known as the MG % of the plasma solution. To calculate the percentage hemolysis due to controlled testing H, it is necessary to subtract from the final value the plasma hemoglobin concentration that was present prior to shearing. This reference value reflects the hemoglobin release due to the blood drawing and pipetting techniques and also the autohemolysis during the blood storage period. The method of calculating H is outlined below:

$$H \equiv \left[\frac{\text{MGM Hgb in final plasma} - \text{MGM Hgb in Ref. plasma}}{\text{MGM Hgb at risk}}\right] \times 100$$

$$H = \left[\frac{\left\{\dfrac{(\text{MG \%})_f - (\text{MG \%})_{\text{Ref}}}{100}\right\} \times \left(\begin{matrix}\text{cc. plasma}\\ \text{in blood sample}\end{matrix}\right)}{325^{*}\,\dfrac{\text{MGM Hgb}}{\text{cc. RBC}} \times \left(\begin{matrix}\text{cc. RBC}\\ \text{in blood sample}\end{matrix}\right)}\right] \times 100$$

$$H = \left[\frac{(\text{MG \%})_f - (\text{MG \%})_{\text{Ref}}}{325}\right]\left(\frac{\text{cc. plasma}}{\text{cc. RBC}}\right)$$

or

$$H = \left[\frac{(\text{MG \%})_f - (\text{MG \%})_{\text{Ref}}}{325}\right]\left(\frac{1 - H}{H}\right)$$

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* From reference 1.

The Calculation of the Critical Locus Curve of a Binary Hydrocarbon System

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A method of calculating the critical properties of binary hydrocarbon systems is presented which is based upon the rigorous thermodynamic equations for the critical point of a binary mixture. By using these equations together with an equation of state, a completely analytical procedure was developed with the aid of a digital computer. The Redlich-Kwong and the Dieterici equations of state were chosen for study. The Redlich-Kwong equation was found superior for predicting critical pressures and temperatures by this method, although the Dieterici equation was better for critical volumes. The two interaction parameters arising from the equation of state were calculated from combining rules or from available experimental critical data on binary systems. To facilitate the latter approach, a mathematical optimization routine was used to find the best values of the interaction parameters for twenty-one binary hydrocarbon systems for which critical data were experimentally determined. The optimum values of the interaction parameters were correlated as functions of the ratio of molecular weights of the components. These correlations enable one to predict quite precisely the critical properties of the binary systems from the pure component data alone.

The critical properties of chemical compounds and their mixtures are of major importance in engineering calculations and design. The critical point defines the temperature and pressure where the liquid and vapor phases have identical properties and is, therefore, a key point in the construction of the phase diagram of a mixture. Also, with a knowledge of the critical properties of the pure components and with the aid of van der Waals' theorem of corresponding states, it is possible to predict the thermodynamic properties of the compounds when these properties have not been determined experimentally. For a number of years, this laboratory has had a continuing research program to determine the factors affecting the critical properties of binary systems. Most of these studies have been carried out on hydrocarbon systems which were chosen to investigate the effect of molecular size, structure, and chemical nature of the components. For this paper, the critical locus curves of twenty-one binary systems composed of mixtures of paraffinic, naphthenic, and aromatic hydrocarbons have been used to develop a method of calculating the critical properties of a mixture of known composition from a knowledge of the critical properties of the pure components. The systems and references

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to the experimental data are given in the following table:

Benzene-*n*-nonane (*13*)
Cyclopentane-methycyclohexane (*13*)
n-pentane-*n*-nonane (*10*)
Cyclopentane-*n*-heptane (*10*)
Cyclopentane-*n*-octane (*10*)
Cyclopentane-*n*-nonane (*10*)
Cyclohexane-*n*-octane (*10*)
Cyclohexane-*n*-nonane (*10*)
Ethyl benzene-*n*-pentane (*9*)
Ethyl benzene-*n*-hexane (*9*)
n-hexane-*n*-heptane (*14*)
n-hexane-*n*-octane (*14*)
n-heptane-*n*-octane (*14*)
Benzene-*n*-octane (*14*)
Benzene-ethyl benzene (*11*)
Benzene-*o*-xylene (*11*)
Propane-*n*-butane (*2*)
Propane-*n*-pentane (*16*)
Propane-*n*-hexane (*17*)
Propane-*n*-heptane (*15*)
Propane-*n*-octane (*7*)

The approach is a thermodynamic one and has possibilities for extension to systems of more than two components and to systems other than hydrocarbons.

THERMODYNAMIC CONDITIONS AT THE CRITICAL POINTS OF A BINARY MIXTURE

Although many of the methods that have been proposed for estimating the critical properties of binary mixtures are essentially empirical, some of the more recent methods (*1, 12, 18*) are based upon the rigorous thermodynamic conditions at the critical point of a binary system, originally derived by Gibbs (*8*), namely

$$\left(\frac{\partial^2 g}{\partial X_1^2}\right)_{P,T} = 0 \tag{1}$$

$$\left(\frac{\partial^3 g}{\partial X_1^3}\right)_{P,T} = 0 \tag{2}$$

When these equations are expressed in terms of the measurable variables P, V, T, and X_1, one obtains

$$\left(\frac{\partial^2 g}{\partial X_1^2}\right)_{P,T} = \frac{RT}{X_1X_2} + \int_V^{V_\infty}\left(\frac{\partial^2 P}{\partial X_1^2}\right)_{V,T} dV - \left(\frac{\partial P}{\partial X_1}\right)_{V,T}\left(\frac{\partial V}{\partial X_1}\right)_{P,T} = 0 \tag{3}$$

and

$$\left(\frac{\partial^3 g}{\partial X_1^3}\right)_{P,T} = \frac{RT(X_1 - X_2)}{X_1^2X_2^2} + \int_V^{V_\infty}\left(\frac{\partial^3 P}{\partial X_1^3}\right)_{V,T} dV - \left(\frac{\partial P}{\partial X_1}\right)_{V,T}\left(\frac{\partial^2 V}{\partial X_1^2}\right)_{P,T} - \left(\frac{\partial V}{\partial X_1}\right)^2_{P,T}\left(\frac{\partial^2 P}{\partial V\partial X_1}\right)_T - 2\left(\frac{\partial V}{\partial X_1}\right)_{P,T}\left(\frac{\partial^2 P}{\partial X_1^2}\right)_{V,T} = 0 \tag{4}$$

EQUATIONS OF STATE

In order to solve Equations (3) and (4), it is necessary to introduce an equation of state relating the variables P, V, T, and X_1. Although an equation of state may have been derived by a sound application of kinetic theory, it is nevertheless an empirical equation because the constants must be evaluated from experimental data. However, at the critical point of a pure substance, the constants in a two-constant equation of state can be calculated by the application of thermodynamic conditions at the critical point of a pure compound, namely

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \tag{5}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \tag{6}$$

For this study, the Redlich-Kwong equation (*19*)

$$P + \frac{a}{T^{1/2}V(V+b)} = \frac{RT}{(V-b)} \tag{7}$$

and the Dieterici equation (*6*)

$$Pe^{a/RTV}(V-b) = RT \tag{8}$$

were chosen for the solution of Equations (3) and (4). The values of the constants a and b calculated by Equations (5) and (6) are for the Redlich-Kwong equation

$$a = 0.42748\,\frac{R^2T_c^{2.5}}{P_c} \tag{9}$$

$$b = 0.086640\,\frac{RT_c}{P_c} \tag{10}$$

and for the Dieterici equation

$$a = \frac{4R^2T_c^2}{e^2P_c} \tag{11}$$

$$b = \frac{RT_c}{e^2P_c} \tag{12}$$

The Redlich-Kwong equation has been used by others (*3, 12, 18*) in attempts to calculate properties of binary mixtures. In many respects it is a good equation, although it predicts a value of the critical compressibility factor of $Z_c = 0.333$, whereas the experimental value for many substances including hydrocarbons is approximately 0.27. On the other hand, the Dieterici equation predicts $Z_c = 0.2707$ but is less convenient to use.

In the application of these equations of state to mixtures, the variation of the constants with composition was represented by the commonly used equations

$$a = a_1X_1^2 + 2a_{12}X_1X_2 + a_2X_2^2 \tag{13}$$

$$b = b_1X_1^2 + 2b_{12}X_1X_2 + b_2X_2^2 \tag{14}$$

The degree to which the calculated critical properties agree with the experimental values depends on the values assigned to these interaction parameters. For their evaluation, two different methods were investigated:

1. a_{12} and b_{12} were calculated by combining rules from the values of a and b for the pure components.
2. The best values of a_{12} and b_{12} were calculated by an optimization technique with experimental critical property data on the binary system.

Given a pair of values of a_{12} and b_{12}, the P-T critical locus curve of the binary system was calculated. For any composition X_1, the two thermodynamic Equations (3) and (4) plus the equation of state provided three equations which were solved for the three critical properties P_c, V_c, and T_c of the mixture. At any given composition, the two thermodynamic equations were solved simultaneously for the critical temperature and volume, and then the critical pressure was calculated from the equation of state.

The integrals of the partial derivatives appearing in Equations (3) and (4), namely

$$\int_V^{V_\infty}\left(\frac{\partial^2 P}{\partial X_1^2}\right)_{V,T} dV \quad \text{and} \quad \int_V^{V_\infty}\left(\frac{\partial^3 P}{\partial X_1^3}\right)_{V,T} dV$$

were evaluated analytically for the Redlich-Kwong equation and numerically by Simpson's rule (*5*) for the Dieterici equation, since for the latter an analytical solution is impossible.

The two thermodynamic equations were solved simultaneously by a modified form of Newton's iterative method for two equations (*4*). The modifications involved replac-

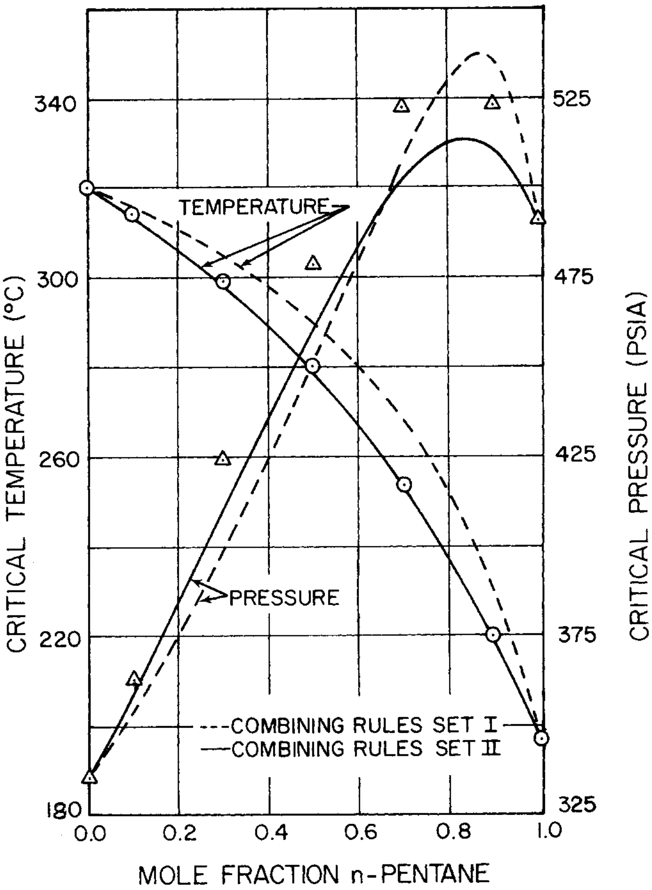

Fig. 1. Calculation of the critical locus curves of binary systems by using the Redlich-Kwong equation of state. *n*-pentane-*n*-nonane. Points are experimental values *(10)*.

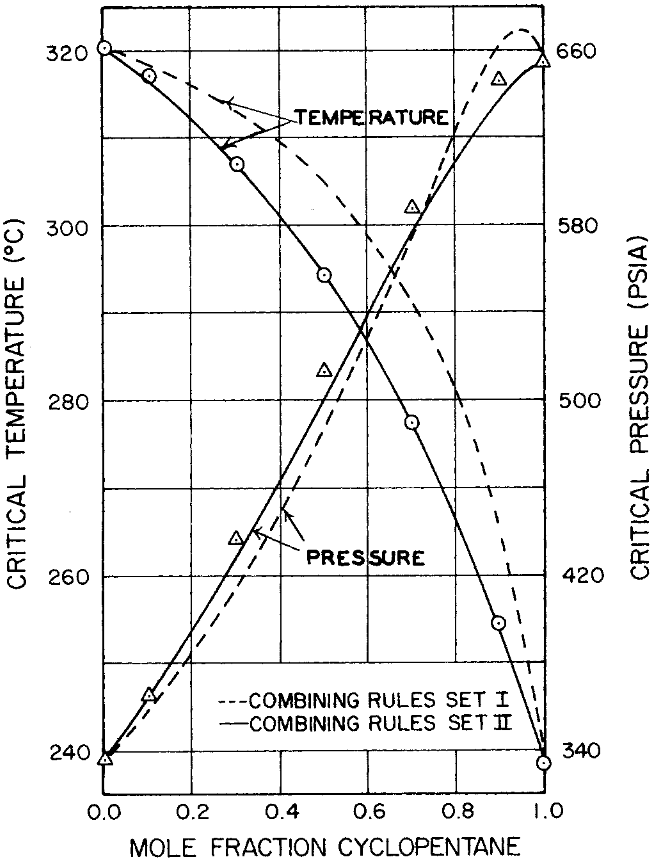

Fig. 2. Calculation of the critical locus curves of binary systems by using the Redlich-Kwong equation of state. Cyclopentane-*n*-nonane. Points are experimental values *(10)*.

ing the derivatives in Newton's method with difference quotients and introducing a procedure to search for suitable initial values of the variables involved. The entire calculation was carried out on an IBM-7094 digital computer.

It is this completely analytical solution of Equations (3) and (4) which distinguishes this work from the previous efforts which have been directed at using the thermodynamic conditions of the critical state to correlate mixture critical properties. Redlich and Kister (*18*) and Ackerman and Redlich (*1*) considered only the two ends of the critical locus, where the pure component Equations (5) and (6) could be used together with Equations (3) and (4) to calculate the limiting slopes of the locus. Joffe and Zudkevitch (*12*) solved Equations (3) and (4) by plotting values of the two free energy derivatives, reading off the zero points, and cross plotting to obtain the simultaneous solution. The completely analytical solution procedure used in this work made it possible to investigate a large number of cases and thereby to establish the utility of this correlational approach.

CALCULATION OF THE CRITICAL LOCUS FROM METHOD 1

Two sets of combining rules for method 1 were investigated:

$$\text{Set I}\quad\begin{cases} a_{12} = \dfrac{1}{2}\,(a_1 + a_2) & (15)\\[2ex] b_{12} = \dfrac{1}{2}\,(b_1 + b_2) & (16)\end{cases}$$

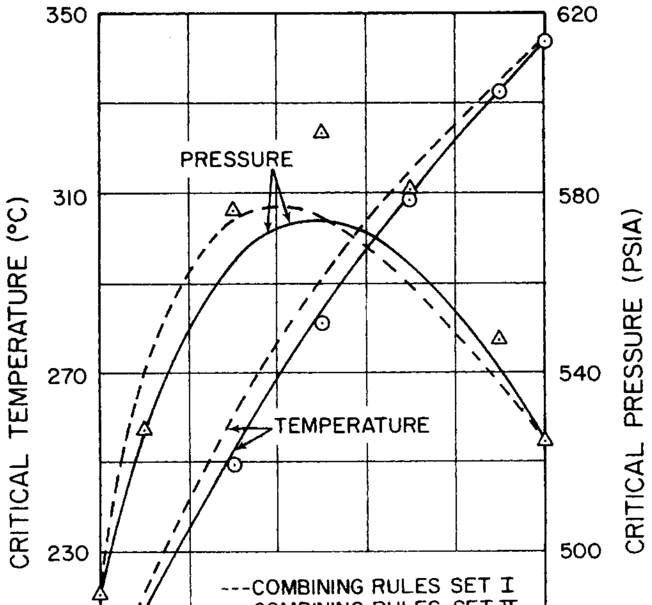

Fig. 3. Calculation of the critical locus curves of binary systems by using the Redlich-Kwong equation of state. Ethyl benzene-*n*-pentane. Points are experimental values *(9)*.

TABLE 1. STATISTICAL COMPARISON OF EXPERIMENTAL AND CALCULATED CRITICAL PROPERTIES BY USING COMBINING RULES

Equation of state	Redlich-Kwong				Dieterici			
Combining rules	Set I		Set II		Set I		Set II	
System	P_D*	T_D†	P_D*	T_D†	P_D*	T_D†	P_D*	T_D†
n-pentane-*n*-nonane	19.0	9.44	15.0	1.02	27.4	12.97	29.6	2.09
Cyclopentane-*n*-nonane	19.2	9.63	9.8	0.37	16.0	17.43	10.9	5.88
Ethyl benzene-*n*-pentane	14.4	7.71	13.7	2.19	36.6	5.44	40.1	0.60
Propane-*n*-pentane	18.9	8.90	11.8	2.68	29.9	10.37	32.8	3.68
Propane-*n*-hexane	38.4	14.56	18.1	2.58	51.3	17.44	30.8	3.37
Propane-*n*-heptane	66.8	22.26	31.4	4.97	76.0	25.55	80.8	9.94
Maximum deviations System	Pressure, lb./sq.in.	Temp., °C.	Pressure, lb./sq.in.	Temp., °C.	Pressure, lb./sq.in.	Temp., °C.	Pressure, lb./sq.in.	Temp., °C.
n-pentane-*n*-nonane	27.8	14.48	21.1	1.81	36.3	18.32	41.1	2.79
Cyclopentane-*n*-nonane	28.0	14.48	13.4	0.71	23.7	24.13	14.4	7.95
Ethyl benzene-*n*-pentane	22.2	10.91	19.5	3.27	49.2	7.50	53.1	1.03
Propane-*n*-pentane	28.0	12.97	19.1	3.86	43.6	14.02	44.5	5.09
Propane-*n*-hexane	56.2	21.32	28.2	3.79	74.0	24.20	39.7	4.72
Propane-*n*-heptane	92.8	32.67	47.8	7.57	111.6	38.45	106.2	13.75

* Root-mean-square pressure deviation, lb./sq.in.
† Root-mean-square temperature deviation, °C.

$$\text{Set II} \quad \left\{ \begin{aligned} a_{12} &= (a_1 a_2)^{1/2} && (17) \\ b_{12} &= \left[\frac{1}{2} (b_1^{1/3} + b_2^{1/3}) \right]^3 && (18) \end{aligned} \right.$$

For both sets of combining rules and for both the Redlich-Kwong and Dieterici equations of state, the critical temperature-composition and critical pressure-composition curves were calculated for a number of systems involving aliphatic, cycloparaffinic, and aromatic hydrocarbons. These curves are presented for three of the most nonideal systems examined in this work, the *n*-pentane-*n*-nonane,

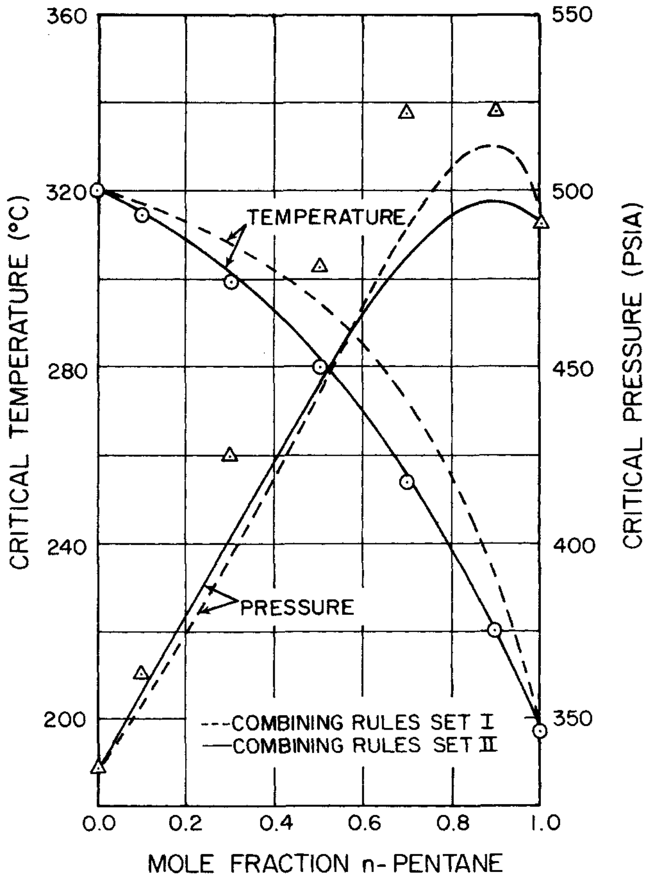

Fig. 4. Calculation of the critical locus curves of binary systems by using the Dieterici equation of state. *n*-pentane-*n*-nonane. Points are experimental values (10).

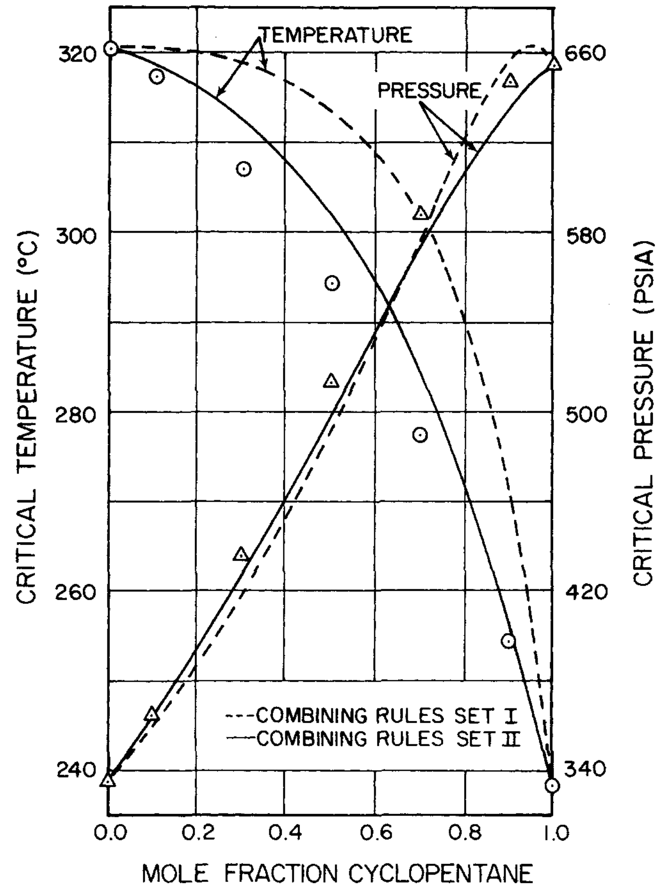

Fig. 5. Calculation of the critical locus curves of binary systems by using the Dieterici equation of state. Cyclopentane-*n*-nonane. Points are experimental values (10).

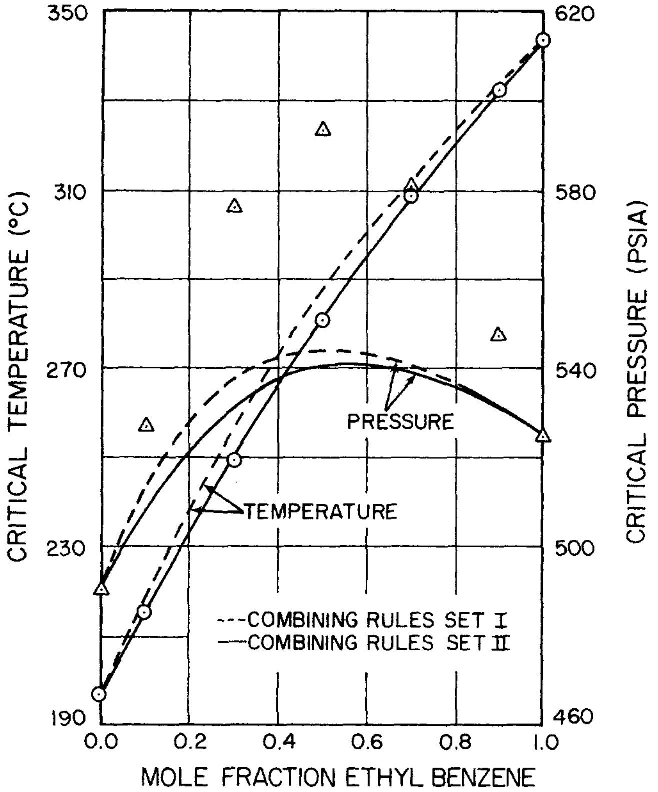

Fig. 6. Calculation of the critical locus curves of binary systems by using the Dieterici equation of state. Ethyl benzene-*n*-pentane. Points are experimental values *(9)*.

cyclopentane-*n*-nonane, and ethyl benzene-*n*-pentane systems.

Comparisons of the calculated curves with the experimental data are shown in Figures 1 through 3 for the Redlich-Kwong equation and 4 through 6 for the Dieterici equation. From these comparisons and by an extensive statistical analysis of the data, shown in Table 1, the following conclusions were reached:

1. When the Redlich-Kwong equation is used, the combining rules of set II yield a considerably better prediction of the critical properties than do the rules of set I. The critical temperature predictions of set I are consistently high, while those predicted by set II are in closer agreement with the experimental values. The critical pressure predictions by set II are also better than those by set I, although the pressures calculated with set II are consistently below the experimental critical pressures.
2. When the Dieterici equation is used, the combining rules of set II yield a better prediction of the critical temperatures than do the rules of set I. However, for the critical pressures the advantage is less clear.

These results indicate that the Redlich-Kwong equation is superior to the Dieterici equation for use in the calculation of the critical pressures and temperatures of hydrocarbon mixtures. However, the Dieterici equation yields a much better prediction of the critical volumes than the Redlich-Kwong equation. This is shown in Figure 7, where the calculated critical volume-composition curves are compared with the experimental data for the propane-*n*-hexane system *(17)*.

CALCULATION OF THE CRITICAL LOCUS FROM METHOD 2

Since the critical properties of a mixture are ultimately determined by the intermolecular forces existing in the solution, one may consider the interaction parameters a_{12} and b_{12} as related to those intermolecular forces. This suggested the use of the experimental critical data to calculate the best values of a_{12} and b_{12}, that is, the values which minimized the difference between the experimental and calculated critical properties. This was a nonlinear optimization problem which was solved by incorporating the critical locus calculation into a direct search or univariate optimization program which varied each parameter separately, preserved improvements, and incorporated strategies for a patterned approach to the optimum. For this work, a direct search optimization program developed by Williamson of this laboratory *(20)* was used.

The problem was complicated in that with one set of interaction parameters both the critical temperatures and critical pressures of the mixtures could be calculated. Thus, a set of interaction parameters could be found to minimize either the root-mean-square pressure deviation or the root-mean-square temperature deviation. However, the objective was to minimize not either one of these deviations but some combination of them which would result in the best critical locus prediction from the standpoint of both pressure and temperature.

The function to be minimized (F) was taken as a linear combination of the root-mean-square pressure and temperature deviations. That is

$$F = P_D + \alpha T_D \tag{19}$$

A direct search optimization study of the *n*-pentane-*n*-nonane system showed that the optimum values obtained for the interaction parameters are relatively insensitive to

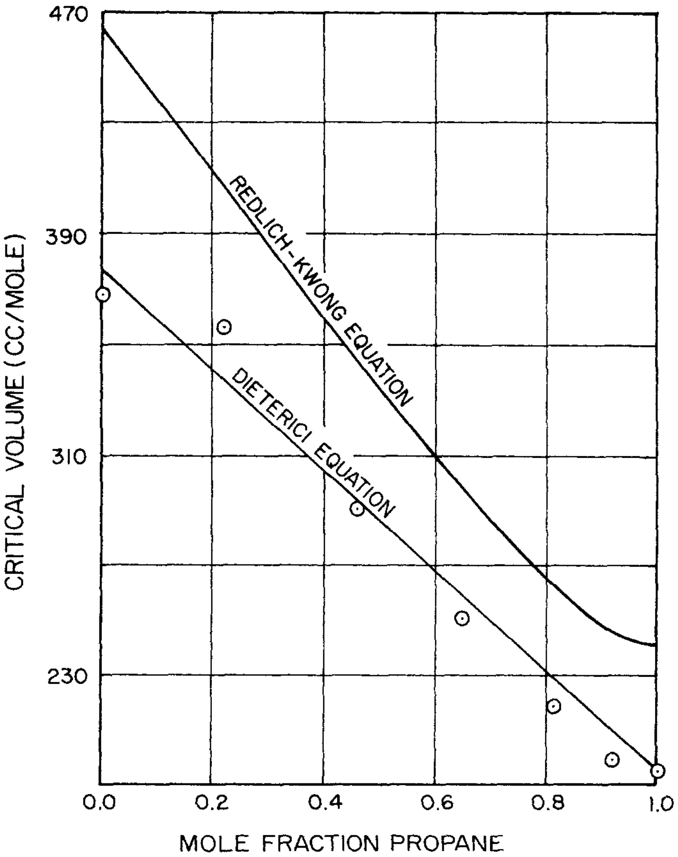

Fig. 7. Calculation of critical volume by the Redlich-Kwong and Dieterici equations of state. Propane-*n*-hexane system. Points are experimental values *(17)*.

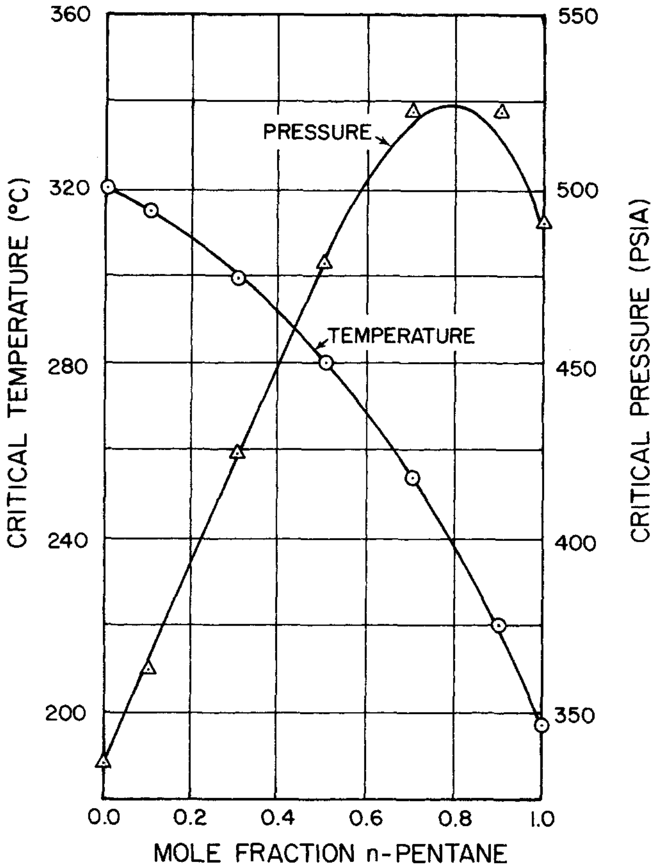

Fig. 8. Calculation of the critical locus curve by the Redlich-Kwong equation by using optimum interaction parameters. *n*-pentane-*n*-nonane system. Points are experimental values *(10)*.

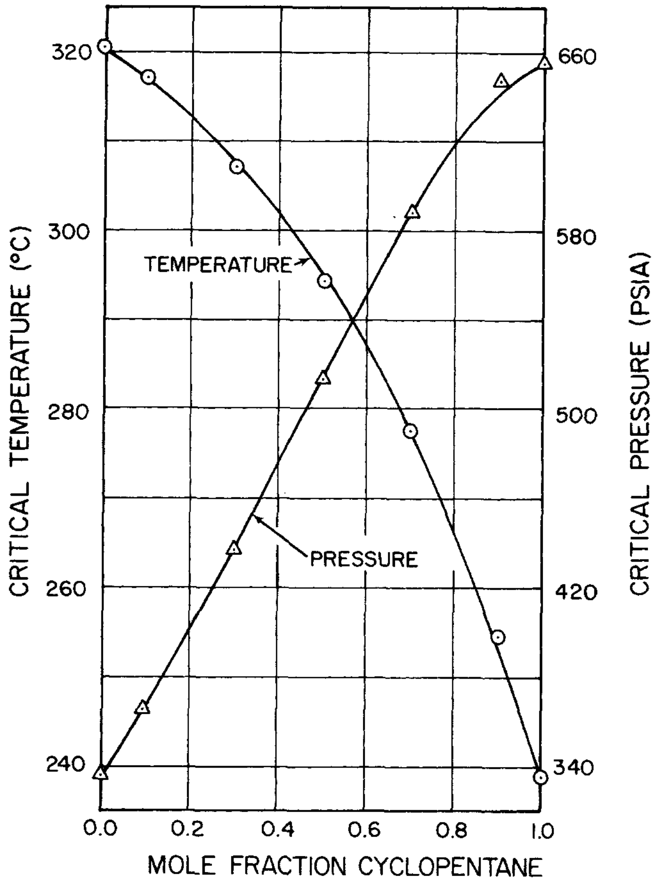

Fig. 9. Calculation of the critical locus curve by the Redlich-Kwong equation by using optimum interaction parameters. Cyclopentane-*n*-nonane system. Points are experimental values *(10)*.

the value of α, and the optimized critical locus calculated from these values is even more insensitive. With a variation of α from 2 to 6, the differences among the calculated critical loci were within about 2 lb./sq.in. in pressure and

TABLE 2. STATISTICAL COMPARISON OF EXPERIMENTAL AND CALCULATED CRITICAL PROPERTIES BY USING OPTIMUM INTERACTION PARAMETERS

System	Parameter m	Reduced interaction parameters a^*_{12}	Reduced interaction parameters b^*_{12}	Root-mean-square deviations P_D†	Root-mean-square deviations T_D††	Maximum deviations Pressure, lb./sq.in.	Maximum deviations Temp., °C.
Benzene-*n*-nonane	0.6420	0.89228	0.94313	0.5	0.29	0.7	0.49
Cyclopentane-methylcyclohexane	0.3999	0.94882	0.97493	0.6	0.27	1.3	0.46
n-pentane-*n*-nonane	0.7775	0.84871	0.91514	3.6	0.95	8.1	1.67
Cyclopentane-*n*-heptane	0.4288	0.94444	0.96717	0.6	0.27	1.2	0.55
Cyclopentane-*n*-octane	0.6288	0.89230	0.93822	0.7	0.49	1.4	0.87
Cyclopentane-*n*-nonane	0.8287	0.84581	0.91213	1.9	0.76	4.3	1.15
Cyclohexane-*n*-octane	0.3573	0.94056	0.95359	2.9	0.18	4.9	0.38
Cyclohexane-*n*-nonane	0.5239	0.92779	0.95478	1.3	0.26	2.8	0.59
Ethyl benzene-*n*-pentane	0.4714	0.89363	0.94937	3.1	0.85	6.5	1.30
Ethyl benzene-*n*-hexane	0.2330	0.94467	0.96895	0.8	0.46	1.3	0.74
n-hexane-*n*-heptane	0.1628	0.97626	0.98063	3.0	0.23	3.8	0.29
n-hexane-*n*-octane	0.3256	0.95387	0.97423	0.6	0.11	1.0	0.22
n-heptane-*n*-octane	0.1400	0.96874	0.97133	2.8	0.32	3.7	0.43
Benzene-*n*-octane	0.4624	0.92300	0.95853	1.0	0.12	1.5	0.14
Benzene-ethyl benzene	0.3591	0.94989	0.97453	0.3	0.15	0.5	0.26
Benzene-ortho xylene	0.3591	0.94301	0.97216	1.0	0.25	1.6	0.46
Propane-*n*-butane	0.3182	0.96080	0.98746	1.2	0.16	1.9	0.29
Propane-n-pentane	0.6364	0.86165	0.94293	2.9	1.07	6.7	1.76
Propane-*n*-hexane	0.9544	0.80081	0.92164	4.7	1.61	11.2	2.44
Propane-*n*-heptane	1.2726	0.72285	0.89480	12.9	3.64	34.3	5.55
Propane-*n*-octane	1.5908	0.65734	0.86371	20.5	5.82	42.9	8.86

† Root-mean-square deviation, lb./sq.in.
†† Root-mean-square temperature deviation, °C.

TABLE 3. STATISTICAL COMPARISON OF EXPERIMENTAL AND CALCULATED CRITICAL PROPERTIES BY USING BACK CALCULATED INTERACTION PARAMETERS

System	Red. interaction param.		Root-mean-square deviations		Maximum deviations	
	a^*_{12}†	b^*_{12}††	P_D**	T_D¶	lb./sq.in.	Temp., °C.
n-pentane-*n*-nonane	0.85067	0.93119	7.8	1.76	14.4	3.07
Cyclopentane-*n*-nonane	0.83716	0.92695	8.3	3.21	15.9	5.05
Ethyl benzene-*n*-pentane	0.92327	0.95653	2.9	3.36	4.9	4.64
Propane-*n*-butane	0.95077	0.96921	5.6	0.90	7.5	1.21
Propane-*n*-pentane	0.88633	0.94287	3.1	3.28	6.2	4.80

† Back calculated from Equation (23).
†† Back calculated from Equation (24).
** Root-mean-square pressure deviation, lb./sq.in.
¶ Root-mean-square temperature deviation, °C.

0.6°C. in temperature. A value of $\alpha = 4$, therefore, was selected for the optimization.

Each evaluation of the function to be minimized involved calculating the critical properties over the entire composition range, comparing these values with the experimental values by calculating the root-mean-square pressure and temperature deviations, and then combining these two deviations according to Equation (19).

Table 2 presents the optimum values of the interaction parameters for the twenty-one systems on which the optimization was performed. For convenience, the parameters in this table are reduced interaction parameters defined as follows:

$$a^*_{12} = 2a_{12}/(a_1 + a_2) \tag{20}$$

$$b^*_{12} = 2b_{12}/(b_1 + b_2) \tag{21}$$

The optimum values of the parameters a^*_{12} and b^*_{12} vary from 0.65 to 0.98 and 0.86 to 0.99, respectively. Figures 8 through 10 compare the experimental critical properties of the three systems with the values calculated by using the Redlich-Kwong equation of state and the optimum values of the interaction parameters. The table and the figures show that the critical properties of even rather highly nonideal systems can be predicted quite accurately by this procedure if the proper values are used for the interaction parameters.

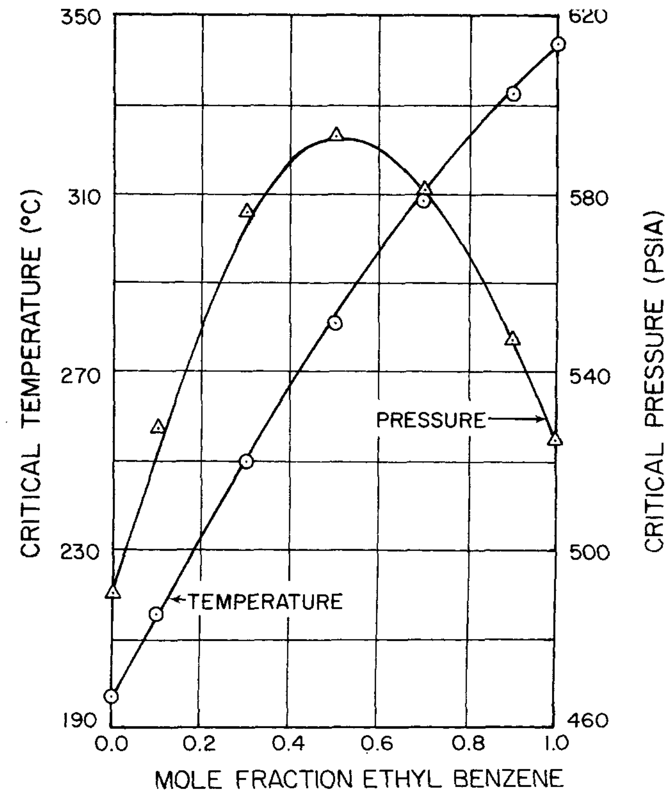

Fig. 10. Calculation of the critical locus curve by the Redlich-Kwong equation by using optimum interaction parameters. Ethyl benzene-*n*-pentane system. Points are experimental values (9).

CORRELATION OF THE REDUCED INTERACTION PARAMETERS

It is well known that the critical properties of mixtures are related to the nonideality of the systems. It was, therefore, not surprising to find that the optimized values of the interaction parameters were related to the nonideality of the system. One of the most important factors affecting the nonideality is the difference in the size of the components, which for simplicity is taken as the difference in molecular weights. In terms of the critical locus curve of a binary system, it was found that the greater the difference between the molecular weights of the components, the greater the deviation of the locus curve from a linear relationship; and for a given difference between the molecular weights of the components, the lower the absolute molecular weight, the greater the deviation from a linear relationship. The following molecular weight function follows both of these trends:

$$\mathcal{M} = M_1/M_2 - 1 \tag{22}$$

The optimum values of the interaction parameters listed in Table 2 were correlated as polynomials in the function $\mathcal{M}$ by using a least-squares regression analysis. The plot of a^*_{12} against $\mathcal{M}$ was clearly *S* shaped, so a third-order

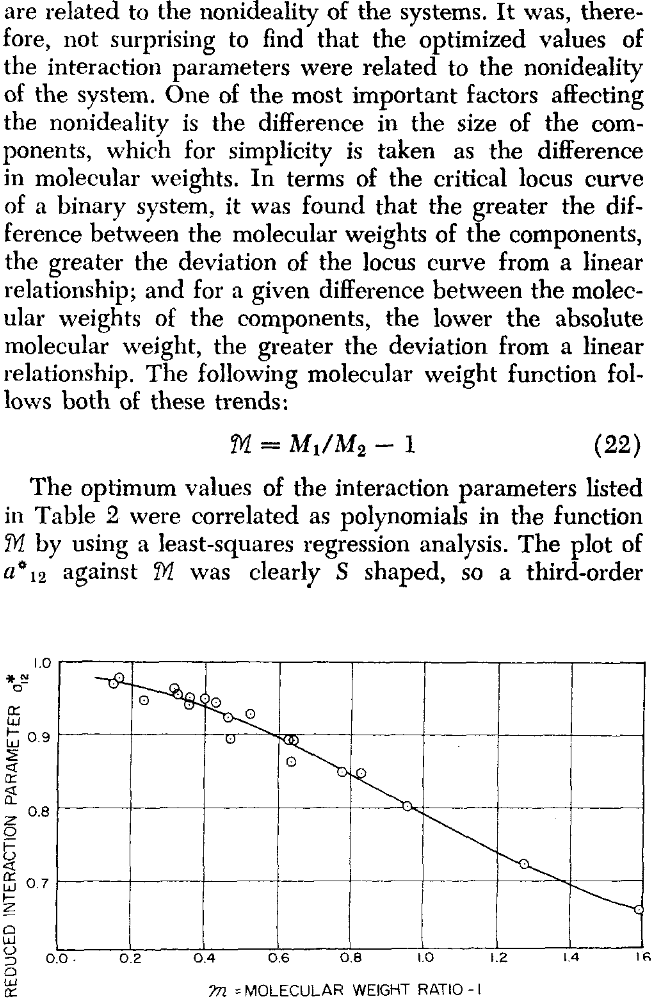

Fig. 11. Correlation of reduced interaction parameters a_{12}^*.

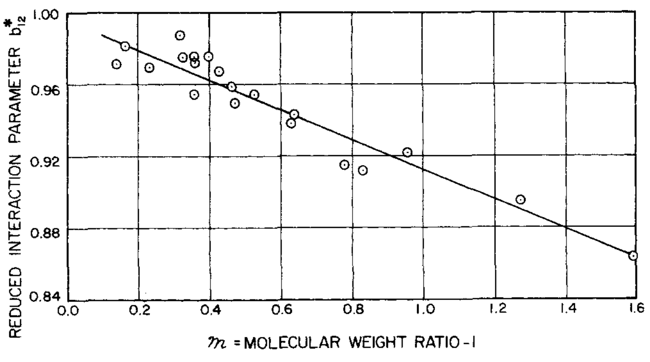

Fig. 12. Correlation of reduced interaction parameters b_{12}^*.

equation was selected to represent this relationship. A first-order equation was selected for b^*_{12}. These equations are

$$a^*_{12} = 0.97754 - 0.004949\mathcal{M} - 0.280326\mathcal{M}^2 + 0.098798\mathcal{M}^3 \quad (23)$$

$$b^*_{12} = 0.99555 - 0.082779 \quad (24)$$

These equations apply over the range

$$0.1 < \mathcal{M} < 1.6$$

Figures 11 and 12 show plots of Equations (23) and (24), respectively. The points are the values from Table 2, and the lines are calculated from the equations. The systems upon which these correlations are based include all possible binary combinations of the three hydrocarbon chemical families: normal paraffins, naphthenes, and aromatics. For these systems, there was no justification for developing separate correlations for the various combinations of chemical families because all the systems followed the same patterns.

TEST OF CORRELATION EQUATIONS

To determine the effect of the scatter in the values of a^*_{12} and b^*_{12} on the calculated critical properties, the five systems for which the corresponding points on Figures 11 and 12 were farthest away from the calculated curves were studied. For these systems, Table 3 presents the interaction parameters calculated by Equations (23) and (24) and the corresponding root-mean-square deviations of the critical properties. A comparison of Table 3 with Table 1 shows that the correlated parameters yield a superior prediction of critical pressures but an inferior prediction of critical temperatures when compared with the best prediction made with combining rules. These five systems are, of course, the worst cases; for most systems, the use of Equations (23) and (24) yields a better prediction of the critical properties than will the use of combining rules.

Equations (23) and (24) should by no means be regarded as the final expressions for the interaction parameters. These equations are based on the twenty-one systems previously mentioned which involve three hydrocarbon chemical families and a wide range of molecular sizes and structures. However, as the approach of optimizing the interaction parameters is applied to more systems on which critical data are available, the expressions for the interaction parameters should be improved.

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NOTATION

a, b = equation of state constants
a_{12}, b_{12} = interaction parameters for equation of state
a^*_{12}, b^*_{12} = reduced interaction parameters
F = function to be minimized
g = molar Gibbs free energy
M = molecular weight
$\mathcal{M}$ = molecular weight correlating parameter
P = pressure
P_D = root-mean-square pressure deviation, lb./sq.in.
R = gas constant
T = temperature
T_D = root-mean-square temperature deviation, °C.
V = volume
X = mole fraction
Z = compressibility factor, PV/RT
α = constant to balance T and P deviations

Subscripts

c = critical state
1, 2 = components 1 and 2
∞ = limiting condition of very high volumes

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A print-out copy of the digital computer programs used to calculate the properties described in this paper may be obtained from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 W. 34th St., New York 10001. Document No. 00962, $2.00 for microfiche or $5.00 for photocopies.

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