LITERATURE CITED

1. Bender, P., G. T. Furukawa, and J. R. Hyndman, *Ind. Eng. Chem.*, **44**, 387 (1952).
2. Chueh, P. L., Ph.D. dissertation, Univ. California, Berkeley (1967).
3. ———, N. K. Muirbrook, and J. M. Prausnitz, *AIChE J.*, **11**, No. 6, 1097 (1965).
4. Chueh, P. L., and J. M. Prausnitz, *ibid.*, **13**, 1107 (1967).
5. Din, F., "Thermodynamic Functions of Gases," Vol. 3, Butterworths, London (1956).
6. Joffe, J., *Ind. Eng. Chem.*, **39**, 837 (1947).
7. ———, and David Zudkevitch, *Ind. Eng. Chem. Fundamentals*, **5**, 455 (1966).
8. Kay, W. B., *Ind. Eng. Chem.*, **28**, 1014 (1936).
9. Kobe, K. A., and R. E. Lynn, *Chem. Rev.*, **52**, 117 (1953).
10. Leland, T. W., P. S. Chappelear, and B. W. Gamson, *AIChE J.*, **8**, 482 (1962).
11. Lyckman, E. W., C. A. Eckert, and J. M. Prausnitz, *Chem. Eng. Sci.*, **20**, 703 (1965).
12. Meissner, H. P., and R. Seferian, *Chem. Eng. Progr.*, **47**, 579 (1951).
13. Riedel, L., *Chem. Ing. Tech.*, **26**, 83, 259, 679 (1954).
14. Rowlinson, J. S., *Trans. Faraday Soc.*, **51**, 1317 (1955).
15. Pitzer, K. S., D. Lippman, R. F. Curl, Jr., C. M. Huggins, and D. E. Petersen, *J. Am. Chem. Soc.*, **77**, 3433 (1955).
16. Pitzer, K. S., and G. O. Hultgren, *ibid.*, **80**, 4793 (1958).
17. Prausnitz, J. M., *AIChE J.*, **8**, 563 (1962).
18. ———, *Chem. Eng. Sci.*, **18**, 613 (1963).
19. ———, C. E. Eckert, R. V. Orye, and J. P. O'Connell, "Computer Calculations for Multicomponent Vapor-Liquid Equilibria," Prentice-Hall, Englewood Cliffs, N.J. (1967).
20. Prausnitz, J. M., and R. D. Gunn, *AIChE J.*, **4**, 430 (1958).
21. Reamer, H. H., B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **42**, 534 (1950).
22. Redlich, O., and J. N. S. Kwong, *Chem. Rev.*, **44**, 233 (1949).
23. Reid, R. C., and T. W. Leland, Jr., *AIChE J.*, **11**, 228 (1965).
24. Sage, B. H., and W. N. Lacey, "Some Properties of The Lighter Hydrocarbons, Hydrogen Sulfide and Carbon Dioxide," American Petroleum Institute (1955).
25. ———, "Thermodynamic Properties of The Lighter Paraffin Hydrocarbons and Nitrogen," American Petroleum Institute (1950).
26. Stewart, W. E., S. F. Burkhardt, and David Voo, paper presented at AIChE Kansas City Meeting (May 18, 1959).

Manuscript received January 24, 1967; revision received March 17, 1967; paper accepted March 23, 1967. Paper presented at AIChE Houston meeting.

Vapor-Liquid Equilibria at High Pressures: Calculation of Critical Temperatures, Volumes, and Pressures of Nonpolar Mixtures

P. L. CHUEH and J. M. PRAUSNITZ
University of California, Berkeley, California

An analysis of critical data for a large number of binary mixtures of normal fluids shows that the critical temperature and the critical volume can each be expressed as quadratic functions of the surface fraction. Each of these functions requires one adjustable parameter characteristic of the binary pair; for any family of chemical components, these parameters, upon suitable reduction, follow definite trends. It was shown that the surface fraction gives much better correlation than any other size-weighted variable. For the critical pressure, however, no quadratic function was adequate. To calculate critical pressures, the correlations for critical temperature and critical volume were used in conjunction with a slightly altered version of the Redlich-Kwong equation.

Generalizations to systems containing more than two components follow without additional assumptions. The methods presented in this paper provide good estimates for critical constants of multicomponent mixtures. These are particularly useful for analyzing and correlating vapor-liquid equilibria in the critical region.

The critical properties of pure fluids have received much attention and as a result of much experimental work, dating back nearly 100 years (*3*, *6*), as well as semiempirical correlations (*56*), it is now possible to make good estimates of the critical temperature, pressure, and volume of most pure fluids encountered in typical chemical engineering work. The critical properties of mixtures, however, are not known nearly as well, although experimental data are available for a surprisingly large number of binary mixtures (*58*).

Critical properties of mixtures are required in petroleum and natural gas engineering and for rational design of separation equipment and chemical reactors at high pressures.

The rising use of high pressures in chemical technology calls for increased knowledge of fluid phase behavior in the critical region. Since our primary aim is to establish thermodynamic methods for calculating vapor-liquid equilibria at high pressures, including the critical region (see preceding paper), it is essential to have available methods for estimating the critical conditions wherein the vapor phase and the liquid phase become identical.

In this work we present correlations for the critical temperatures and volumes of binary mixtures, and we present an equation-of-state method for calculating critical pressures using critical temperatures and volumes. In a very straightforward way, we generalize our results for estimating critical properties of mixtures containing any number of components. Our attention is restricted to normal fluids [as defined by Pitzer (*47*)]; that is to molecules which have zero (or small) dipole moments, no tendency to associate by hydrogen bonding or similar chemical forces, and which have sufficiently large mass to permit neglect of quantum corrections.

Several authors (*1, 14, 17, 19, 21, 22, 34, 36, 44, 45, 63, 64*) have reported correlations of the critical temperature or critical pressure of mixtures but these, by and large, have been confined to a particular chemical class of substances (usually paraffins). Very little work has been reported on the correlation of critical volumes of mixtures (*22*). While the critical volume seldom enters directly into engineering calculations, it is of more fundamental significance than the critical pressure, and it is needed to provide estimates of the very large effect of pressure on liquid phase activity coefficients in the critical region.

CRITICAL TEMPERATURES

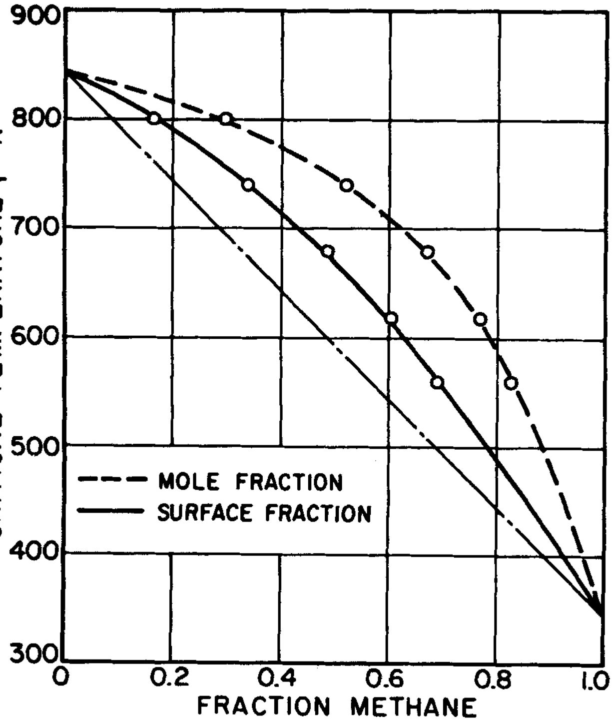

Fig. 1. Critical temperatures of the methane–*n*-pentane system as a function of mole fraction and of surface fraction.

Rowlinson (*58*) has shown that for a binary mixture of components 1 and 2, the critical temperature of the mixture is, to a good approximation, a simple quadratic function of the mole fraction, provided components 1 and 2 consist of simple, spherically symmetric molecules of nearly the same size. Rowlinson writes

$$T_{cT} = x_1 T_{c_1} + x_2 T_{c_2} + 2x_1 x_2 \Delta T_{12} \tag{1}$$

where ΔT_{12} is a known function of T_{c_1}, T_{c_2}, v_{c_1} and v_{c_2}, and a parameter which depends on the two exponents used in the potential function for describing the intermolecular forces. In addition, ΔT_{12} depends on the energy characteristic of the 1–2 interaction; it is common to assume that this characteristic energy is given by the geometric mean of the pure-component characteristic energies, but this assumption, unfortunately, can often lead to appreciable error. The important simplifying element of Rowlinson's treatment lies in his assumption of pairwise additivity of intermolecular energies; the potential energy of a multibody assembly is given by the sum of the potential energies of all nearest neighbor pairs. As a result, the critical temperature of the mixture is a quadratic function of the mole fractions. Rowlinson's treatment is not useful for mixtures whose components differ appreciably in molecular size. For such mixtures, the thermodynamic properties are quadratic functions of the mole fraction only at moderate densities (second virial coefficients); at liquid-like densities, it has been common practice to express the thermodynamic properties of such mixtures in terms of volume fractions. The critical density is intermediate between that of liquids and that wherein the second virial coefficient gives a sufficiently good approximation. We propose, therefore, to correlate experimentally determined critical temperatures as a quadratic function of the surface fraction θ defined by

$$\theta_i = \frac{x_i v_{c_i}^{2/3}}{\sum_i x_i v_{c_i}^{2/3}} \tag{2}$$

For a binary mixture, the critical temperature is given by

$$T_{cT} = \theta_1 T_{c_1} + \theta_2 T_{c_2} + 2\theta_1\theta_2 \tau_{12} \tag{3}$$

where τ_{12} is a parameter characteristic of the 1–2 interaction. Equation (3) is a one-parameter equation. By expressing the mixture's critical temperature as a function of surface fraction, we find that the quadratic term $2\theta_1\theta_2\tau_{12}$ makes a comparatively small contribution. For mixtures whose components differ very much in molecular size, the contribution of the quadratic term is smaller when surface fractions are used; it is significantly larger if the critical temperature is expressed by quadratic functions in mole fraction. To illustrate, Figure 1 shows that the critical temperatures of the methane–*n*-pentane system are more nearly linear and symmetric when plotted against surface fraction rather than mole fraction. As a result, the correlating parameter τ_{12} in Equation (3) is smaller than ΔT_{12} in Equation (1); uncertainties in τ_{12}, therefore, lead to smaller error than comparable uncertainties in ΔT_{12}. For the methane–*n*-pentane system the experimental data (*62*) are correlated by Equation (3) (using $\tau_{12} = 78.8$°K.) with an average error of 0.73%. On the other hand, the optimum fit of the data with Equation (1) (using $\Delta T_{12} = 127.8$°K.) produces an average error of 4.08%.

Equation (3) has been used to correlate the critical temperatures of sixty-five binary systems; Table 1 gives the parameters τ_{12} in reduced form for these systems. The average deviation of all experimental and fitted critical temperatures is 0.4%.

For a given family of chemical systems, the reduced parameters follow a trend which can form the basis for interpolation and cautious extrapolation. For example, for paraffin-paraffin systems (for which experimental data are most plentiful) the reduced parameter is a smooth function of the absolute value of $(T_{c_1} - T_{c_2})/(T_{c_1} + T_{c_2})$ as illustrated in Figure 2. Paraffin-olefin systems follow the same

TABLE 1. CALCULATED AND EXPERIMENTAL CRITICAL TEMPERATURES, VOLUMES, AND PRESSURES OF BINARY SYSTEMS

(Critical pressures are calculated from revised Redlich-Kwong equation)

System	Avg. Dev. in T_{CT}, %	$\frac{2\tau_{12}}{T_{c_1}+T_{c_2}}$	Avg. Dev. in v_{CT}, %	$\frac{2\nu_{12}}{v_{c_1}+v_{c_2}}$	k_{12}^*	Avg. Dev.† in P_{CT}, %	Ref.
Methane–argon	0.05	0.0044					*24*
Methane–nitrogen	0.33	0.0198	‡	−0.07	0.03	1.4, 1.7	*24, 5, 11*
Methane–oxygen	0.51	−0.0400					*24*
Methane–propane	1.39	0.1237					*1a*
Methane–propane	0.28	0.1410	1.9	−0.3653			*61*
Methane–propane	0.39	0.1775			0.02	4.9	*50*
Methane–*n*-butane	0.81	0.1826	1.4	−0.6975	0.04	5.5	*59*
Methane–iso-butane	0.45	0.1444	0.3	−0.6503	0.05	3.1	*43*
Methane–*n*-pentane	0.73	0.2378	3.4	−0.7153	0.06	2.3	*62*
Methane–iso-pentane	0.02	0.1953			0.07	3.7	*2*
Methane–*n*-heptane	3.39	0.2773	5.9	−0.9808	0.10	6.8	*54*
Acetylene–ethane	0.20	−0.0866			0.08	1.8	*33*
Acetylene–ethylene	0.84	−0.0545			0.06	2.4**	*10*
Acetylene–propane	0.62	−0.0468			0.09	5.2**	*38*
Acetylene–propylene	0.17	−0.0304			0.07	5.6**	*38*
Ethane–propane	0.13	0.0211			0	3.7**	*35*
Ethane–propylene	0.24	−0.0078	0.4	−0.1057	0	1.3	*39*
Ethane–*n*-butane	0.13	0.0267	0.8	−0.2753	0.01	1.7	*26*
Ethane–*n*-pentane	0.73	0.0438	1.0	−0.5250	0.02	3.6**	*55*
Ethane–cyclohexane	0.47	0.0695	2.9	−0.5931	0.03	3.2**	*29*
Ethane–*n*-heptane	0.61	0.0743	3.9	−0.6826	0.04	6.0	*25*
Ethylene–ethane	0.17	0.0006					*37*
Ethylene–propylene	0.14	0.0241					*23*
Ethylene–*n*-heptane	0.69	0.0799	4.8	−0.8327	0.04	10.9	*28*
Propane–*n*-butane	0.12	0.0144	1.3	−0.0061	0	1.1	*41*
Propane–*n*-pentane	0.14	0.0092			0.01	1.1**	*60*
Propane–iso-pentane	0.06	0.0088	1.1	−0.2991	0	1.4	*65*
n-Butane–nitrogen	1.80	0.3500	‡	−0.95	0.12	4.0	*57*
n-Butane–*n*-heptane	0.03	0.0192	1.9	−0.3042	0	1.1	*27*
n-Pentane–neo-pentane	0.02	0.0038					*46*
n-Pentane–*n*-hexane	0.06	0.0031					*46*
n-Pentane–cyclohexane	0.03	0.0201					*46*
n-Pentane–*n*-heptane	0.05	0.0076			0	1.4	*13*
neo-Pentane–*n*-hexane	0.09	0.0064					*46*
neo-Pentane–cyclohexane	0.05	0.0047					*46*
n-Hexane–cyclohexane	0.03	0.0013					*46*
Benzene–ethane	0.82	0.0526	3.8	−0.5588	0.03	2.6**	*31*
Benzene–propane	1.16	0.0264			0.02	2.0	*20*
Benzene–*n*-pentane	0.71	−0.0066					*46*
Benzene–neo-pentane	0.44	−0.0258					*46*
Benzene–*n*-hexane	0.14	−0.0182					*46*
Benzene–cyclohexane	0.01	−0.0128					*46*
Benzene–toluene	0.03	0.0008					*46*
Toluene–*n*-pentane	0.14	−0.0302					*46*
Toluene–*n*-hexane	0.09	−0.0028	0.0	−0.1141			*46, 66*
Toluene–cyclohexane	0.04	−0.0061					*46*
Carbon dioxide–methane	1.61	0.0472			0.07	2.4	*15*
Carbon dioxide–ethane	0.10	−0.0911					*33*
Carbon dioxide–propane	0.99	−0.0573			0.10	6.5	*48*
Carbon dioxide–propane	0.67	−0.0693	3.0	−0.3418			*52*
Carbon dioxide–*n*-butane	0.91	−0.0313					*48*
Carbon dioxide–*n*-butane	0.74	−0.0707	1.0	−0.4513	0.18	7.0	*42*
Carbon dioxide–*n*-pentane	2.42	0.0156					*48*
Carbon monoxide–argon	0.13	−0.0015					*24*
Carbon monoxide–oxygen	0.07	−0.0005					*24*
Carbon monoxide–nitrogen	0.06	−0.0054					*24*
Carbon monoxide–methane	0.16	0.0220					*24*
Carbon monoxide–propane	0.20	0.3560					*67*
Hydrogen sulfide–methane	0.84	0.0577	2.7	−0.6063	0.06	1.6	*51*
Hydrogen sulfide–ethane	0.36	−0.0683	0.5	−0.1279	0.06	1.7	*30*
Hydrogen sulfide–propane	0.04	−0.0748	1.0	−0.1746	0.08	1.2	*32*
Hydrogen sulfide–*n*-pentane	1.75	−0.0168¶	2.1	−0.5030	0.10	9.1	*53*
Hydrogen sulfide–carbon dioxide	0.14	−0.0666	0.8	−0.0760	0.08	2.1	*4*
Nitrogen–argon	0.08	0.0098					*24*
Nitrogen–oxygen	0.05	0.0163					*24*
Argon–oxygen	0.03	−0.0090					*24*

*Values of k_{12} are obtained from second virial coefficient (B_{12}) data or saturated liquid volume data of binary mixtures.

†In calculating v_{CT} and T_{CT} values of τ_{12} and ν_{12} were taken from this table unless otherwise noted.

‡No critical volumes of mixtures available for these systems. Values of ν_{12} are back-calculated from critical pressure of mixture.

**Value of ν_{12} for these systems were taken from the smoothed curves of Figure 4.

¶This parameter does not follow the trend of other hydrogen sulfide-paraffin systems shown in Figure 2.

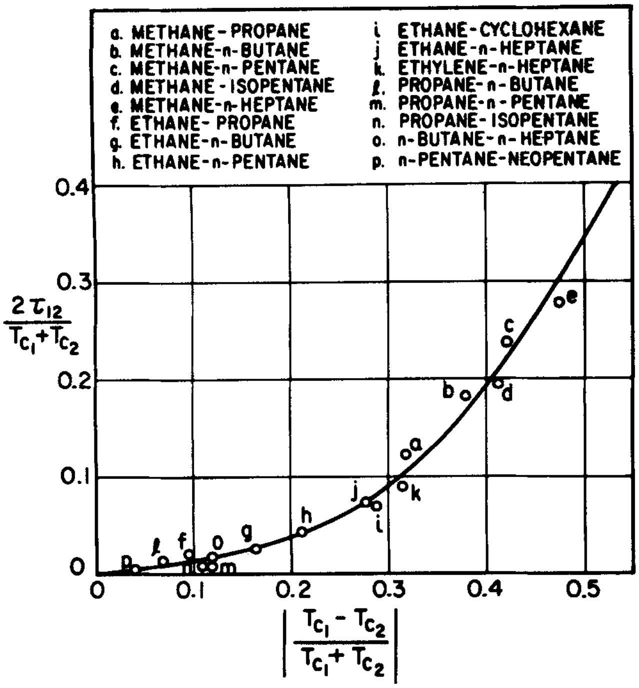

Fig. 2. Correlating parameter τ_{12} for critical temperatures of some binary systems containing satuated hydocarbons.

trend as paraffin-paraffin systems. Systems containing acetylene with a paraffin (or olefin), however, do not follow the paraffin-paraffin curve (see Table 1), due to the large quadrupole moment of acetylene. Figure 3 gives plots for paraffin-aromatic, paraffin-carbon dioxide, and paraffin-hydrogen sulfide systems.

The uncertainties in τ_{12} follow, in part, from experimental uncertainties. For example, three different investigators have reported critical temperatures for the system methane-propane. When fitted to Equation (3), we obtain $2\tau_{12}/(T_{c_1} + T_{c_2})$ equal to 0.1775 from reference *50*, 0.1410 from reference *61*, and 0.1237 from reference *1a*. When compared with experimental results for other paraffin-paraffin systems (Figure 2), it appears that the data of reference *1a* are the most reliable.

CRITICAL VOLUMES

If we utilize the simplifying assumption that the configurational thermodynamic properties of a dense system are due to two-body, nearest-neighbor interactions, we can express the critical volume of a mixture as a quadratic function of the composition. However, the composition can be specified in many ways and for components of significantly different molecular size, the mole fraction is inadequate. As for the critical temperature, we have found that the surface fraction [Equation (2)] provides the most useful measure of composition. Table 2 presents average deviations for the critical volumes of ten systems when experimental data are fitted to quadratic functions of four measures of composition: mole fraction, diameter fraction,* surface fraction, and volume fraction. The surface fraction gives the minimum deviation. The critical volume of a binary mixture therefore is written as

$$v_{cT} = \theta_1 v_{c_1} + \theta_2 v_{c_2} + 2\theta_1\theta_2 v_{12} \tag{4}$$

where v_{12} is a correlating parameter characteristic of the 1, 2 binary. Experimental data for critical volumes of binary mixtures are not nearly as plentiful as those for critical temperatures nor, because of experimental difficulties, are they as accurate. Table 1 gives the parameter v_{12} in reduced form as determined from experimental data for twenty-five systems. For these systems, Equation (4) correlated the data with an overall average deviation of 1.9%. Since accurate experimental determination of critical volumes is not simple, this deviation in many cases is of the same order as the experimental uncertainty.

TABLE 2. AVERAGE PERCENT DEVIATIONS IN CORRELATING CRITICAL VOLUMES OF BINARY MIXTURES WITH DIFFERENT WEIGHTING OF MOLECULAR SIZE*

	Type of weighting			
System	Mole fract.	Diameter fract.	Surface fract.	Volume fract.
Methane–*n*-heptane	24.27	16.79	5.89	8.06
Methane–*n*-pentane	7.50	5.09	3.43	4.86
Methane–*n*-butane	2.70	0.94	1.41	4.14
Methane–iso-butane	4.27	2.36	0.34	2.59
Ethane–benzene	6.09	5.01	3.81	3.39
Ethane–*n*-heptane	6.16	4.33	3.91	6.54
Ethane–*n*-pentane	3.34	1.70	0.97	2.97
Ethane–*n*-butane	1.56	1.03	0.80	0.89
Hydrogen sulfide–*n*-pentane	2.60	1.79	2.09	5.30
Carbon dioxide–*n*-butane	2.96	1.99	1.00	2.96

*In each case a one-parameter quadratic function is used for correlation.

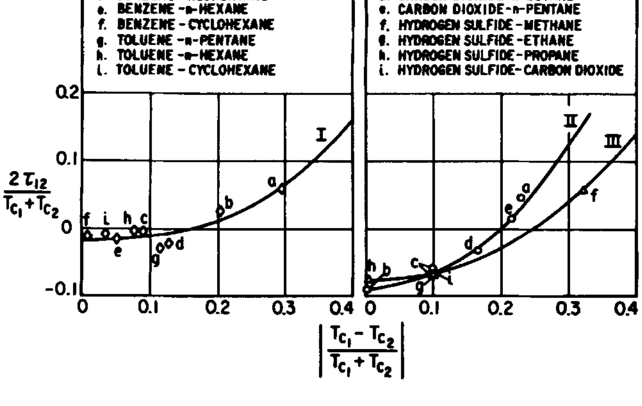

Fig. 3. Correlating parameter τ_{12} for critical temperatures of some binary systems: I. aromatic paraffin II. Carbon dioxide-paraffin III. Hydrogen sulfide-paraffin.

Figure 4 presents the reduced correlating parameter as a function of the absolute value of $(v_{c_1}^{2/3} - v_{c_2}^{2/3})/(v_{c_1}^{2/3} + v_{c_2}^{2/3})$. Definite trends can be observed for different chemical families; Figure 4, therefore, should be useful for estimating critical volumes of systems where experimental data are lacking. The paraffin-paraffin curve for v_{12} may be used for systems consisting of paraffins, olefins, and acetylenes.

CRITICAL PRESSURES

Having correlated critical temperatures and critical volumes with quadratic functions of the surface fraction, one is tempted to try a similar correlation for the critical pressure. Such a correlation was tried and failed. Previous workers (*64*) have noted that the dependence of the critical pressure on composition is much more strongly nonlinear

---

*Diameter fraction weights the mole fraction of component i with $v_{c_i}^{1/3}$.

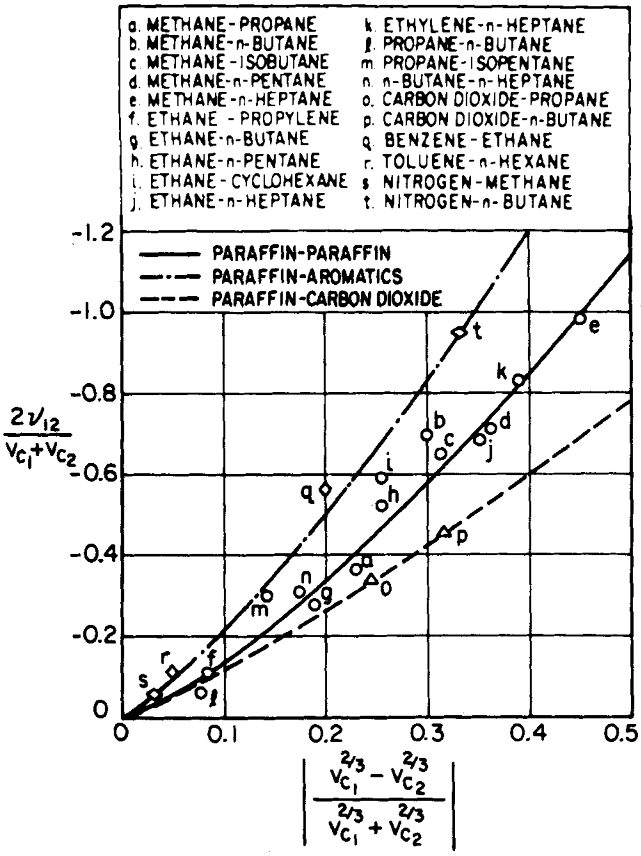

Fig. 4. Correlating parameter ν_{12} for critical volumes of some binary systems.

than that of the critical temperature and the critical volume; in many systems a plot of critical pressure vs. mole fraction shows a sharp maximum and a point of inflection. The more complicated behavior of the critical pressure follows from its nonfundamental nature; subject to well-defined assumptions, both critical temperatures and critical volumes can be related directly to the intermolecular potential, but the critical pressure can be related to the intermolecular potential only indirectly through the critical temperature and critical volume.

To express the critical pressure as a function of composition, we propose to use our correlations for critical temperature and critical volume coupled with an equation of state. We have adopted the Redlich-Kwong equation of state (*1*) with certain alterations. The Redlich-Kwong equation is

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}v(v+b)} \tag{5}$$

For a pure component, the constants a and b are related to the critical temperature and pressure of that component by

$$a = \frac{\Omega_a R^2 T_c^{2.5}}{P_c} \tag{6}$$

$$b = \frac{\Omega_b R T_c}{P_c} \tag{7}$$

The dimensionless constants Ω_a and Ω_b may be found (as is commonly done) by equating to zero the first two isothermal derivatives of pressure with respect to volume at the critical point. This procedure gives $\Omega_a = 0.4278$ and $\Omega_b = 0.0867$. To do so, however, puts a severe strain on the equation of state, leading to a value of z_c which is too large. Since any two-parameter equation of state is necessarily approximate when applied to a wide range of temperature and density, it is best to determine the dimensionless parameters Ω_a and Ω_b from experimental data available in the region of temperature and density where the equation of state is to be used. Toward that end, we have previously (*7, 9*) evaluated the parameter Ω_b for a variety of fluids from pure-component volumetric data, once for saturated liquids and once for saturated vapors. For our present purpose, we use for Ω_b for each substance the arithmetic mean of the two values obtained from saturated liquid and saturated vapor volumes. For a variety of normal fluids, this Ω_b may be represented by a function of the acentric factor ω (*47, 9*):

$$\Omega_b = 0.0867 - 0.0125\,\omega + 0.011\,\omega^2 \quad (0 \le \omega < 0.6) \tag{8}$$

To force agreement for each pure component at the critical point, Ω_a is determined by the experimental critical temperature, pressure, and volume of that component according to

$$\Omega_a = \left(\frac{RT_c}{v_c - b} - P_c\right)\frac{P_c v_c (v_c + b)}{(RT_c)^2} \tag{9}$$

where b is given by Equations (7) and (8).

To apply Equation (5) to mixtures, we require mixing rules for a and b. We propose, as before (*9*), to use

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (a_{ij} \neq \sqrt{a_{ii}a_{jj}}) \tag{10}$$

$$b = \sum_i x_i b_i \tag{11}$$

where

$$a_{ii} = \frac{\Omega_{a_i} R^2 T_{c_i}^{2.5}}{P_{c_i}} \tag{12}$$

$$b_i = \frac{\Omega_{b_i} R T_{c_i}}{P_{c_i}} \tag{13}$$

$$a_{ij} = \frac{\frac{1}{4}(\Omega_{a_i} + \Omega_{a_j}) R T_{c_{ij}}^{1.5} (v_{c_i} + v_{c_j})}{0.291 - 0.04(\omega_i + \omega_j)} \tag{14}$$

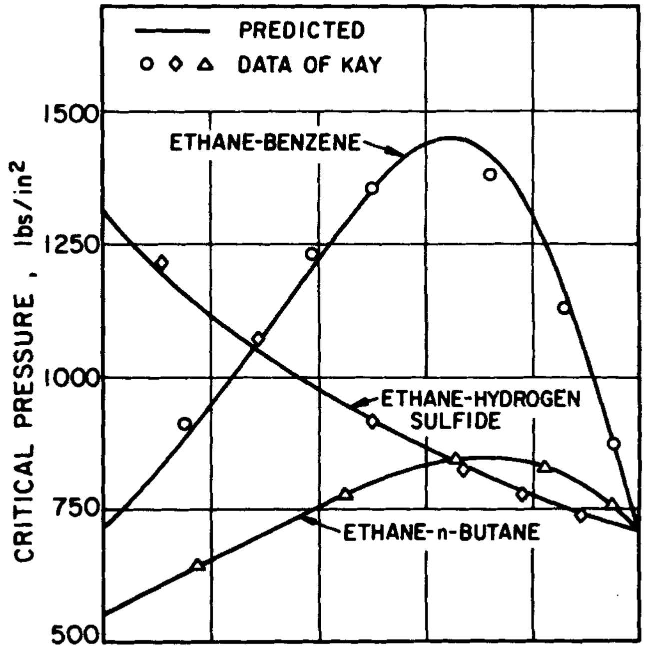

Fig. 5. Critical pressures of three binary systems containing ethane.

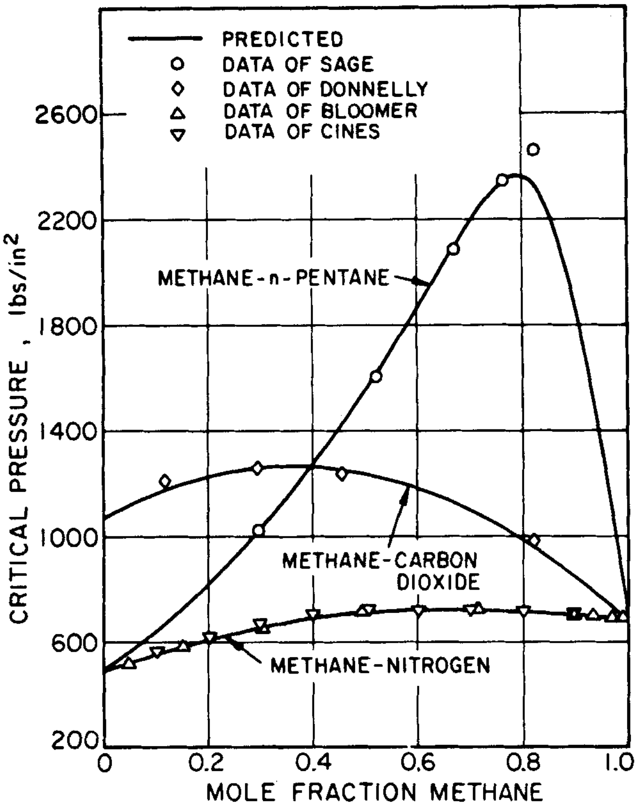

Fig. 6. Critical pressures of three binay systems containing methane.

$$T_{c_{ij}} = \sqrt{T_{c_{ii}} T_{c_{jj}}}\,(1 - k_{ij}) \tag{15}$$

The constant k_{ij} is a small number (usually positive and of the order 10^{-2} or 10^{-1}) which is characteristic of the *i-j* interaction. To a good approximation, it is independent of temperature, density, and composition; it can be determined from a variety of experimental data for the *i-j* mixture including second virial coefficients and liquid-phase properties (*8*, *9*, *16*, *49*). Table 1 gives k_{ij} for thirty-six systems as determined from *i-j* mixture data. (Critical properties of mixtures were not used.)

Using the equation of Redlich and Kwong together with the previously established correlations for critical temperatures and critical volumes, we calculated critical pressures and compared them with experimental results for the thirty-six systems listed in Table 1. The mean of the average deviations is 3.6%. In these calculations, critical temperatures and volumes of mixtures were calculated from Equations (3) and (4); experimental critical temperatures and volumes of mixtures were not used directly in the Redlich-Kwong equation.

Typical results are shown in Figure 5 for three binary systems containing ethane and in Figure 6 for three binary systems containing methane. The system ethane-hydrogen sulfide is unusual, because, unlike the behavior of most systems, the critical pressures fall below a straight line joining the pure component critical pressures.

To illustrate the importance of k_{ij}, Figure 7 gives critical pressures for the *n*-butane-nitrogen system. Experimental results are compared with two sets of calculations; in one set k_{ij} was zero and in the other it was 0.12 as found from second virial coefficient data (*49*). Figure 6 shows that marked improvements can be obtained when small corrections are applied to the (rough) rule that the temperature characteristic of the 1-2 interaction is given by the geometric mean of the pure-component critical temperatures.

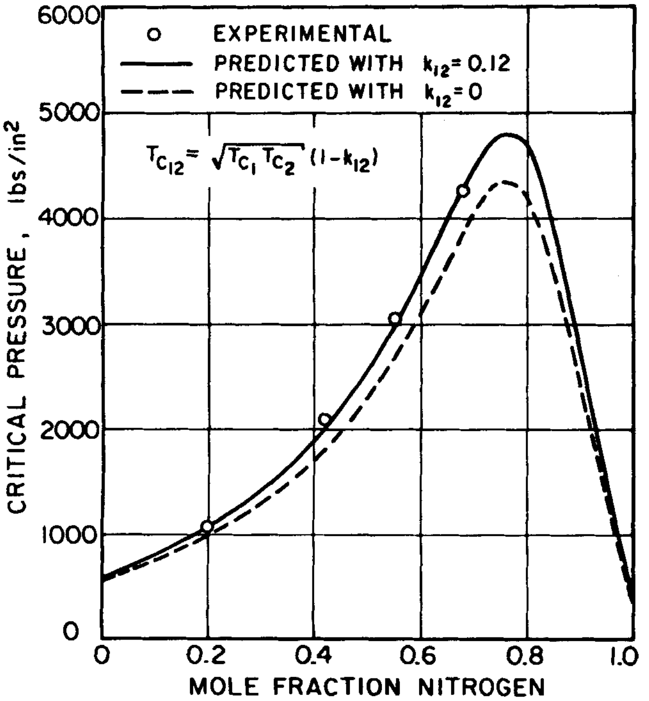

Fig. 7. Effect of correction to geometric mean on predicted critical pressures of the nitrogen–*n*-butane system. (k_{12} obtained from second virial coefficient data.)

MULTICOMPONENT SYSTEMS

Equations (3) and (4) are readily generalized to mixtures containing any number of components. The generalized equations are

$$T_{cT} = \sum_i \theta_i T_{c_i} + \sum_i \sum_j \theta_i \theta_j \tau_{ij} \tag{16}$$

$$v_{cT} = \sum_i \theta_i v_{c_i} + \sum_i \sum_j \theta_i \theta_j \nu_{ij} \tag{17}$$

where $\tau_{ii} = \nu_{ii} = 0$.

The critical pressure of a multicomponent mixture is found from the equation of state, Equation (5), with the mixing rules given by Equations (10) to (15).

For systems containing more than two components, directly measured critical temperatures and critical pressures are scarce, and directly measured critical volumes have not been reported at all. Critical constants obtained by extrapolation of vapor-liquid equilibrium (*K* factor) data are generally not reliable and in some cases may lead to large error, as pointed out by Sutton (*64*). With only directly measured experimental results, calculated and observed critical temperatures and critical pressures have been compared for six ternary systems (*12*, *18*, *19*, *40*), two quaternary systems (*19*), and two quinary systems (*19*). The average deviation for the critical temperature was 0.4% and that for the critical pressure, 4.3%. It appears therefore that the accuracy for calculating critical constants of multicomponent systems is very close to that for calculating critical constants of binary mixtures.

CONCLUSION

With the correlations presented in this work, good estimates can be made of the critical properties of a wide variety of mixtures of normal fluids (including paraffins, olefins, acetylene, aromatics, nitrogen, oxygen, carbon dioxide, and hydrogen sulfide) containing any number of components. Such estimates should be useful for technical calculations required in the petroleum, natural gas, and related industries. Since the correlations are in analytical form, they can easily be implemented in an electronic computer. Critical temperatures and critical volumes are of particular interest in establishing techniques for analyzing and correlating high-pressure vapor-liquid equilibria in the critical region, as discussed in the previous paper.

ACKNOWLEDGMENT

For financial support, the authors are grateful to the National Science Foundation, to the donors of the Petroleum Research Fund, and to the Miller Institute for Basic Science. We also thank the Computer Center, University of California, Berkeley, for the use of its facilities.

NOTATION

a, b = constants in Redlich-Kwong equation of state
k_{ij} = characteristic constant for i-j interaction
P = pressure
P_{c_i} = critical pressure of component i
P_{cT} = critical pressure of a mixture
R = gas constant
T = temperature
T_{c_i} = critical temperature of component i
$T_{c_{ij}}$ = characteristic temperature of i-j interaction
T_{cT} = critical temperature of a mixture
v = molar volume
v_{c_i} = critical volume of component i
v_{cT} = critical volume of a mixture
x = mole fraction

Greek Letters

θ = surface fraction
τ_{ij} = correlating parameter for critical temperature
ν_{ij} = correlating parameter for critical volume
ω = acentric factor
Ω_a, Ω_b = dimensionless constants in Redlich-Kwong equation, as given by Equations (9) and (8)

Subscripts

c = critical
i, ii = pure component i
ij = i-j pair
M = mixture

LITERATURE CITED

1. Ackerman, F. J., and O. Redlich, *J. Chem. Phys.*, **38**, 2740 (1963).
1a. Akers, W. W., J. F. Burns, and W. R. Fairchild, *Ind. Eng. Chem.*, **46**, 2531 (1954).
2. Amick, E. H. Jr., W. B. Johnson, and B. F. Dodge, *Chem. Eng. Progr. Symp. Ser. No. 3*, **48**, 65 (1952).
3. Andrews, T., *Phil. Trans.*, **159**, 575 (1869).
4. Bierlein, J. A., and W. B. Kay, *Ind. Eng. Chem.*, **45**, 618 (1953).
5. Bloomer, O. T., and J. D. Parent, *Chem. Eng. Progr. Symp. Ser. No. 6*, **49**, 11 (1953).
6. Cailletet, L., and E. Mathias, *Compt. Rend., Paris*, **102**, 1202 (1886); **104**, 1563 (1887).
7. Chueh, P. L., and J. M. Prausnitz, *Ind. Eng. Chem. Fundamentals*, **6**, 492 (1967).
8. ———, and J. M. Prausnitz, *AIChE J.*, **13**, 896 (1967).
9. ———, *ibid.*, **13**, 1099 (1967).
10. Churchill, S. W., W. G. Collamore, and D. L. Katz, *Oil Gas J.*, 33 (Aug. 6, 1942).
11. Cines, M. R., J. T. Roach, R. J. Hogan, and C. H. Roland, *Chem. Eng. Progr. Symp. Ser. No. 6*, **49**, 1 (1953).
12. Cota, H. M., and George Thodos, *J. Chem. Eng. Data*, **7**, 62 (1962).
13. Cummings, L. W. T., F. W. Stones, and M. A. Volante, *Ind. Eng. Chem.*, **25**, 728 (1933).
14. Davis, P. C., A. F. Bertuzzi, T. L. Gore, and F. Kurata, *J. Petrol. Technol.*, **6**, 37 (1954).
15. Donnelly, H. G., and D. L. Katz, *Ind. Eng. Chem.*, **46**, 511 (1954).
16. Eckert, C. A., H. Renon, and J. M. Prausnitz, *Ind. Eng. Chem. Fundamentals*, **6**, 58 (1967).
17. Eilerts, C. K., et al., "Phase Relations of Gas-Condensate Fluids," Vol. 1, Monograph No. 10, U.S. Bur. Mines (1957).
18. Ekiner, O., and George Thodos, *J. Chem. Eng. Data*, **11**, 457 (1966).
19. Etter, D. O., and W. B. Kay, *J. Chem. Eng. Data*, **6**, 409 (1961).
20. Glanville, J. W., B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.*, **42**, 508 (1950).
21. Grieves, R. B., and George Thodos, *AIChE J.*, **6**, 561 (1960).
22. *Ibid.*, **9**, 25 (1963).
23. Haselden, G. G., F. A. Holland, M. B. King, and R. F. Strickland-Constable, *Proc. Roy. Soc.*, (*London*), **240** 1 (1957).
24. Jones, I. W., and J. S. Rowlinson, *Trans. Faraday Soc.*, **59**, 1702 (1963).
25. Kay, W. B., *Ind. Eng. Chem.*, **30**, 459 (1938).
26. *Ibid.*, **32**, 353 (1940).
27. *Ibid.*, **33**, 590 (1941).
28. *Ibid.*, **40**, 1459 (1948).
29. ———, and R. E. Albert, *Ind. Eng. Chem.*, **48**, 422 (1956).
30. Kay, W. B., and D. B. Brice, *ibid.*, **45**, 615 (1953).
31. Kay, W. B., and T. D. Nevens, *Chem. Eng. Progr. Symp. Ser. No. 3*, **48**, 108 (1952).
32. Kay, W. B., and G. M. Rambosek, *Ind. Eng. Chem.*, **45**, 221 (1953).
33. Kuenen, J. P., *Phil. Mag.*, **44**, 174 (1897).
34. Kurata, F., and D. L. Katz, *Trans. Am. Inst. Chem. Engrs.*, **38**, 995 (1942).
35. Matschke, E., and George Thodos, *J. Chem. Eng. Data*, **7**, 232 (1962).
36. Mayfield, F. D., *Ind. Eng. Chem.*, **34**, 843 (1942).
37. McCurdy, J. L., and D. L. Katz, *ibid.*, **36**, 675 (1944).
38. ———, *Oil Gas J.*, 102 (Mar. 17, 1945).
39. McKay, R. A., H. H. Reamer, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **43**, 2112 (1951).
40. Nelson, J. M., and D. E. Holcomb, *Chem. Eng. Progr. Symp. No. 7*, **49**, 93 (1953).
41. Nysewander, C. N., B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **32**, 118 (1940).
42. Olds, R. H., H. H. Reamer, B. H. Sage, and W. N. Lacey, *ibid.*, **41**, 475 (1949).
43. Olds, R. H., B. H. Sage, and W. N. Lacey, *ibid.*, **43**, 2112 (1951).
44. Organick, E. I., *Chem. Eng. Progr. Symp. Ser. No. 6*, **49**, 81 (1953).
45. ———, and G. G. Brown, *Chem. Eng. Progr. Symp. Ser. No. 2*, **48**, 97 (1952).
46. Partington, E. J., J. S. Rowlinson, and J. F. Weston, *Trans. Faraday Soc.*, **56**, 479 (1960).
47. Pitzer, K. S., *J. Am. Chem. Soc.*, **77**, 3427, 3433 (1955).
48. Poettman, F. H., and D. L. Katz, *Ind. Eng. Chem.*, **37**, 847 (1945).
49. Prausnitz, J. M., and R. D. Gunn, *AIChE J.*, **4**, 430 (1958).
50. Reamer, H. H., B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **42**, 534 (1950).
51. *Ibid.*, **43**, 976 (1951).
52. *Ibid.*, 2515.
53. *Ibid.*, **45**, 1805 (1953).
54. ———, *J. Chem. Eng. Data*, No. 1, 29 (1956).
55. *Ibid.*, **4**, 44 (1959).
56. Reid, R. C., and T. K. Sherwood, "The Properties of Gases and Liquids," 2 ed., McGraw-Hill, New York (1966).
57. Roberts, L. R., and J. J. McKetta, *AIChE J.*, **7**, 173 (1961).
58. Rowlinson, J. S., "Liquids and Liquid Mixtures," Butterworth, London (1959).
59. Sage, B. H., B. L. Hicks, and W. N. Lacey, *Ind. Eng. Chem.*, **32**, 1085 (1940).
60. Sage, B. H., and W. N. Lacey, *ibid.*, **32**, 992 (1940).
61. ———, and J. G. Schaafsma, *ibid.*, **26**, 214 (1934).
62. Sage, B. H., H. H. Reamer, R. H. Olds, and W. N. Lacey, *ibid.*, **34**, 1108 (1942).
63. Smith, R. L., and K. M. Watson, *ibid.*, **29**, 1408 (1937).
64. Sutton, J. R., "Advances in Thermophysical Properties at Extreme Temperatures and Pressures," p. 76, Am. Soc. Mech. Engrs., New York (1965).
65. Vaughn, W. E., and F. C. Collins, *Ind. Eng. Chem.*, **34**, 885 (1942).
66. Watson, L. M., and B. F. Dodge, *Chem. Eng. Symp. Ser. No. 3*, **48**, 73 (1952).
67. Widdoes, L. C., and D. L. Katz, *Ind. Eng. Chem.*, **40**, 1742 (1948).

Manuscript received January 24, 1967; revision received March 17, 1967; paper accepted March 23, 1967. Paper presented at AIChE Salt Lake City meeting.