0.33	313 70	316.56	2.86	0.91	Yarborough & Smith
19	5 341	5 540	199	3.72	199.26	201.21	1.95	0.97	Gonzalez & Lee
20	4 932	5 046	114	2.30	193.87	195.65	1.77	0.91	Gonzalez & Lee
21	5 180	5 352	172	3.31	196.53	198 98	2.44	1.24	Gonzalez & Lee
22	5 456	5 720	264	4.83	199 54	202.05	2.51	1.25	Gonzalez & Lee
23	3 093	3 085	−8	−0.25	541.26	540.65	−0.61	−0 11	Hissong
24	13 748	14 597	849	6 17	310.53	321.96	11.42	3.67	Hanson & Brown
25	13 700	14 664	964	7.04	308.42	320 80	12.37	4 01	Hanson & Brown
26	7 220	7 041	−178	−2.47	387.03	393.75	6.71	1.73	Etter & Kay
27	5 624	5 577	−47	−0.82	385.42	388.95	3.52	0.91	Etter & Kay
28	6 536	6 455	−80	−1.23	376.42	381.43	5 01	1.33	Etter & Kay
29	7 846	7 880	34	0.43	313.70	318 62	4.91	1 56	Yarborough & Smith
30	5 578	5 904	325	5.83	201.09	202.44	1.35	0.67	Gonzalez & Lee
31	3 539	3 291	−248	−7.00	543.37	542.36	−1.00	−0.18	Hissong
32	6 708	6 791	83	1.23	188.87	184.26	−4.61	−2.44	Davis et al.
Average differences:		Absolute	173	2.33			4.25	1.31	
		Arithmetic	39	+0.13			3.86	1.14	

where it is understood that the independent variables on the right-hand side of Equations (7) and (8) are T, V, x_1, x_2, ..., and x_{n-1}. When n equals 2, Equations (7) and (8) reduce immediately to those given by Rowlinson (1969) for a binary mixture. All of the partial derivatives required in the above equations can be readily derived from the pressure explicit equation of state. Consequently, the two determinant equations take the final form

$$U(T, P) = 0 \tag{9}$$

$$M(T, P) = 0 \tag{10}$$

because, for a given mixture, the molar volume V is a function of temperature and pressure only.

CALCULATION METHOD

It is quite clear that Newton's method can be utilized to solve the simultaneous Equations (9) and (10) because both U and M are defined and continuously differentiable throughout the entire physically meaningful (T, P) plane. This can be done following standard procedures described by Henrici (1964), and from this we obtain

$$T^{(r+1)} = T^{(r)} - \frac{U^{(r)}\left(\frac{\partial M}{\partial P}\right)_T^{(r)} - M^{(r)}\left(\frac{\partial U}{\partial P}\right)_T^{(r)}}{J} \tag{11}$$

$$P^{(r+1)} = P^{(r)} - \frac{M^{(r)}\left(\frac{\partial U}{\partial T}\right)_P^{(r)} - U^{(r)}\left(\frac{\partial M}{\partial T}\right)_P^{(r)}}{J} \tag{12}$$

where

$$J = \left(\frac{\partial U}{\partial T}\right)_P^{(r)}\left(\frac{\partial M}{\partial P}\right)_T^{(r)} - \left(\frac{\partial M}{\partial T}\right)_P^{(r)}\left(\frac{\partial U}{\partial P}\right)_T^{(r)}$$

Although it was possible to calculate the derivatives of the determinants exactly from rigorous mathematical theory, unfortunately it became infeasible when the number of components reached the order of ten or more. This was because for each iteration there were $(n^2 - 2n + 3)(2n - 1)$ determinants of order $n - 1$ to be solved. For a ten-component system, one would have to evaluate 1 577 ninth-order determinants. To reduce the computing time we calculated

$$\left(\frac{\partial U}{\partial P}\right)_T, \left(\frac{\partial U}{\partial T}\right)_P, \left(\frac{\partial M}{\partial P}\right)_T, \text{ and } \left(\frac{\partial M}{\partial T}\right)_P$$

by numerical differentiation and evaluated $\left(\frac{\partial U}{\partial x_i}\right)$ analytically. By this means the number of determinants was reduced to 3 $(n^2 - 2n + 3)$. The step sizes used in the numerical differentiations were 10^{-4} K and 10^{-2} kPa, respectively. These were chosen because they were considered to be small enough to maintain the sense of the derivatives and at the same time large enough not to cause excessive roundoff errors during the computing process.

It is known that Newton's method does not always guarantee the convergence to the correct solution when used to solve systems of nonlinear equations. The highly nonlinear characteristics of U and M make them more vulnerable for divergence to occur. However, the iterative procedure used in this study usually converged reliably and was not unusually sensitive to the initial values chosen. With error bounds of 0.01 K and 1 kPa for T and P, respectively, the critical point could be found within twenty iterations, although generally it could be obtained within ten iterations when a reasonable initial value was used. The computing time varied from approximately 0.02 s/iteration for three-component systems to 0.7 s/iteration for twelve-component systems on an AMDHAL computer. The computing time could be further reduced if Broyden's method (1965) were used to calculate the correction vectors.

RESULTS AND DISCUSSION

Critical temperatures and critical pressures have been calculated for a total of thirty-two multicomponent mixtures containing three or more components for which experimental critical properties were available. As shown in Table 1, these mixtures included fourteen three-component, seven four-component, six five-component, two six-component, two seven-component, and one twelve-component mixture. The compositions included paraffin hydrocarbons from methane through n-decane, nitrogen, carbon dioxide, and hydrogen sulfide. It is worth noting that the reliability of the method for systems containing nonhydrocarbons appears to be as good as it is for the pure hydrocarbon mixtures. This is significant because many of the existing empirical procedures do not provide at all for the inclusion of carbon dioxide or hydrogen sulfide, both of which are common components in reservoir fluids. Values of the fitted binary interaction parameters δ_{ij} required for treating the nonhydrocarbon-hydrocarbon mixtures were obtained from binary vapor-liquid equilibrium data by matching the experimental bubble point curve with that predicted from the equation.

When we consider that the range of compositions included in the comparisons and the fact that there is over a fourfold variation in critical pressure and almost a threefold variation in critical temperature, the agreement between experimental and predicted values is considered to be remarkably good. Although the predicted critical temperatures show a slightly positive bias, that is, an arithmetic average deviation of +1.14% compared to an absolute average deviation of 1.31%, the predicted critical pressures are almost uniformly distributed about the experimental values, that is, an arithmetic average deviation of +0.13% compared to an absolute average deviation of

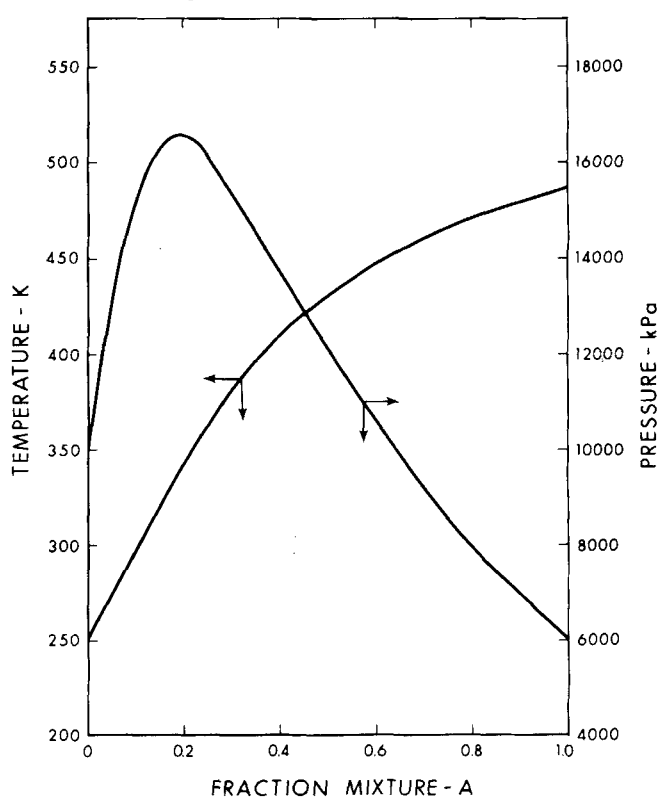

Fig. 1. Critical states for synthetic five-component mixtures.

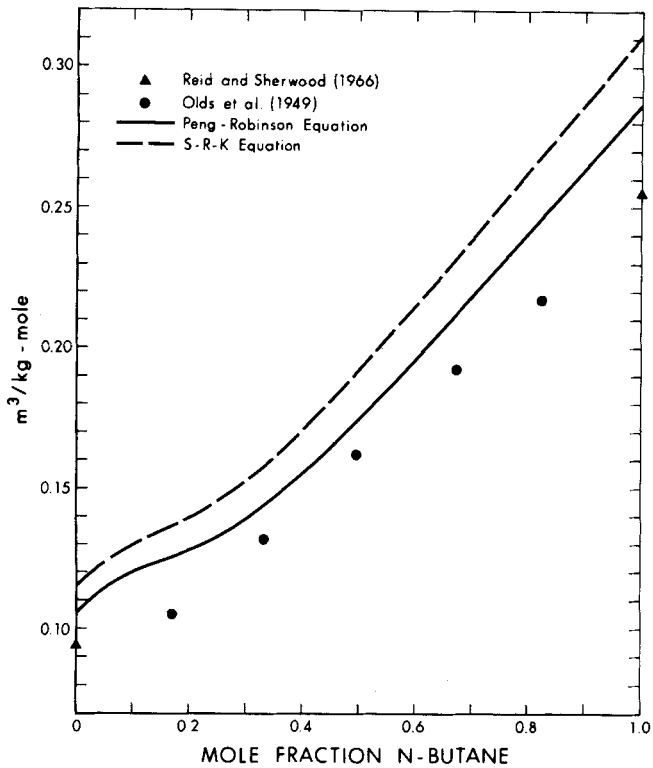

Fig. 2. Critical volumes of mixtures of carbon dioxide and *n*-butane.

2.33%. In view of the experimental difficulties involved in determining the critical state, it is believed that the reliability of the predictions is comparable to that of the experimental data.

Many hydrocarbon mixtures have a critical locus which is characterized by a simple continuous curve when projected onto a *P-T* plane. When plotted on a *T-x* plane, the critical locus for these systems exhibits a critical temperature which varies monotonically with composition. On the other hand, the critical pressure, when represented on a *P-x* plane, usually exhibits a maximum which is greater than the critical pressure for either pure component. This phenomenon has been observed and systematically studied for many binary systems. There seems to be a lack of information based on a similar study for any multicomponent system. However, the methods for predicting the critical state developed in this work can be used to develop the multicomponent analogy of the binary critical locus. Figure 1 shows the predicted critical loci for a binary system made from pure components that are each five-component paraffin hydrocarbon mixtures. The composition of these mixtures is given in Table 2. The critical loci represented in the figure were obtained by calculating the critical state for each of the five-component mixtures together with several mixtures obtained by taking various proportions of each original mixture.

Table 2. Composition of Systems Used to Prepare the Series of Mixtures for which the Critical States are Represented in Figure 1

Component	System A mole fraction	System B mole fraction
Methane	0.156	0.762
Ethane	0.111	0.152
Propane	0.108	0.058
n-pentane	0.246	0.022
n-heptane	0.379	0.006

It may be observed from the figure that the monotonic variation in T_c with composition and the maximum in P_c are similar to those obtained for true binaries. These predictions also emphasize the capability of the proposed method for predicting critical temperatures over a wide range in temperature and for predicting critical pressure in systems where the critical state may occur at temperatures either above or below the temperature corresponding to the cricondenbar.

The primary objective of this paper is to demonstrate the practicability of using an equation of state together with the critical state criteria formulated by Gibbs to predict the critical properties of multicomponent systems. However, even though other investigators have discussed the use of the rigorous approach for predicting the critical properties of binary mixtures, we considered it worthwhile to illustrate the use of the Peng-Robinson (1976) equation of state for one binary hydrocarbon-nonhydrocarbon system. We chose the *n*-butane-carbon dioxide system for this purpose, primarily because it had already been used as an example by Spear et al. (1969). The experimental critical temperatures, pressures, and volumes of five mixtures for this system are presented in Table 3, together with the values predicted by the Soave-Redlich-Kwong (Soave, 1972) and Peng-Robinson (1976) equations of state. The critical volume values are also shown in Figure 2.

It will be noted that the prediction of critical temperature and pressure is good by both methods but that the *P-R* predictions of critical volumes are better by a factor of about 2 compared to the *S-R-K* predictions. This is to be expected because of the improved critical compressibility factor of the *P-R* model.

The above comparison for the *n*-butane-carbon dioxide binary is typical of many comparisons that were made on both hydrocarbon and nonhydrocarbon binary systems from our equation of state. The predictions were at least as good and usually better than those obtained from other equations of state.

Table 3. Critical Temperatures, Pressures, and Volumes for the *n*-Butane-Carbon Dioxide System

Mole fraction *n*-butane	Critical temperature K			Critical pressure kPa			Critical volume m³/kg-mole		
	Exp.	S-R-K	P-R	Exp.	S-R-K	P-R	Exp.	S-R-K	P-R
0.1694	325.9	326.8	325.0	7 908	7 743	7 628	0.1049	0.1358	0.1252
0.3334	351.7	356.3	353.8	8 170	8 150	8 090	0.1317	0.1579	0.1441
0.4984	377.2	381.7	379.5	7 536	7 428	7 439	0.1623	0.1914	0.1746
0.6740	398.8	401.5	400.2	6 281	6 131	6 159	0.1929	0.2316	0.2120
0.8273	412.3	414.3	413.6	5 109	4 973	4 992	0.2172	0.2682	0.2465
Average error		+2.9	+1.2		−116	−139		+0.0352	+0.0187
Average % error		0.78	0.32		1.66	1.99		22.1	11.8

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NOTATION

A = molar Helmholtz free energy
a = attraction parameter
b = van der Waals covolume
C_p = heat capacity at constant pressure
G = molar Gibbs free energy
M = critical state determinant
n = number of components
P = pressure
R = gas constant
T = temperature
U = critical state determinant
V = molar volume
x = mole fraction
α = scaling factor
δ = interaction coefficient
κ = characterization constants
ω = Pitzer's acentric factor

Superscript

(r) = r^{th} iteration
* = ideal gas state

Subscripts

c = critical property
i, j, k = component identifications
o = reference state

LITERATURE CITED

Broyden, C. G., "A Class of Methods for Solving Nonlinear Simultaneous Equations," *Mathematics of Computations* **19**, 577 (1965).

Chueh, P. L., and J. M. Prausnitz, "Vapor-Liquid Equilibria at High Pressures: Calculation of Critical Temperatures, Volumes, and Pressures of Non-Polar Mixtures," *AIChE J.*, **13**, 1107 (1967).

Davis, P. C., A. F. Bertuzzi, T. L. Gore, and F. Kurata, "The Phase and Volumetric Behavior of Natural Gases at Low Temperatures and High Pressures," *Petrol. Trans. A.I.M.E.*, **201**, 245 (1954).

Ekiner, O., Ph.D. dissertation, Northwestern Univ., Evanston, Ill. (1965).

———, and G. Thodos, "Critical Temperatures and Pressures of the Ethane-n-Pentane-n-Heptane System," *J. Chem. Eng. Data*, **11**, 457 (1966).

Etter, D. O., and W. B. Kay, "Critical Properties of Mixtures of Normal Paraffin Hydrocarbons," *ibid.*, **6**, 409 (1961).

Gibbs, J. W., "On the Equilibrium of Heterogeneous Substances" (October 1876-May 1877), "Collected Works," Vol. 1, p. 55, Yale Univ. Press, New Haven, Conn. (1928).

Gonzales, M. H., and A. L. Lee, "Dew and Bubble Points of Simulated Natural Gases," *J. Chem. Eng. Data*, **13**, 172 (1968).

Henrici, P., "Elements of Numerical Analysis," pp. 105-107, Wiley, New York (1964).

Hissong, D. W., Ph.D. dissertation, Ohio State Univ. (1968).

———, and W. B. Kay, "The Calculation of the Critical Locus Curve of a Binary Hydrocarbon System," *AIChE J.*, **16**, 580 (1970).

Joffe, J., and D. Zudkevitch, "Predictions of Critical Properties of Mixtures: Rigorous Procedure for Binary Mixtures," *Chem. Eng. Progr. Symposium Ser. No. 81*, **63**, 43 (1967).

Kurata, F., and D. L. Katz, "Critical Properties of Volatile Hydrocarbon Mixtures," *Trans. Am. Inst. Chem. Engrs.*, **38**, 995 (1942).

Olds, R. H., H. H. Reamer, B. H. Sage, and W. N. Lacey, "Phase Equilibria in Hydrocarbon Systems: The n-Butane-Carbon Dioxide System," *Ind. Eng. Chem.*, **41**, 475 (1949).

Organick, E. I., "Prediction of Critical Temperatures and Critical Pressures of Complex Hydrocarbon Mixtures," *Chem. Eng. Progr. Symposium Ser. No. 6*, **49**, 81 (1953).

Peng, D., and D. B. Robinson, "A New Two-Constant Equation of State," *Ind. Eng. Chem. Fundamentals*, **15**, 59 (1976).

Prausnitz, J. M., and P. L. Chueh, "Computer Calculations for High Pressure Vapor Liquid Equilibria," Prentice Hall, Englewood Cliffs, N.J. (1968).

Reid, R. C., and T. K. Sherwood, "The Properties of Gases and Liquids," 2 ed., McGraw-Hill, New York (1966).

Robinson, D. B., and J. A. Bailey, "The Carbon Dioxide-Hydrogen Sulfide-Methane System, Part I: Phase Behavior at 100°F," *Can. J. Chem. Eng.*, **35**, 151 (1957).

Rowlinson, J. S., "Liquids and Liquid Mixtures," 2 ed., pp. 190-192, Butterworth, London, England (1969).

Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," *Chem. Eng. Sci.*, **27**, 1197 (1972).

Spear, R. R., R. L. Robinson, Jr., and K. C. Chao, "Critical States of Mixtures and Equations of State," *Ind. Eng. Chem. Fundamentals*, **9**, 2 (1969).

———, "Critical States of Ternary Mixtures and Equations of State," *ibid.*, **10**, 591 (1971).

Spencer, C. F., T. E. Daubert, and P. D. Danner, "A Critical Review of Correlations for the Critical Properties of Defined Mixtures," *AIChE J.*, **19**, 522 (1973).

Yarborough, L., and L. R. Smith, "Solvent and Driving Gas Compositions for Miscible Slug Displacement," *Soc. Petrol. Eng. J.*, **10**, 298 (1970).

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A Group Contribution Molecular Model of Liquids and Solutions

A group contribution molecular model is developed for the thermodynamic properties of polar and nonpolar liquids and their solutions, including energy of vaporization, pVT relations, excess properties, and activity coefficients. The model is based on the cell theory in which the repulsive forces of molecules are expressed with a modified cell partition function derived from the Carnahan-Starling equation of state for hard spheres. The attractive forces are made up of group pair interaction contributions. Group and interaction properties have been determined for methyl, methylene, hydroxyl, and carbonyl. Extensive comparisons are made of predictions of the model with data for pure liquids and their solutions.

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SCOPE

The objective of this work is twofold:

1. To develop a comprehensive theory of group contribution for the estimation of various thermodynamic properties of polar and nonpolar liquids and their solu-

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