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The Gas-Liquid Critical Properties of Binary Mixtures

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Contents

I. Introduction

A. Scope of Article

The prediction of gas-liquid critical properties and phase behavior of nonpolar mixtures at high pressures received considerable attention at the turn of the century. This interest was superseded by new developments, and very little experimental or theoretical work was attempted until the forties. However, more recently, partly because of the increased industrial importance of high-pressure processes and particularly the widespread use of natural gas, the measurement and prediction of gas-liquid critical properties has received increased attention.

One of the simplest definitions of the gas-liquid critical point of a pure substance is a point at which the liquid phase has the same density as the gaseous phase in equilibrium with it. For a pure substance it is the state coincident with the highest pressure and temperature at which the coexistence of gaseous and liquid phases is possible. The critical state for mixtures is defined in a similar manner as for pure substances. It is the state at which two phases coexisting in equilibrium become indistinguishable from one another with reference to all their intensive properties. However, in general, for mixtures it is neither the highest pressure nor the highest temperature at which two phases may coexist in equilibrium.

The critical points found experimentally for "simple" binary mixtures have been conventionally put into two distinct categories.[1] At temperatures well below the critical temperature of the more volatile component, so-called liquid-liquid critical points are observed, which when studied as a function of composition and plotted on a p,T projection are often found to give a locus nearly parallel to the p axis. Secondly, at temperatures near the

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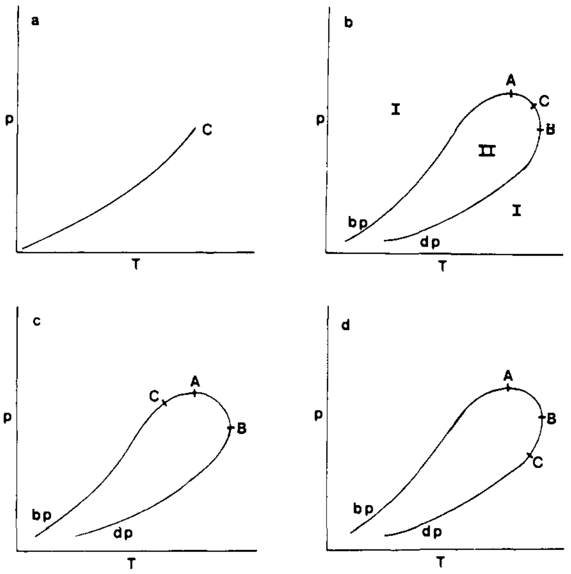

Figure 1. Phase diagrams for a pure substance and mixtures of constant composition. (a) Vapor-pressure line for a pure substance: (b–d) bubble point-dew point loci for mixtures. A, point of maximum pressure on p,T locus, cricondenbar of maxcondenbar; B, point of maximum temperature on p,T locus, cricondentherm or maxcondentherm; C, critical point; I, one-phase region; II, two-phase region; bp, bubble point; dp, dew point.

critical temperatures of the two components, gas–liquid critical points are observed, so-called because if studied as a function of composition and plotted in p,V,T space their locus passes smoothly between the gas–liquid critical points of the two pure components.

There is no absolute distinction between liquid–liquid and gas–liquid critical points for binary mixtures; they are both defined by the limits of diffusional stability. Some systems have critical points which are intermediate between liquid–liquid and gas–liquid critical points as classified above.[2]

This article will be concerned almost exclusively with those systems for which the gas–liquid critical point is a continuous function of composition. There are several reviews of the systems in which the critical point is not a continuous function of composition including the systems which exhibit so-called gas–gas immiscibility.[1,3,4] Phase diagrams for such systems have been discussed by Rowlinson[1] and Schneider.[2,3]

In this article more emphasis will be placed on the thermodynamic description and theoretical discussion of the critical locus than on detailed description of the many different types of apparatus employed in the measurement of critical properties. We shall not consider in detail the useful but purely empirical correlations used by chemical engineers. The usefulness of these correlations will decrease as more progress is made with the theoretical prediction of critical properties. We shall also omit any discussion of the critical point exponents of either pure substances or of simple binary mixtures. This topic is adequately treated elsewhere in recent reviews.[5-8]

B. Retrograde Condensation

It is desirable to point out some phenomena which occur in mixtures which do not occur in pure substances. By far the most important of these is retrograde condensation.[9,10] This phenomena is conveniently discussed in terms of pressure *vs.* temperature diagrams at fixed composition. Figure 1 shows the pressure *vs.* temperature diagram of a pure substance and a mixture at constant composition. Figure 1a is simply the vapor pressure of a pure substance curve which ends abruptly at the critical point. In Figure 1, I is a one-phase region and II the two-phase (liquid + gas) region. AC is the bubble point curve and CB the dew point curve. It is obvious that for a mixture the critical point C is neither a point of maximum pressure A nor a point of maximum temperature B on the one–two phase boundary curve. The points A and B have been given various names, but the terms cricondenbar[11] or maxcondenbar[12] and cricondentherm[11] or maxcondentherm,[12] respectively, are the most widely used. It is not necessary for the points to occur in the order ACB. The two situations illustrated in Figures 1c and 1d are also possible.

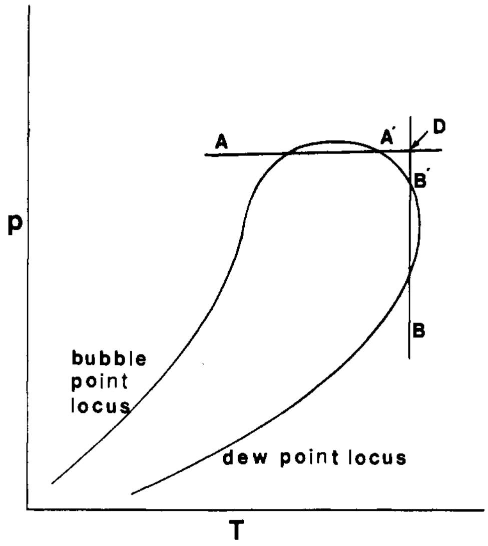

Figure 2. Diagram showing paths along which isobaric (AA′) and isothermal (BB′) retrograde vaporization/condensation occur.

Near the critical point it is possible for the mixture to exhibit unusual properties. For example, consider a mixture heated at constant pressure along the path AA′ in Figure 2. On crossing the bubble point locus into the two-phase region, a vapor phase appears which on further heating attains a maximum volume and then diminishes upon further heating until the mixture is again completely condensed. This is known as retrograde vaporization, and the reverse, a retrograde condensation, occurs when going along A′A in the opposite direction. Similarly on compressing the mixture at constant temperature along the path BB′ a liquid phase appears when the process enters the two-phase region. With increasing pressure the quantity of liquid phase first increases then diminishes until the mixture is completely vaporized again. Strictly the terms vapor and liquid are not meaningful, as the state at point D would be called liquid if reached along AA′ and vapor if approached along BB′.

Another remarkable phenomenon called the baratropic effect also occurs in some mixtures. When certain mixtures are compressed isothermally, the gaseous phase becomes more dense than the liquid phase and sinks to the bottom of the vessel. Such inversion of the phases was first found by Onnes[13] in 1906 for the helium + hydrogen system. The nitrogen + ammonia[14] system and some fluorocarbon + hydrocarbon mixtures[15] also exhibit this effect.

C. Criticality Conditions

The critical point of a pure substance is governed by the thermodynamic conditions

$$p > 0, \ (\partial p/\partial v)_T = 0 \text{ and } (\partial^2 p/\partial v^2)_T = 0 \qquad (1)$$

whereas the thermodynamic conditions for the existence of the critical state in a binary mixture are that the second and third derivatives of the molar free energy, G, with respect to composition at constant temperature and pressure must vanish. For a binary system of components 1 and 2, those conditions are given by

$$(\partial^2 G/\partial x_2^2)_{T,p} = 0 \text{ and } (\partial^3 G/\partial x_2^3)_{T,p} = 0 \qquad (2)$$

where x_2 is the mole fraction of the second component. Since all equations of state capable of describing the coexistence of liquid and gas phases at the same temperature have several roots for volume at some pressure but a unique value of pressure for every volume, it is more convenient to use v, the molar volume of the mixture, and T as the independent variables than p and T. For this reason the alternative expression of the criticality condition in terms of A, the molar Helmholtz free energy of the mixture, is generally preferred,[2] being

$$(\partial^2 A/\partial x^2)_{v,T} - (\partial^2 A/\partial x \partial v)_T{}^2/(\partial^2 A/\partial v^2)_{x,T} = 0 \qquad (3)$$

$$(\partial^3 A/\partial x^3)_{v,T} - 3(\partial^3 A/\partial x^2 \partial v)_T Q + 3(\partial^3 A/\partial x \partial v^2)_T Q^2 - (\partial^3 A/\partial v^3)_{x,T} Q^3 = 0 \qquad (4)$$

where

$$Q = (\partial^2 A/\partial x \partial v)_T/(\partial^2 A/\partial v^2)_{x,T}$$

The derivation of eq 3 and 4 from eq 2 involves the application of the standard change of constraint partial differentiation theorem. The critical points described by eq 3 and 4 may be thermodynamically stable, metastable, or unstable with respect to a separation into two or more phases at the same temperature and pressure.

The solution of eq 3 and 4 for critical points requires that we are able to evaluate over a range of volume, temperature, and composition either $A(v,T,x)$ or all of the necessary derivatives of A.

II. Experimental Methods

A. Methods for Pure Components

The experimental methods for determining critical properties of pure substances have been reviewed by Rowlinson[1] and by Kudchadker, Alani, and Zwolinski.[16]

1. Critical Temperature

The most commonly used method is the observation of the disappearance of the meniscus in a system with an overall density approximately equal to the critical.[17] If a sealed tube containing a liquid and its vapor is heated uniformly, then one of three things will happen. If the overall density is less than the critical, the meniscus will fall and eventually all the liquid will evaporate. If the overall density is greater than the critical, the meniscus will rise and eventually the liquid will completely fill the tube. However, if the density is close to the critical density, then the meniscus will rise slowly until it is near the center of the tube where it will become flat and faint and will eventually vanish at the critical temperature. There is no great need for the overall density to be exactly the critical density for measurements of moderate precision (0.1 K) since the meniscus will move up or down and vanish at a height at which the local density is equal to the critical.[16] For more precise measurements of T^c of the order of 0.01 K or better, the density must be within 1% of the critical and the tube must be well stirred and short and the final heating (or cooling) must be carried out very slowly.[16] The critical temperature, pressure, and volume can be determined from the isotherm for which $(\partial p/\partial v) = 0$.[18] However, such measurements are time consuming and do not, in general, give critical temperature as accurately as the direct observation of the disappearance or reappearance of the meniscus.

2. Critical Pressure

The critical pressure may be measured with little more trouble than the critical temperature. The most commonly used apparatus consists of a tube which is sealed at the upper end in which the sample is confined over mercury.[19,20] The pressure on the sample can be varied by a screw press and measured by a high-precision gauge or a dead weight pressure tester. This type of apparatus was originally developed by Andrews[21] and later by Young[22] and Ambrose and coworkers.[19]

3. Critical Volume

The lack of sensitivity of the temperature of disappearance of the meniscus to the overall density means that the disappearance of the meniscus cannot be used for any but the roughest measurements of critical volume. The best method for measuring critical volumes and the method most commonly used is to extrapolate the mean of the orthobaric liquid and gas densities up to the critical temperature. It can be shown that the classical description of the critical region requires that law of rectilinear diameters is true; hence the critical density should be equal to the mean of the orthobaric densities at temperatures just below the critical.[1]

This was shown to be so experimentally by Caillet and Mathias[23] who originally proposed the law of rectilinear diameters. Schneider and coworkers[24] have shown that this law holds at least up to a few thousandths of a degree from the critical temperature. This law is often applied[20,25,26] to density measurement between 3 and 50 K below the critical temperature since the mean of the orthobaric densities is almost linear in temperature. The slope of the density *vs.* temperature line is small.

B. Methods for Mixtures

For mixtures it is usual to determine the critical temperature only or the critical temperature and critical pressure together or all three critical properties in the one experiment. In contrast to work on pure substances, many different types of apparatus have been used to determine critical properties of mixtures. We shall discuss only the most commonly used methods. In many experiments[27,28] the critical properties have been determined as part of a more general study of the equilibrium ratios for vapor–liquid equilibrium. Since these methods have been discussed elsewhere, our treatment of them will be brief.

The most commonly used techniques for measuring critical properties may be divided into five types depending on the apparatus employed. These five types may be grouped in two classes depending on whether the critical composition is fixed by the initial loading of the sample or whether it is variable and determined by some method of analysis.

1. Sealed Tube Method

Critical temperatures of mixtures[29-35] may be determined from the disappearance of a meniscus on slow heating through the critical point or the reappearance of a meniscus on slow cooling. This method is completely analogous to the method used for pure substances. A typical apparatus for this method has been described by Powell, *et al.*[29] The furnace consisted of an aluminum cylinder 300 mm long and 160 mm in diameter heated by Nichrome wire, suitably lagged and enclosed in a large asbestos jacket. The sample was sealed in heavy-walled Pyrex tubes approximately 150 mm long and 1.6 mm internal diameter. The sample tubes were inserted into a vertical hole drilled down the axis of the aluminum cylinder and viewed through a small horizontal hole. The tubes were illuminated from behind by a small focused light. It is customary to note the reappearance of the meniscus as this is usually a sharper phenomenon than the disappearance.

It is possible in principle to determine critical volumes using a sealed tube technique by measuring bubble point and dew point densities as a function of temperature for mixtures for which the critical point of maximum temperature and point of maximum pressure are within 0.5 K. However the "paired tube" method[19] which is generally applicable for pure substances is not satisfactory for mixtures although it has been used.[36] For this method to be applicable, it would be necessary for liquid and vapor samples in both of the paired tubes to have the same composition which cannot occur in practice.

2. *Open-Ended Tube with Visual Observation*

Critical temperatures and/or critical pressures and/or critical volumes may be determined by measuring the bubble and dew point properties for a mixture of fixed composition near the critical point.[37-39] The bubble and dew points and critical point are determined visually.[38]

The critical volume is usually determined[40] by extrapolating the dew and bubble point volumes to the critical temperature.

A typical apparatus for such measurements has been described by Kay.[41] The sample was confined over mercury and heated by condensing vapors in a jacket surrounding the sample tube. The temperature of the condensing vapors could be varied over a limited range by changing the pressure using a simple pressure regulator. A range of organic substances enabled temperatures in the range 55–305° to be maintained constant to about 0.01°. The pressure on the sample could be varied by a screw press and measured by a gauge. A steel ball bearing moving in the sample provided adequate stirring.

The authors[39] have used a similar type of apparatus but replaced the vapor bath by an aluminum block furnace.

3. *Open-Ended Cell without Windows*

This is the same technique as in section 2 except that the dew and bubble points are determined by the change in slope of a plot of volume against pressure at a series of temperatures. The critical point is determined by construction of a smooth curve through the dew and bubble points at various compositions and then drawing the critical pressure–temperature locus and determining the points of contact.[43]

4. *Isothermal-Variable Composition Method*[44-47]

In this method the pressure exerted by a mixture at constant temperature is measured together with the gas- and liquid-phase compositions. The critical point is that point at which $(\partial p/\partial x_2)_T$ changes sign through zero (a maximum or minimum) at those temperatures where the curve exists over a limited range of composition.

5. *Isobaric-Variable Composition Method*[27]

In this method the composition of the gas and liquid phases is determined as a function of temperature at a fixed pressure. The critical temperature is determined as that point for which $(\partial T/\partial x_2)_p$ changes sign through zero at those pressures where the temperature *vs.* composition curve only exists over a limited range of composition.

It is difficult to compare the various methods in terms of reproducibility because of the difference in the range of pressure and temperature involved for different mixtures. The sealed tube method is capable of a reproducibility of approximately 0.05 K provided the tubes are filled within 3% of the critical volume, and this method is certainly the most accurate method for determining critical temperatures as a function of composition. The open-ended tube method with visual observation of the bubble and dew points is probably the best method for determining all three critical properties in the same experiment. It is capable of reproducing critical temperature, pressure, and volume to ±0.1 K, $\pm 0.02 \times 10^5$ Pa, and ±3% respectively, for simple mixtures. The variable composition isothermal and isobaric methods are, however, often used for determining equilibrium ratios as the primary objective in the same experiment as the critical properties are measured.

C. Factors Affecting the Accuracy of Measurements

1. *Mercury Vapor*

Often mercury is used as a pressure-transferring medium in apparatus used for determining critical properties. If the sample is confined above mercury at temperatures for which the vapor pressure of mercury is appreciable, the measured pressure may be considerably in error. Relatively little work has been undertaken on the effect of mercury on the gas–liquid critical properties. Firstly, there is a possibility of reaction either between mercury and the sample or a catalytic effect on slow reactions which take place in the sample. Secondly, the partial pressure of mercury may differ considerably from the vapor pressure of mercury at the same temperature. Jepson and Rowlinson[46] have discussed this problem, and Kay and coworkers[47,48] have made measurements with the sample confined over mercury and then over gallium. The vapor pressure of gallium at the critical temperatures of hydrocarbons is negligible. Kay and Pak suggested that for hydrocarbon mixtures the partial pressure of mercury could be calculated from the equation

$$\log P_{\mathrm{Hg}} = 5.92822 - 3037.6/T \qquad (5)$$

where P_{Hg} is the partial pressure of Hg in lb in.$^{-2}$.

2. *Effect of Dissolved Air*

The presence of dissolved air in a sample can give rise to two effects: (a) a reaction between the sample and the dissolved air and (b) a "multicomponent mixture" effect. Kay and coworkers[47] have shown that for pure air saturated components usually the critical pressure is most affected and often by as much as $0.2\text{–}0.3 \times 10^5$ Pa.

3. *Decomposition of the Sample*

Most substances decompose near their critical point, and it is obviously important to be sure that the decomposition or reactions of the components in a mixture are kept to a minimum and that the extent of reaction is known. The simple check of making critical property measurements on the pure components and one mixture as a function of the time the sample has been kept near the critical point can usually indicate if the decomposition is seriously affecting the measurements.

III. Theory

A. Introduction

The critical properties of mixtures may be predicted using three major assumptions.

(1) There is a hypothetical equivalent substance which has the same configurational properties as the mixture, the properties of which are determined from a "recipe" or "prescription" which is a function of composition and energy and volume parameters characterizing interactions between like and unlike molecules.

(2) The unlike energy and volume parameters can be calculated from the like energy and volume parameters by means of combining rules.

(3) The equivalent substance, mixture, and pure components obey the same reduced equation of state. That is, they are conformal or obey the principle of corresponding states. A reasonably accurate analytic form of this equation of state must be known.

Published studies[49-53] have been confined to six different equations of state of which only the Bak and Bjerre equation[54] and a double Taylor series expansion are reasonably accurate for pure substances near the critical point.[55]

B. Corresponding States for Pure Substances

The solution of the criticality conditions requires that we are able to evaluate over a range of volume, temperature, and composition either the free energy or all the necessary derivatives of free energy (see section I.C). The calculation of the total free energy of the mixture is, at our present state of knowledge, an impossible task, but by making a number of simplifying assumptions we may derive expressions for all the terms in the criticality conditions. The most important of these assumptions is that of corresponding states which we discuss for pure substances before considering for mixtures.

The principle of corresponding states[56] enables us to relate the configurational properties of one pure substance to those of another. The principle had a long empirical history[57,58] before it was given a theoretical basis[59,60] by the arguments of Pitzer and Guggenheim. If the intermolecular potential of a pure substance (1) may be related to that of a reference substance (0) by

$$u_{11}(\rho) = f_{11}u_{00}(\rho/g_{11}) \qquad (6)$$

where ρ is the intermolecular distance, $f_{11} = \epsilon_{11}/\epsilon_{00}$, and $g_{11} = \sigma_{11}/\sigma_{00}$, and ϵ_{ii} and σ_{ii} are the characteristic energy and distance, respectively, of an interaction between two molecule of species i, and, if the phase integral may be "factorized" into a molecular and configurational part, then, in classical statistical mechanics, the configurational free energies of the two substances are related by[1]

$$A_1^*(v,T) = f_{11}A_0^*(v/h_{11},T/f_{11}) - RT\ln h_{11} \qquad (7)$$

where

$$h_{11} = g_{11}^3 \qquad (8)$$

The molecular part of the phase integral is assumed to be independent of density, although a function of temperature, and so although eq 7 is applicable only to the configurational free energy, differentiation with respect to volume at constant temperature gives the principle of corresponding states in terms of pressure.

$$p_1(v,T) = (f_{11}/h_{11})\, p_0(v/h_{11},T/f_{11}) \qquad (9)$$

If the principle of corresponding states is valid, then the reducing ratios f and h may equally well be defined by the ratios of the temperature and volume at any singular point on the p,v,T surface. It is usual and particularly convenient to use the critical properties of the pure substance to define f and h, so we may write

$$f_{11} = T_{11}^{c}/T_{00}^{c} \qquad (10a)$$

$$h_{11} = V_{11}^{c}/V_{00}^{c} \qquad (10b)$$

The empirical justification and accuracy of the principle of corresponding states has been frequently considered.[1,61,62] The permanent gases are found to follow very similar reduced equations of state for their p,v,T properties[63] (except He and H_2 for which quantum effects are not negligible), but deviations tend to appear with larger, nonsymmetric, or polar molecules.[64,65]

C. Corresponding States for Mixtures

One of the basic assumptions in the derivation of the principle of corresponding states for pure substances is that the molecular part of the phase integral is independent of density. For mixtures it is also necessary to assume that it is independent of environment, that is of the adjacent molecular species, so that the contribution to the total free energy of the mixture is linear in composition.

The distinguishability of the molecular species in a mixture, quite apart from specific differences in the intermolecular potentials, contributes a term to the free energy which is not present in the phase integral for pure substances. It is usual to assume that this, the combinatorial contribution, may be factorized out separately from the configurational and molecular parts and that it is independent of density.

In a mixture the interaction between the molecules are not all described by the same intermolecular potential, although to apply corresponding states we require that they are conformal, so that they may be related to that of a common reference substance by

$$u_{ij}(\rho) = f_{ij}u_{00}(\rho/g_{ij}) \qquad (11)$$

which is a generalization of eq 6 to include interactions between unlike molecules, so that $f_{ij} = \epsilon_{ij}/\epsilon_{00}$, $g_{ij} = \sigma_{ij}/\sigma_{00}$, ϵ_{ij} and σ_{ij} being the characteristic energy and distance of the interaction of a molecule of species i with a molecule of species j.

It is not known how the configurational integral depends upon the various intermolecular interactions, and to proceed it is necessary to propose an averaging of the interactions or of the thermodynamic consequences of the individual interactions, by some model. The most general classification of the averaging processes which have been used is that which divides them into one, two, and three fluid models for binary mixtures.[66-71]

1. One-Fluid Model

In the one-fluid model the configurational free energy of the mixture is identified with that of a hypothetical pure substance, the equivalent substance, which has an intermolecular potential averaged from those in the mixture. Thus the equivalent substance reducing ratios f_{es} and h_{es} are usually functions of mixture composition. We have

$$A_m^* = A_{es}^* = f_{es}A_0^*(v/h_{es},T/f_{es}) - RT\ln h_{es} \qquad (12)$$

2. *Two-Fluid Model*

The averaging for the two-fluid model is made partly on the intermolecular interactions, and partly on the configurational free energy. The average intermolecular interaction for both molecular species is calculated and used to generate configurational free energies. These are then averaged on a mole fraction basis, so we have

$$A_m{}^* = (1-x)[f_1A_0{}^*(v/h_1,T/f_1) - RT\ln h_1] + x[f_2A_0{}^*(v/h_2,T/f_2) - RT\ln h_2] \quad (13)$$

where the average reducing ratios for species i, f_i, and h_i are usually functions of composition. An alternative, but nonequivalent, model may be defined in terms of the averaging of the configurational Gibbs free energies.

3. *Three-Fluid Model*

The averaging is made on the configurational free energies

$$A^* = (1-x)^2A_{11}{}^* + 2x(1-x)A_{12}{}^* + x^2A_{22}{}^* \quad (14)$$

where

$$A_{ij}{}^*(v,T) = f_{ij}A_0{}^*(v/h_{ij},T/f_{ij}) - RT\ln h_{ij} \quad (15)$$

An alternative form may be written by averaging the configurational Gibbs free energy.

Scott[71] has pointed out that this is a model more appropriate to gaseous densities than those of a liquid. Of the three averaging processes, the one which is most commonly used and easiest to apply to the prediction of mixture critical points is the one-fluid model.[72-75] The three-fluid model predicts that critical points, if they do occur, can only exist at absolute zero.

D. Total Free Energy of a Mixture

If we employ the one-fluid model and assume that the molecular part of the phase integral for each species is independent of both density and environment, then for the total free energy of the mixture we may write

$$A = A_{es}{}^* + A_{cb} + (1-x)A_1{}^\dagger(T) + xA_2{}^\dagger(T) \quad (16)$$

where $A_i{}^\dagger$ is the contribution of the molecular part of the phase integral to the free energy of species i, which is unaffected by the mixing process. The difference in free energy between the mixture and the separated components is then

$$A - (1-x)A_1 - xA_2 = A_{es}{}^* - (1-x)A_1{}^* - xA_2{}^* + A_{cb} \quad (17)$$

$A_1{}^\dagger$ and $A_2{}^\dagger$ having subtracted out, so that the change in free energy and the excess property depend only on the configurational free energies and A_{cb}. Similarly, the critical points are independent of $A_i{}^\dagger$ which may be shown by writing eq 16 in the alternative Gibbs free energy form

$$G = G_{es}{}^*(p,T,x) + A_{cb}(T,x) + (1-x)A_1{}^\dagger(T) + xA_2{}^\dagger(T) \quad (18)$$

Differentiation of this equation with respect to composition at constant temperature and pressure shows that the diffusional stability conditions are independent of $A_i{}^\dagger$. The critical points given by solution of the simultaneous conditions may be thermodynamically unstable, since for critical phase stability we must have[76]

$$(\partial^4G/\partial x^4)_{p,T} > 0 \quad (19)$$

but clearly this too is independent of $A_i{}^\dagger$. Similarly the boundary between stable and metastable fluid regions may be shown to be independent of A_i. Therefore, it is only necessary to consider the configurational and combinatorial contributions to the free energy of the mixture.

For a perfect gas, and an ideal liquid mixture, the combinatorial free energy of the mixture, A_{cb}, has the value

$$A_{cb} = RT\{(1-x)\ln(1-x) + x\ln x\} \quad (20)$$

When the molecules differ in size, this equation is inadequate at liquid densities. The Flory equation is more appropriate when chain molecules made up of like segments are considered[77,78]

$$A_{cb} = RT\{(1-x)\ln(1-\phi) + x\ln\phi\} \quad (21)$$

where ϕ is the volume or segment fraction of the second species, defined by

$$\phi = rx/(1-x+rx) \quad (22)$$

r being the ratio of molar volumes[79] (2:1) or the ratio of semiarbitrarily defined segments, depending upon the particular treatment.[80-81] For simplicity r should be defined so as to be independent of pressure in the region under discussion.

The Flory combinatorial free energy has been applied to discussions of many different classes of molecular species, but its validity for mixtures of globular molecules has recently been questioned. It is inapplicable to the dilute gas so that r cannot be truly independent of pressure. The effect of varying r on the predicted critical properties has been investigated by the authors.[82]

E. Prescriptions for the Equivalent Substance Parameters

The equivalent substance of the one-fluid model is characterized either by its critical properties $T_{es}{}^c$ and $V_{es}{}^c$ or by its reducing ratios f_{es} and h_{es}. Many different prescriptions have been proposed for the calculation of the critical temperature and volume (or f_{es} and h_{es}) of the equivalent substances. The prescriptions for the pseudo-critical properties of a mixture used by chemical engineers are really prescriptions for f_{es} and h_{es}. Similarly the so-called mixing rules for equation of state parameters such as

$$a_m = x_1{}^2a_{11} + 2x_1x_2a_{12} + x_2{}^2a_{22} \quad (23)$$

$$b_m = x_1{}^2b_{11} + 2x_1x_2b_{12} + x_2{}^2b_{22} \quad (24)$$

proposed by van der Waals[83] for the a and b parameters are also really prescriptions for f_{es} and h_{es}. (Since a and b are differently related to T^c and V^c in different equations of state, the rules 23 and 24 will correspond to different prescriptions of f_{es} and h_{es} for each equation of state.)

Prescriptions for f_{es} and h_{es} are usually based upon simple statistical models and are frequently intuitive rather than rigorous in their logic. Their success is judged by the quality of their predictions, the favorite testing ground in the past having been the prediction of the excess thermodynamic properties of fluid mixtures.[67-71,84] However, it may be argued that gas–liquid critical properties are superior for testing the various prescriptions.

Most prescriptions, but not all, require values of the unlike interaction reducing ratios for f_{12} and h_{12}. The estimation of these is a topic quite separate from the statistical models for f_{es} and h_{es} and will be treated in the section on combining rules.

1. *Kay Prescription*[85]

The most straightforward mixture prescription for f_{es} and h_{es} is that proposed by Kay[85] which makes a quadratic mole fraction combination of the f_{ij} and h_{ij} characteristic of each molecular interaction in the mixture. For a binary mixture we have

$$f_{es} = (1-x)^2 f_{11} + 2x(1-x)f_{12} + x^2 f_{22} \qquad (25)$$

$$h_{es} = (1-x)^2 h_{11} + 2x(1-x)h_{12} + x^2 h_{22} \qquad (26)$$

The simplicity of this particular prescription has encouraged its use when a fuller calculation would not be justified. Its use has mainly been confined to predictive methods in chemical engineering.

2. *Random Mixture Prescription*[86]

More sophisticated prescriptions than that of Kay are based upon the averaging of the intermolecular energy rather than of the reducing ratios directly. If we assume random mixing, so that the probability is x_j that a molecule in a particular position relative to a molecule of species i is of species j, then the average interaction energy of a pair of molecules in a binary mixture a distance ρ apart is given by

$$u_{es}(\rho) = (1-x)^2 u_{11}(\rho) + 2x(1-x)u_{12}(\rho) + x^2 u_{22}(\rho) \qquad (27)$$

If we assume that all the potential functions in eq 27 are conformal, and further are Lennard-Jones (12,6) potential functions[87]

$$u(\rho) = 4\epsilon[(\sigma/\rho)^{12} - (\sigma/\rho)^6] \qquad (28)$$

then we derive the random mixture prescription for f_{es} and h_{es} (eq 29 and 30). The prescription can be written

$$f_{es} = \frac{[(1-x)^2 f_{11}h_{11}^2 + 2x(1-x)f_{12}h_{12}^2 + x^2 f_{22}h_{22}^2]^2}{[(1-x)^2 f_{11}h_{11}^4 + 2x(1-x)f_{12}h_{12}^4 + x^2 f_{22}h_{22}^4]} \qquad (29)$$

$$h_{es} = \left[\frac{(1-x)^2 f_{11}h_{11}^4 + 2x(1-x)f_{12}h_{12}^4 + x^2 f_{22}h_{22}^4}{(1-x)^2 f_{11}h_{11}^2 + 2x(1-x)f_{12}h_{12}^2 + x^2 f_{22}h_{22}^2}\right]^{1/2} \qquad (30)$$

in a more general form in terms of the Lennard-Jones (m,n) potential. The random mixture overemphasizes the effect of size difference and leads to poor predictions of the excess thermodynamic properties.[1,67,69] The effect of size difference also appears in the predicted gas-liquid critical properties, and this has led to the Kay prescription being preferred by some workers.[29,30]

3. *van der Waals Prescription*

It is common practice[49,83,88] when applying the van der Waals equation to the configurational properties of mixtures to derive the values of the constants a and b for the equivalent substance by

$$a_{es} = (1-x)^2 a_{11} + 2x(1-x)a_{12} + x^2 a_{22} \qquad (31)$$

$$b_{es} = (1-x)^2 b_{11} + 2x(1-x)b_{12} + x^2 b_{22} \qquad (32)$$

This was the procedure originally suggested by van der Waals, doubtless primarily because of its simplicity, and the same form has been used for the combination of the constants a and b which appear in most closed equations of state. In the cases of the van der Waals, Dieterici,[89] and Guggenheim[90,91] equations of state, the constant a is proportional to T^cV^c and the constant b to V^c (a and b may also be written in terms of R, T^c, and p^c) so that eq 31 and 32 may equivalently be written

$$f_{es}h_{es} = (1-x)^2 f_{11}h_{11} + 2x(1-x)f_{12}h_{12} + x^2 f_{22}h_{22} \qquad (33)$$

$$h_{es} = (1-x)^2 h_{11} + 2x(1-x)h_{12} + x^2 h_{22} \qquad (34)$$

This particular prescription has been brought from the field of chemical engineering expedience (tied to particular equations of state) into the realm of theoretical significance by the work of Leland, Chappelear, and Gamson[92] who showed that it can be deduced from an expansion of the radial distribution function of a system of soft spheres about that for hard spheres. Although now separated from the van der Waals equation of state, this particular prescription has been named, somewhat confusingly, after van der Waals, and has recently been the subject of much discussion. Leland, Rowlinson, and Sather[67] showed that the leading term in size difference in a series expansion for the excess free energy of mixing, given by the van der Waals prescription, is very similar to that given by solution of the Percus-Yevick equation for soft spheres.[93] They used the van der Waals prescription together with the reference fluid proposed by Bellemans, Mathot, and Simon[94] to predict the excess thermodynamic functions of permanent gas mixtures and found it to be superior to the random mixing prescription. McGlashan[69] repeated this comparison but using the van der Waals and Guggenheim equations of state as reference fluids and came to the same conclusion—the van der Waals prescription is better than the random mixture prescription. Marsh, *et al.*,[70,84] extended this work to other equations of state.

When equal size molecules are considered, the random mixture and van der Waals prescriptions are completely equivalent. That the van der Waals model is less sensitive to size differences than the random mixture prescription may be demonstrated by series expansions of eq 30 and 33. This difference may be attributed to the different intermolecular potential assumed in each case.[67]

4. *Congruence Prescription for n-Alkane Mixtures*

Members of homologous series usually display a regular progression in their properties as their chain length is increased. The principle of congruence[95-97] exploits this regularity to calculate the properties of a mixture of members of a homologous series by supposing that the equivalent substance is also a member of the series, and further that it may be identified by

$$n_{es} = \sum_i x_i n_i \qquad (35)$$

where x_i is the mole fraction of the ith species, n_i is the chain length parameter (carbon number for the n-alkanes), and n_{es} is the chain length parameter for the equivalent substance.

Several correlation procedures for the critical temperatures and volumes of the n-alkanes as a function of carbon number have been explored[98,99] with the intention of using these for the equivalent substance. The congruence prescription is defined by

$$T_{es}^c = T_{es}^c(n_{es}) \qquad (36)$$

$$V_{es}^c = V_{es}^c(n_{es}) \qquad (37)$$

$$n_{es} = (1-x_2)n_1 + x_2 n_2 \qquad (38)$$

F. Combining Rules

All the prescriptions for f_{es} and h_{es} discussed, with the exception of the congruence prescription, require an estimate for the unlike interaction reducing ratios f_{12} and h_{12}. It may be regarded as one of the advantages of the congruence prescription that it requires no such estimate. Unlike f_{ii} and h_{ii}, the unlike interaction reducing ratios are not available from experimental measurements on pure substance critical properties representing as they do interactions which only occur in a mixture.

The estimation of f_{12} and h_{12} is not only central to the prediction of critical properties, but it is important in the calculation of the thermodynamic, transport, and surface properties of both liquid and gaseous mixtures.

Measurements on cross-term second virial coefficients, B_{12}, enable f_{12} and h_{12} to be evaluated for small spherically symmetric molecules, but such measurements have been made with the necessary accuracy and reliability[100] on very few systems. Usually because of experimental error it is possible to fit cross-term second virial coefficients with a fairly wide range of f_{12} and h_{12}. Secondly, second virial coefficients are sensitive to small deviations from corresponding states[101] and, even when the deviation has been estimated for the pure substance, the deviation for the mixture has to be decided in an arbitrary manner.

Therefore we may choose to treat f_{12} and h_{12} as adjustable parameters in the theory or use pure substance properties to estimate them *via* combining rules.

1. Combining Rules for h_{12}

We have very little theoretical idea of how h_{12} may be related to h_{11} and h_{22} except by a hard-sphere estimate, the Lorentz combining rule

$$h_{12} = \tfrac{1}{8}(h_{11}^{1/3} + h_{22}^{1/3})^3 \tag{39}$$

Occasionally the alternative arithmetic mean combining rule[49,53]

$$h_{12} = \tfrac{1}{2}(h_{11} + h_{22}) \tag{40}$$

or the geometric mean combining rule[53,101]

$$h_{12} = (h_{11}h_{22})^{1/2} \tag{41}$$

have been used. There is some evidence that the geometric mean rule is superior to the widely used Lorentz rule.[101]

2. Combining Rules for f_{12}

The most commonly used combining rule for f_{12} is the Berthelot or geometric mean rule[1]

$$f_{12} = (f_{11}f_{22})^{1/2} \tag{42}$$

It is sometimes stated[102] that eq 42 may be justified theoretically, while elsewhere[103] it is asserted that a harmonic mean rule

$$f_{12} = 2f_{11}f_{22}/(f_{11} + f_{22}) \tag{43}$$

may be derived from the London formula for dispersion forces.[104] Both these statements are equally misleading. Hudson and McCoubrey[105] have shown that elimination of polarizabilities from the London dispersion force expressions for like and unlike interactions gives

$$f_{12} = (f_{11}f_{22})^{1/2}\frac{2(I_1I_2)^{1/2}}{(I_1 + I_2)}\left[\frac{h_{11}h_{22}}{h_{12}^2}\right] \tag{44}$$

where I_i is the first ionization potential of species i, while Munn[106] has shown that the elimination of the I_i gives

$$f_{12} = \frac{2f_{11}f_{22}P_1P_2}{(f_{11}h_{11}^2P_2 + f_{22}h_{22}^2P_1)}\left[\frac{h_{11}h_{22}}{h_{12}}\right]^2 \tag{45}$$

where P_i is the polarizability of species i.

Fender and Halsey[107] have shown that eliminating polarizabilities from the Kirkwood–Muller expression[108] gives the combining rule

$$f_{12} = \frac{2f_{11}f_{22}D_1D_2}{f_{11}(h_{11}D_2)^2 + f_{22}(h_{22}D_1)^2}\left[\frac{h_{11}h_{22}}{h_{12}}\right]^2 \tag{46}$$

where D_i is the diamagnetic susceptibility of species i. Similarly, it may be shown that eliminating diamagnetic susceptibilities from the Kirkwood–Muller expression gives the Munn combining rule, as does the elimination of the effective number of outer shell electrons, z_i, from the Slater–Kirkwood formulation.[109] Elimination of polarizabilities from the Slater–Kirkwood formulation gives

$$f_{12} = \frac{2(f_{11}f_{22})^{2/3}(z_1z_2)^{1/3}(h_{11}h_{22})^{4/3}}{[(f_{11}h_{11}^2z_2^2)^{1/3} + (f_{22}h_{22}^2z_1^2)^{1/3}]h_{12}^2} \tag{47}$$

It is clear that the geometric mean rule may only be "deduced" from dispersion force theory by neglecting the terms in I_i and h_{ij} in eq 44 in which case the harmonic mean rule, deducible from eq 45 and 46 by similarly questionable methods, is equally valid as is

$$f_{12} = \frac{2(f_{11}f_{22})^{2/3}}{(f_{11})^{1/3} + (f_{22})^{1/3}} \tag{48}$$

from eq 47.

The reason why these apparently incompatible rules may be "validated" by dispersion force theory is that the last step of arbitrarily neglecting terms implies in the theories that the f_{ii} are equal, and this is the precise point at which the geometric mean rule, the harmonic mean rule, and eq 48 agree on the value of f_{12}.

The justification of the geometric mean combining rule for f_{12} is its empirical success. It is noteworthy, however, that the Hudson and McCoubrey rule gives an f_{12} which is smaller than the geometric mean whenever the I_i and h_{ii} in eq 44 differ. This suggests that the geometric mean gives an upper limit to f_{12} if the intermolecular attractive forces are dominated by dispersion forces. Possibly for this reason the harmonic mean rule, itself always smaller than the geometric mean, has been found in some cases to be an improvement on the geometric mean for f_{12}.

van der Waals proposed a geometric mean combining rule for the a in his equation of state which appears to be superior to the geometric mean in some cases[110]

$$a_{12} = (a_{11}a_{22})^{1/2} \tag{49}$$

Equation 49 is equivalent to

$$f_{12} = (f_{11}f_{22})\left(\frac{h_{11}h_{22}}{h_{12}^2}\right)^{1/2} \tag{50}$$

It can easily be shown that, if h_{12} is given by eq 39, then the van der Waals rule f_{12} always lies between the values given by the Hudson and McCoubrey and the geometric mean rule.

G. Reduced Equations of State

To solve the criticality conditions for the critical point of a binary mixture using the one-fluid model, we must assume an equation of state for the equivalent substance. The equation of state may be that of another reference substance from which we derive that of the equivalent substance by means of corresponding states, or it may be a reduced equation of state based on theory, experiment, or both. It is convenient to use a reduced equation of state

$$\tilde{p} = \tilde{p}(\tilde{v},\tilde{T})$$

as the criticality conditions are conveniently expressed throughout in terms of reduced equation of state properties.

Several different equations of state have been used to solve the criticality conditions. Here we shall briefly discuss the major inadequacies of each in turn.

1. *van der Waals Equation*

This has been widely used to solve the criticality conditions. The major disadvantage is that this equation

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \tag{51}$$

(where a and b are constants independent of temperature and volume) predicts a value of Z^c of 0.375 instead of the experimental values of ~(0.290 to 0.270). It fits neither the liquid- or vapor-phase properties well if a and b are chosen to fit the critical data.

2. *Redlich–Kwong Equation*

This equation has also been widely used to solve the criticality conditions.

$$p = RT/(v - b) - a/T^{1/2}(v + b)v \tag{52}$$

It suffers from similar disadvantages to the van der Waals equation, but if a and b are fitted to liquid-phase properties, it is more accurate than the van der Waals equation.

3. *Dieterici,[111] Kay–Redlich–Ngo,[112] and Bak and Bjerre[54] Equations of State*

These equations of state are respectively

$$p = RT/e^{a/RTv}(v - b) \tag{53}$$

$$p = 3Z^cRT/(v - b) - a/T^{1/2}(v + b)v \tag{54}$$

$$p = RT/(v - b) - a/T^{1/2}(v + \tfrac{3}{2}b)^2 \tag{55}$$

They have the advantage over the van der Waals and Redlich–Kwong equations of state that they give Z^c in better agreement with experiment. Bak and Bjerre claimed eq 55 fitted the experimental critical, liquid, and gas phase properties better than any other two parameter closed equations of state of the nine they considered.

It may be argued that it would be more correct to credit Martin[157] with this equation. He discussed several equations of state including the equation referred to above as the Bak and Bjerre equation (with minor differences in the numerical constants). Martin also suggested an equation which gives a better fit to the experimental critical, liquid, and gas phase properties.

4. *Davis and Rice Equation of State[55]*

There are two other "equations of state" which may be useful in solving the criticality conditions. The tables of compressibility factor Z as a function of reduced pressure and temperature can be regarded as an accurate nonanalytic two-parameter equation of state[113] and could be possibly used to create a analytic two-parameter equation valid in a very limited range. No work has been attempted on the application of this equation of state to critical properties.

A second accurate but very limited equation of state has been proposed by Davis and Rice.[55]

These workers wrote the reduced pressure of a one-component system in the region of its gas–liquid critical point as a Taylor series expansion in reduced temperature and reduced density, $\tilde{\rho}$, and found that two separate Taylor series were required to describe the gas and liquid single-phase regions. They tested the suggestion of Widom and Rice[114] that $(\partial^3\tilde{p}'\partial\tilde{\rho}^3)_{T^c} = 0$ and that $(\partial^4\tilde{p}/\partial\tilde{\rho}^4)_{T^c} = 0$ is discontinuous, as this would account for the existence of a cubic coexistence curve. They found that this suggestion was apparently compatible with the experimental facts and went on to evaluate the coefficients of the leading terms in the two Taylor series.

Strictly the work of Davis and Rice is not a theory of the critical point and, as they indicate, would be valid so long as there is a point within a small increment δ on each side of the critical point about which a Taylor series expansion may be made. Whatever its ultimate validity, it does give us an accurate reduced equation of state for the near-critical region.

Davis and Rice[55] derived the coefficients of their two Taylor series mainly by the method of limiting gradients, for a number of pure substances, and then recommended values of the coefficients for the "ideal" or "corresponding states" fluid of Guggenheim.[60] The authors have calculated higher terms in the series from the experimental data on argon.[99]

The Taylor series expansions appear to be valid for $\tilde{p}$ within the range $|\tilde{T} - 1| < 0.3$ and $|\tilde{\rho} - 1| < 0.3$. Almost all systems with continuous gas–liquid critical lines have those lines lying entirely within this range.

The only two difficulties caused by the restricted range of validity are, firstly, the treatment cannot be used for those cases where the gas–liquid critical line is not continuous in pTx space. Secondly, it is necessary to evaluate the configurational energy, U_{es}, to solve the criticality conditions. This requires an integration from $v = \infty$ down to $v = v$ which cannot be calculated using the Davis and Rice equation of state. Instead it has always been calculated using the Beattie–Bridgeman equation of state,[116] with the general coefficients determined by Su and Chang[117] which enables the equation of state to be written in reduced form. A small error in U_{es} does not affect the solutions to the criticality conditions to any significant extent.

IV. Solution of the Criticality Conditions

A. Approximate Solution of the Criticality Conditions

The criticality conditions have been given in section I.C; here we give an approximate and more general solution to those conditions for a one-fluid model.

Gas–liquid critical points of binary mixtures are known to be usually close to the equivalent substance critical points from experimental evidence so that Q^{-1} in eq 4 should be small at the critical point. The first-order solution uses this to simplify eq 4 by dividing throughout by Q^3 and neglecting terms multiplied by Q^{-2} and Q^{-3}. If additionally $(\partial^2A_{es}/\partial x^2)_{v,T}$ is neglected in comparison with $(\partial^2A_{cb}/\partial x^2)_{v,T}$ then we may rewrite eq 3 and 4 in the form

$$(\partial^2A_{cb}/\partial x^2)_{v,T}Q^{-1} + (\partial p/\partial x)_{v,T} = 0 \tag{56}$$

$$-3(\partial^2p/\partial x\partial v)_TQ^{-1} + (\partial^2p/\partial v^2)_{x,T} = 0 \qquad (57)$$

and

$$Q = (\partial^2A/\partial x\partial v)_T/(\partial^2A/\partial v^2)_{x,T} \qquad (58)$$

$$= (\partial p/\partial x)_{v,T}/(\partial p/\partial v)_{x,T} \qquad (59)$$

Rearranging eq 56 gives

$$(\partial p/\partial v)_{x,T} = -(\partial p/\partial x)_{v,T}{}^2/(\partial^2A_{\mathrm{cb}}/\partial x^2)_{v,T} \qquad (60)$$

An expression for $(\partial p/\partial x)_{T,v}$ may be arrived at as follows

$$A_{\mathrm{es}} = A(f_{\mathrm{es}},h_{\mathrm{es}}) \qquad (61)$$

where f_{es} and h_{es} are temperature and volume reducing parameters, respectively. Then

$$(\partial A_{\mathrm{es}}/\partial x)_{T,v} = (\partial A_{\mathrm{es}}/\partial f_{\mathrm{es}})_{T,v,h_{\mathrm{es}}}(\partial f_{\mathrm{es}}/\partial x) + (\partial A_{\mathrm{es}}/\partial h_{\mathrm{es}})_{T,v,f_{\mathrm{es}}}(\partial h_{\mathrm{es}}/\partial x) \qquad (62)$$

which may be written in short as

$$(\partial A_{\mathrm{es}}/\partial x)_{T,v} = A_ff_{\mathrm{es}}' + A_hh_{\mathrm{es}}' \qquad (63)$$

$$\therefore (\partial p/\partial x) = (\partial/\partial v(\partial A_{\mathrm{es}}/\partial x)_{T,v} = (\partial A_f/\partial v)_{T,x}f_{\mathrm{es}}' + (\partial A_h/\partial v)_{T,x}h_{\mathrm{es}}' \qquad (64)$$

From thermodynamics

$$fA_f = U = A - T(\partial A/\partial T) \qquad (65)$$

$$\therefore f(\partial A_f/\partial v)_{T,x} = (\partial A_{\mathrm{es}}/\partial v)_{T,x} - T(\partial^2A/\partial T\partial v)_x \qquad (66)$$

$$= -p - T(\partial p/\partial T)_{v,x} \qquad (67)$$

also

$$hA_h = pv - RT \qquad (68)$$

$$\therefore h(\partial A_h/\partial v)_{T,x} = p + v(\partial p/\partial v)_{T,x} \qquad (69)$$

Substituting eq 66 and 69 in eq 64

$$\frac{\partial p}{\partial x} = \frac{f_{\mathrm{es}}'}{f_{\mathrm{es}}}\left[p - T\left(\frac{\partial p}{\partial T}\right)_{v,x}\right] - \frac{h_{\mathrm{es}}'}{h_{\mathrm{es}}}\left[p + v\left(\frac{\partial p}{\partial v}\right)\right] \qquad (70)$$

Expressing $(\partial p/\partial v)_{T,x}$ as a first-order Taylor series expansion about $T = T_{\mathrm{es}}{}^{\mathrm{c}}$, $v = v_{\mathrm{es}}{}^{\mathrm{c}}$, and as $(\partial^2p/\partial v^2) = 0$ at $T = T_{\mathrm{es}}{}^{\mathrm{c}}$ $v = v_{\mathrm{es}}{}^{\mathrm{c}}$, we obtain

$$(\partial p/\partial v)_{T,x} = (\partial^2p/\partial v\partial T)(T^{\mathrm{c}} - T_{\mathrm{es}}{}^{\mathrm{c}}) \qquad (71)$$

Combining eq 20, 70, and 71 gives eq 72.

$$\left(\frac{\partial^2p}{\partial v\partial T}\right)^{\mathrm{c}}(T - T_{\mathrm{es}}{}^{\mathrm{c}}) = -\frac{x_1x_2}{RT}\left\{\frac{f_{\mathrm{es}}'}{f_{\mathrm{es}}}\left[p - T\left(\frac{\partial p}{\partial T}\right)_{v,x}\right] - \frac{h_{\mathrm{es}}'}{h_{\mathrm{es}}}\left[p + v\left(\frac{\partial p}{\partial v}\right)_{T,x}\right]\right\}\frac{(x_1 + rx_2)^2}{(x_1 + r^2x_2)} \qquad (72)$$

As a first approximation we set p, all the derivatives of p, and T except in the term $(T - T_{\mathrm{es}}{}^{\mathrm{c}})$ to their values at the equivalent substance critical point. In fact, except for $(\partial^2p/\partial vdT)$ and $T_{\mathrm{es}}{}^{\mathrm{c}}$, they refer to the critical point of the mixture. Rearranging eq 72 and setting $(\partial p/\partial v)_{T,x} = 0$ and writing T and p as $T_{\mathrm{m}}{}^{\mathrm{c}}$ and $p_{\mathrm{m}}{}^{\mathrm{c}}$, we get

$$\frac{(T_{\mathrm{m}}{}^{\mathrm{c}} - T_{\mathrm{es}}{}^{\mathrm{c}})}{T_{\mathrm{es}}{}^{\mathrm{c}}} = -x_1x_2Z_{\mathrm{es}}{}^{\mathrm{c}}\left[\frac{f_{\mathrm{es}}'}{f_{\mathrm{es}}}\left\{1 - \frac{T_{\mathrm{es}}{}^{\mathrm{c}}}{p_{\mathrm{es}}{}^{\mathrm{c}}}\left(\frac{\partial p}{\partial T}\right)^{\mathrm{c}}\right\} - \frac{h_{\mathrm{es}}'}{h_{\mathrm{es}}}\right]^2\frac{(x_1 + rx_2)^2}{(x_1 + r^2x_2)}\Bigg/\left(\frac{\partial^2\tilde{p}}{\partial\tilde{v}\partial\tilde{T}}\right)^{\mathrm{c}} \qquad (73)$$

where

$$Z_{\mathrm{es}}{}^{\mathrm{c}} = p_{\mathrm{es}}{}^{\mathrm{c}}\,V_{\mathrm{es}}{}^{\mathrm{c}}/RT_{\mathrm{es}}{}^{\mathrm{c}} \qquad (74)$$

By a Taylor series expansion

$$\frac{p_{\mathrm{m}}{}^{\mathrm{c}} - p_{\mathrm{es}}{}^{\mathrm{c}}}{p_{\mathrm{es}}{}^{\mathrm{c}}} = \frac{T_{\mathrm{m}}{}^{\mathrm{c}} - T_{\mathrm{es}}{}^{\mathrm{c}}}{T_{\mathrm{es}}{}^{\mathrm{c}}}\left(\frac{\partial \ln p_{\mathrm{es}}}{\partial \ln T}\right)_{v,x}^{\mathrm{c}} \qquad (75)$$

Although eq 73 and 75 are only approximate, they have been derived without reference to any equation of state. However, to make use of them it is necessary to assume an equation of state or evaluate the various derivatives in these equations from experimental data. If the van der Waals equation of state is assumed, eq 73 and 75 may be written as

$$T_{\mathrm{m}}{}^{\mathrm{c}} = T_{\mathrm{es}}{}^{\mathrm{c}}\left[1 + \frac{x(1 - x)}{16}\left\{3\left(\frac{f_{\mathrm{es}}'}{f_{\mathrm{es}}}\right) + \left(\frac{h_{\mathrm{es}}'}{h_{\mathrm{es}}}\right)\right\}^2\right] \qquad (76)$$

and

$$p_{\mathrm{m}}{}^{\mathrm{c}} = p_{\mathrm{es}}{}^{\mathrm{c}}\{1 + 4[(T_{\mathrm{m}}{}^{\mathrm{c}}/T_{\mathrm{es}}{}^{\mathrm{c}}) - 1]\} \qquad (77)$$

Similar approximation in eq 57 enables an expression to be derived for $V_{\mathrm{m}}{}^{\mathrm{c}}$ after eq 76 has been used to eliminate $(T_{\mathrm{m}}{}^{\mathrm{c}}/T_{\mathrm{es}}{}^{\mathrm{c}} - 1)$

$$V_{\mathrm{m}}{}^{\mathrm{c}} = V_{\mathrm{es}}{}^{\mathrm{c}}\left[1 - \frac{x(1 - x)}{8}\right]\left[\left(\frac{3f_{\mathrm{es}}'}{f_{\mathrm{es}}}\right)^2 - \left(\frac{h_{\mathrm{es}}'}{h_{\mathrm{es}}}\right)^2\right] \qquad (78)$$

B. General Solution of the Criticality Conditions

For the one-fluid model we may rewrite eq 3 and 4 as

$$(\partial^2A_{\mathrm{cb}}/\partial x^2)_{v,T} + (\partial^2A_{\mathrm{es}}/\partial x^2)_{v,T} + (\partial p/\partial x)_{v,T}Q = 0 \qquad (79)$$

$$(\partial^3A_{\mathrm{cb}}/\partial x^3)_{v,T} + (\partial^3A_{\mathrm{es}}/\partial x^3)_{v,T} + 3(\partial^2p/\partial x^2)_{v,T}Q - 3(\partial^2p/\partial x\partial v)_TQ^2 + (\partial^2p/\partial v^2)_{x,T}Q^3 = 0 \qquad (80)$$

The superscript * has been omitted from the configurational free energy of the equivalent substance for simplicity. The derivatives of A_{cb} with respect to composition may be easily calculated when a specific expression is assumed, for example, those given in section III.D.

A_{es} and hence p [*i.e.*, $(\partial A_{\mathrm{es}}/\partial v)_{x,T}$], is a function of composition solely through the reducing ratios f_{es} and h_{es}, and consequently we may write

$$(\partial A_{\mathrm{es}}/\partial x)_{v,T} = (\partial A_{\mathrm{es}}/\partial f_{\mathrm{es}})_{v,T,h_{\mathrm{es}}}(\partial f_{\mathrm{es}}/\partial x) + (\partial A_{\mathrm{es}}/\partial h_{\mathrm{es}})_{v,T,f_{\mathrm{es}}}(\partial h_{\mathrm{es}}/\partial x) \qquad (81)$$

which we may write in the short-hand form

$$(\partial A_{\mathrm{es}}/\partial x)_{v,T} = A_ff_x + A_hh_x \qquad (82)$$

where the subscripts on the right-hand side denote partial differentiation with respect to the subscripting variable and the identifying subscript "es" has been omitted. Further differentiation with respect to composition at constant temperature and volume gives expressions for the second and higher derivatives of A_{es} in terms of A_{2f}, A_{2h}, A_{fh}, etc., and f_x, f_{2x}, h_{2x}, etc. The derivatives with respect to f_{es} and h_{es} of A_{es} may be expressed in terms of standard thermodynamic functions using eq 12 by making use of the fact that if y is a function of s/t, then

$$(\partial y/\partial t)_s = -(s/t)(\partial y/\partial s)_t \qquad (83)$$

We illustrate this by deriving expressions for A_f and A_h

$$A_f = \frac{\partial}{\partial f_{\mathrm{es}}}[f_{\mathrm{es}}A_0(v/h_{\mathrm{es}},\ T/f_{\mathrm{es}}) - RT\ln h_{\mathrm{es}}] \qquad (84)$$

$$= A_0 + f_{\mathrm{es}}\frac{\partial}{\partial f_{\mathrm{es}}}[A_0(v/h_{\mathrm{es}},\ T/f_{\mathrm{es}})] \qquad (85)$$

which using eq 83 may be written

$$A_f = A_0 - T(\partial A_0/\partial T)_{v,h_{\mathrm{es}}f_{\mathrm{es}}} \qquad (86)$$

$$A_f = [A_{es} - T(\partial A_{es}/\partial T)_{v,h_{es},f_{es}}]/f_{es} \qquad (87)$$

$$= U_{es}/f_{es} \qquad (88)$$

$$A_h = \frac{\partial}{\partial h_{es}}[f_{es}A_0(v/h_{es}, T/f_{es}) - RT \ln h_{es}] \qquad (89)$$

$$= f_{es}\frac{\partial}{\partial h_{es}}[A_0(v/h_{es}, T/f_{es})] - RT/h_{es} \qquad (90)$$

Substitution for A_0 in terms of A_{es} using eq 12 gives

$$A_h = (pv - RT)/h_{es} \qquad (91)$$

Similar differentiation gives the required derivatives of A_{es} with respect to f_{es} and h_{es} up to the third order. These are set out in Table I.

Division of the derivatives of A_{es} with respect to x by RT enables them all to be written in terms of reduced variations $\tilde{p}$ $\tilde{v}$ $\tilde{T}$ and the ratios h_x/h_{es}, etc., where

$$\tilde{p} = p/p_{es}^c, \tilde{v} = v/V_{es}^c, \tilde{T} = T/T_{es}^c \qquad (92)$$

$$Z_{es}^c = (p_{es}^c V_{es}^c)/(RT_{es}^c) \qquad (93)$$

where p_{es}^c, v_{es}^c, and T_{es}^c are the critical pressure, volume, and temperature, respectively, of the equivalent substance. For example

$$(\partial A_{es}/\partial x)/RT = (U_{es}/RT)(f_x/f_{es}) + (pv/RT - 1)(h_x/h_{es}) \qquad (94)$$

If the ratios of the critical temperature and volume are used to define f and h, we have

$$(f_x/f_{es}) = (\partial T_{es}^c/\partial x)/T_{es}^c \qquad (95)$$

$$(h_x/h_{es}) = (\partial v_{es}^c/\partial x)/v_{es}^c \qquad (96)$$

$$(h_{2x}/h_{es}) = (\partial^2 v_{es}^c/\partial x^2)/v_{es}^c \qquad (97)$$

etc. We can now effectively eliminate the reference substance from our discussion and replace it by the reduced equation of state to generate $A_f/(RT)$, $A_h/(RT)$, etc. In this sense the reference substance is still present in the theory since we could choose for the reduced equation of state one determined experimentally for any suitable substance.

Equations 79 and 80 require, in addition to derivatives of A_{cb} and A_{es} with respect to x, $(\partial p/\partial x)_{v,T}$, $(\partial^2 p/\partial x^2)_{v,T}$, and $(\partial^2 p/\partial x \partial v)_T$. These may be calculated from $(\partial A_{es}/\partial x)_{v,T}$ and $(\partial^2 A_{es}/\partial x^2)_{v,T}$ by

$$(\partial p/\partial x)_{v,T} = -(\partial^2 A_{es}/\partial v \partial x)_T \qquad (98)$$

$$(\partial^2 p/\partial x^2)_{v,T} = -(\partial^3 A_{es}/\partial v \partial x^2)_T \qquad (99)$$

$$(\partial^2 p/\partial x \partial v)_T = -(\partial^3 A_{es}/\partial v^2 \partial x)_T \qquad (100)$$

and so, for example

$$(\partial p/\partial x)_{v,T} = -(\partial A_f/\partial v)_{x,T}(f_x/f_{es}) - (\partial A_h/\partial v)_{x,T}(h_x/h_{es}) \qquad (101)$$

which using A_f and A_h from Table I gives

$$\left(\frac{\partial p}{\partial x}\right)_{v,T} = \left[p - T\left(\frac{\partial p}{\partial T}\right)_{x,v}\right]\frac{f_x}{f_{es}} - \left[p + v\left(\frac{\partial p}{\partial v}\right)_{x,T}\right]\frac{h_x}{h_{es}} \qquad (102)$$

TABLE I. Derivatives of A_{es} with Respect to f_{es} and h_{es} at Constant Temperature and Volume

Derivative	Expression as derivatives of A_{es}	Expression in specific forms
$f_{es}A_f$	$A_{es} - T(\partial A_{es}/\partial T)_v$	U_{es}
$f_{es}^2A_{2f}$	$T^2(\partial^2 A_{es}/\partial T^2)_v$	$-T(\partial U_{es}/\partial T)_v$
$f_{es}^3A_{3f}$	$-3T^2(\partial^2 A_{es}/\partial T^2)_v - T^3(\partial^3 A_{es}/\partial T^3)_v$	$2T(\partial U_{es}/\partial T)_v + T^2(\partial^2 U_{es}/\partial T^2)_v$
$h_{es}A_h$	$-v(\partial A_{es}/\partial v)_T - RT$	$pv - RT$
$h_{es}^2A_{2h}$	$2v(\partial A_{es}/\partial v)_T + v^2(\partial^2 A_{es}/\partial v^2)_T + RT$	$-2pv - v^2(\partial p/\partial v)_T + RT$
$h_{es}^3A_{3h}$	$-6v(\partial A_{es}/\partial v)_T - 6v^2(\partial^2 A_{es}/\partial v^2)_T - v^3(\partial^3 A_{es}/\partial v^3)_T - 2RT$	$6pv + 6v^2(\partial p/\partial v)_T + v^3(\partial^2 p/\partial v^2)_T - 2RT$
$f_{es}h_{es}A_{fh}$	$-v(\partial A_{es}/\partial v)_T + vT(\partial^2 A_{es}/\partial v \partial T)$	$pv - vT(\partial p/\partial T)_v$
$f_{es}h_{es}^2A_{f2h}$	$2v(\partial A_{es}/\partial v)_T - 2vT(\partial^2 A_{es}/\partial v \partial T) + v^2(\partial^2 A_{es}/\partial v^2)_T - v^2T(\partial^3 A_{es}/\partial v^2 \partial T)$	$-2pv + 2vT(\partial p/\partial T)_v - v^2(\partial p/\partial v)_T + v^2T(\partial^2 p/\partial v \partial T)$
$f_{es}^2h_{es}A_{2fh}$	$-vT^2(\partial^3 A_{es}/\partial v \partial T^2)$	$vT^2(\partial^2 p/\partial T^2)_v$
Also	$U_{es} = \int_\infty^v \{T(\partial p/\partial T)_v - p\}dv$ and this expression enables the configurational energy, U_{es}, to be calculated from a p,v,T equation of state	

It has already been noted that division of the derivatives of A_{es} by RT enables them to be written in reduced form, and the same applies to the criticality conditions, which when so written may be shown to be functions solely of $(1/RT)(\partial^2 A_{cb}/\partial x^2)_{v,T}$, $(1/RT)(\partial^3 A_{cb}/\partial x^3)_{v,T}$, (f_x/f_{es}), (f_{2x}/f_{es}), (f_{3x}/f_{es}), (h_x/h_{es}), (h_{2x}/h_{es}), (h_{3x}/h_{es}). Consequently under the assumption of a particular equation of state, all mixtures, whatever their composition, with identical values of these parameters have critical points which coincide when they are written in terms of reduced variables, $\tilde{p}$, $\tilde{v}$, and $\tilde{T}$. This does not guarantee the thermodynamic stability of all such critical points for all mixtures. Usually the number of parameters can be reduced from eight if a particular form of A_{cb} is assumed, together with a prescription for f_{es} and h_{es}. Thus the ideal combinatorial free energy is a function only of x, while the Flory expression is a function of x and r. Most of the usual prescriptions for f_{es} and h_{es} enable (f_x/f_{es}), (h_x/h_{es}), etc., to be written as functions of x and the four parameters f_{22}/f_{11}, f_{12}/f_{11}, h_{22}/h_{11}, and h_{12}/h_{11}.

C. Theoretical Work on Phase Behavior

Most work on the phase equilibria of nonbinary mixtures has concentrated on vapor-liquid equilibrium or on the prediction of the gas-liquid critical points. Before the advent of modern computers, rigorous solution of the criticality conditions was impossible except in special essentially trivial cases and so an approximate first-order solution valid only for $\tilde{v}$ and $\tilde{T}$ close to unity was developed. Because of this restricted range of validity the first-order solution given in section IV.A, originally presented by Rowlinson[1] and attributed to Byers Brown, is applicable only to the prediction of simple gas-liquid critical points. It admits only one critical point at any composition, alternative roots having been suppressed in the approximations of the derivation.

1. Approximate Solutions

Equations 76, 77, and 78 have been widely used for the prediction of the gas-liquid critical points of binary mixtures, but are not particularly successful in predicting the critical pressures and volumes, although the critical temperatures given by eq 76 are reasonably close to experimental values for "simple" mixtures if reasonable prescriptions for f_{es} and h_{es} are chosen. The critical pressure loci predicted by eq 77 do not have maxima at all close to those observed experimentally, and this has prompted several workers to propose empirical modifications.

Chueh and Prausnitz[118] retained the form of eq 77 and 78, but introduced surface fractions in the place of mole fractions in f_{es} and h_{es} and empirically altered the resulting expression. It proved possible to reproduce experimental critical temperatures and pressures by the suitable choice of arbitrary parameters, but this is essentially a correlation procedure of little theoretical interest.

Kreglewski[119] adhered more closely to the form of eq 76 and 78 but introduced modifications, neglecting (h_x/h_{es}) in eq 76 and replacing the resulting coefficient of the right-hand side 9/16 by 2.2 since this gives a closer agreement with experiment when $T_{es}{}^{c}$ is taken to be linear in x. He also argued that it was more correct to consider the surface of molecules instead of merely their number when evaluating configurational properties. In a subsequent note, Kreglewski[120] modified eq 77, replacing the coefficient 4 by 5.808, this being the experimental value of $(\partial\tilde{p}/\partial\tilde{T})_{\tilde{v}}$ at the critical point of a "corresponding states" pure fluid.

In a later paper Kreglewski and Kay[103] reinstated the coefficient 9/16 in eq 76 but retained the modified, experimentally determined coefficient of eq 77. This procedure gives agreement within experimental error for both critical temperatures and pressure (if the differences in T^c's are not too large) but poor agreement for critical volumes. The modification of the coefficients could be criticized in that van der Waals equation is assumed in the derivation of eq 76 and 78 but abandoned in favor of an experimentally determined quantity in eq 77 alone. However, it should be remembered that eq 76, 77, and 78 are only approximate solutions.

2. *General Solution*

All the published methods of rigorously solving the criticality conditions assume the one-fluid model with the equivalent substance following a closed equation of state, and take A_{cb} to be given by the ideal expression, eq 20.

Spear, Robinson, and Chao[51] have presented an interesting way of solving for the critical points of a binary mixture. They assume a particular temperature and then trace the locus defined by eq 56 in the v,x plane. It has been shown by Kuenen[121] that along this locus a maximum or a minimum in pressure defines a critical state of a binary mixture, and so by evaluating the pressure along the locus, the critical volume, composition, and pressure at that temperature may be evaluated. This technique was applied to the prediction of gas–liquid critical points assuming that the equivalent substance obeyed the Redlich–Kwong equation of state, with the constants a and b of this equation being estimated for the equivalent substance by mole fraction combination of the a and b for like and unlike interactions, so that

$$a_{es} = (1 - x)^2 a_{11} + 2x(1 - x)a_{12} + x^2 a_{22}$$
$$b_{es} = (1 - x)^2 b_{11} + 2x(1 - x)b_{12} + x^2 b_{22}$$

where a_{ij} and b_{ij} are the parameters characteristic of the interaction between an i and a j molecule, the unlike interaction parameters being estimated by

$$a_{12} = \Omega(a_{11}a_{22})^{1/2} \qquad (103)$$

$$b_{12} = (b_{11}b_{22})^{1/2} \qquad (104)$$

with a_{ii} and b_{ii} calculated from the pure substance properties by the usual relationships

$$a = 0.4278R^2T^{c2.5}/p^c \qquad (105)$$

$$b = 0.0867RT^c/p^c \qquad (106)$$

Calculations were made using Ω both as unity and as an adjustable parameter. In both cases predicted critical temperatures and pressures are in reasonable agreement with experiment, but the critical volumes are not. This was not unexpected as the Redlich–Kwong equation of state does not reproduce critical volumes of pure substances well if a and b are estimated by means of eq 105 and 106.

The particular procedure employed to locate critical points in that work is not completely satisfactory as the critical temperature is assumed at the outset and the composition corresponding to this temperature is calculated. Kay and Hissong[53] have used an iterative procedure to solve the criticality conditions for a given composition, and they have predicted the gas–liquid critical points of binary mixtures using the Redlich–Kwong and Dieterici equation of states and then, in a later publication, the Redlich–Ngo equation of state. They used eq 105 and 106 together with different estimates of a_{12} and b_{12}, firstly taking both as the arithmetic mean of a_{ii} and b_{ii}, and secondly using

$$a_{12} = (a_{11}a_{22})^{1/2} \qquad (107)$$

$$b_{12} = \tfrac{1}{8}(b_{11}{}^{1/3} + b_{22}{}^{1/3})^3 \qquad (108)$$

Finally a_{12} and b_{12} were treated as adjustable parameters, being varied simultaneously to give a best fit to the experimental gas–liquid critical temperatures and pressures. The Redlich–Kwong equation was superior to the Dieterici, and the use of the arithmetic mean for a_{12} and b_{12} was found to be inferior to the use of eq 107 and 108, but again, even when the a_{12} and b_{12} were treated as adjustable parameters, the experimental critical volumes were not well reproduced.

Dalton and Barieau[52,58] have reported the use of the van der Waals equation of state for the prediction of the phase equilibria of binary mixtures, a_{es} and b_{es}, the constants of the equation for the equivalent substance, being given by eq 31, 32, 107, and 108. This work is not as yet completed, and no comparison with experiment is available, but the fundamental theory[52] and a specialized part of the critical point calculations relating to the limiting behavior of the partial molal volume as $x \rightarrow 1$ have already been reported.[88]

The most complete study of all those of the phase behavior given by the assumption of an equation of state for the equivalent substance has been made by van Konynenburg[122] for the van der Waals equation. He has shown that if complete freedom in the choice of a_{ij} and b_{ij} is allowed for both like and unlike interactions, the van der Waals equation is capable of reproducing qualitatively most of the varied types of phase behavior observed experimentally in the fluid state. The technique of solution of the criticality conditions is to write eq 79 and 80 in terms of variables reduced by the properties of component 1, so that

$$p_r = p/p_{11}{}^c,\ v_r = v/v_{11}{}^c,\ T_r = T/T_{11}{}^c \qquad (109)$$

If A_{cb} is given by the ideal combinatorial free energy of mixing, b_{12} is set equal to the arithmetic mean of b_{11} and b_{22} and eq 31 and 32 are used for a_{es} and b_{es}, the reduced criticality conditions may be shown to be a function of x and three parameters: a_{12}/a_{11}, a_{22}/a_{11}, and b_{22}/b_{11}.

Lengthy algebraic manipulation of the criticality condi-

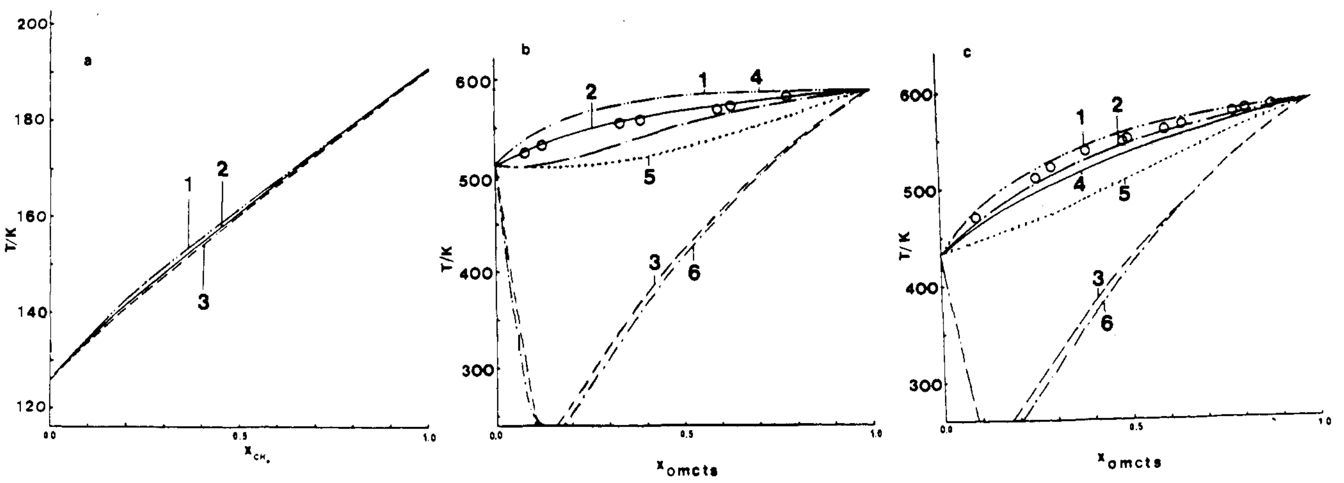

Figure 3. Comparison between critical temperatures predicted from the random mixing Kay and van der Waals prescription for the equivalent substance properties using the ideal combinatorial free energy and the first-order approximate solution.
(a) Methane + nitrogen system; the experimental points are not shown for the sake of clarity. The experimental error is such that the points straddle the lines. The Hudson-McCoubrey rule gives results virtually the same as the geometric mean rule. (b) Octamethylcyclotetrasiloxane + cyclopentane system. (c) Octamethylcyclotetrasiloxane + neopentane system. (1) van der Waals prescription, geometric mean rule. (2) Kay prescription, geometric mean rule. (3) Random mixing prescription, geometric mean rule. (4) van der Waals prescription, Hudson-McCoubrey rule. (5) Kay prescription, Hudson-McCoubrey rule. (6) Random mixing prescription, Hudson-McCoubrey rule.

tions as simultaneous equations for v_r and T_r enables an equation which is independent of T_r, of 15th order in x, eighth order in v_r, and a function of the three parameters, to be derived, together with an explicit expression for T_r as a function of v_r, x, and the three parameters. The roots of the equation for v_r may be found by scanning the value of a functional rearrangement, which is zero at a root, for successive values of v_r.

van Konynenburg calculated p,T,x phase diagrams, which he classified in a manner similar to that of Rowlinson,[1] both for $b_{22}/b_{11} = 1$ and $b_{22}/b_{11} = 2$, with a_{12}/a_{11} and a_{22}/a_{11} covering a wide range of values. It was found convenient for the presentation of results to replace the parameters b_{22}/b_{11}, a_{12}/a_{11}, and a_{22}/a_{11} by the new parameters

$$\xi = (b_{22} - b_{11})/(b_{22} + b_{11}) \tag{110}$$

$$\eta = \frac{(a_{22}/b_{22}^2 - a_{11}/b_{11}^2)}{(a_{22}/b_{22}^2 + a_{11}/b_{11}^2)} \tag{111}$$

$$\lambda = \frac{(a_{22}/b_{22}^2 + a_{11}/b_{11}^2 - 2a_{12}/(b_{11}b_{22}))}{(a_{22}/b_{22}^2 - a_{11}/b_{11}^2)} \tag{112}$$

as ξ and η must both lie in the range -1 to $+1$.

It is then possible to depict graphically the ranges of these parameters which give particular characteristic p,T,x phase diagrams. Some of these results have been described by Scott and van Konynenburg,[5,122] but no real comparison with experiment has been made in quantitative terms, it being admitted that this is poor. The purpose and importance of the work lie in its demonstration that almost the entire range of phase behavior observed experimentally can be reproduced by an equation of state as straightforward as that of van der Waals.

The solution to the criticality conditions van Konynenburg uses depends upon algebraic manipulations which are specific to the van der Waals equation. Although it is, in principle, possible to carry out analogous calculations using another equation of state, it is not certain that the elimination of temperature from the equations is feasible in all cases.

V. *Comparison of Theory and Experiment*

There are several possible variables in the theory of the critical point of mixtures such as the equation of state, the mixture prescription, the form of the combinatorial free energy, and the combining rule for f_{12} and h_{12}. Generally workers have decided, often in a rather arbitrary manner, which variables to fix and which to allow as adjustable when comparing theory and experiment. Here we attempt to fix certain of the variables in a way which is not rigorous but at least reasonable in the light of our knowledge of intermolecular forces. Unfortunately it is still not possible to choose all the variables unambiguously since a change in one variable can usually be offset by a different choice of another variable.

We shall not follow exactly the solution of the criticality conditions used by any other workers but will compare the various equations of state, combining rules, etc., used by them. Our main aim in the next three sections is to compare various choices of one of the variables under conditions where all the other variables are the same.

A. Prediction of Critical Temperatures with Various Prescriptions for the Equivalent Substance Parameters

Elsewhere[39] we have shown that the difference between the first-order solution to the criticality conditions and the more general solution is small for many mixtures provided only critical temperatures are considered.

We now consider the random mixture (eq 29 and 30), the Kay (eq 25 and 26), and the van der Waals one-fluid model (eq 33 and 34) prescriptions for the properties of the equivalent substance using the first-order approximate solution. The critical temperatures of the permanent gas mixture, methane + nitrogen, and the essentially "hydrocarbon" mixture, octamethylcyclotetrasiloxane (OMCTS) + cyclopentane and OMCTS + neopentane (as typical of mixtures for which the size difference of the component molecules is moderately large), are considered here. The Lorentz-Berthelot (geometric mean), eq 39 and 42, and Lorentz-Hudson and McCoubrey, eq 39 and 44, combining rules have been used together with the ideal combinatorial entropy. The various prescriptions are compared in Figure 3. It can be seen that the random mixing prescription is grossly in error, with either the Lorentz-Berthelot or Lorentz-Hudson and McCoubrey combining rules. Similar conclusions have been reached

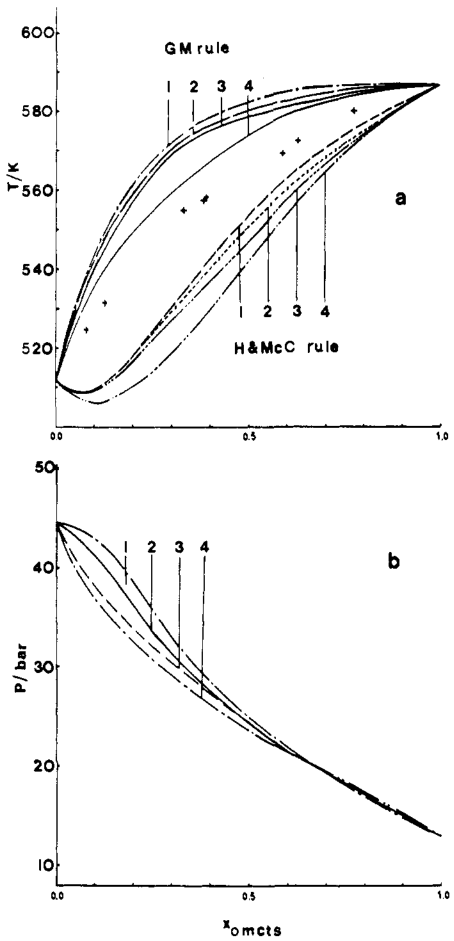

Figure 4. Critical temperature and critical pressure as a function of composition for the system octamethylcyclotetrasiloxane + cyclopentane calculated from the first-order approximate solution using various values of the size ratio, r, in the combinatorial free energy term: (a) critical temperature; (b) critical pressure. (1) r = 1, (2) r = 2, (3) r = 3, (4) r = ratio of molar volumes at 293.15 K.

by other workers[67,68,123] by comparing experimental free energies, heats, and volume of mixing near room temperature with those predicted by the random mixing prescription. The Kay and van der Waals prescriptions do not appear to be badly in error. However, unlike the van der Waals rules, the Kay rule is purely empirical and will not be considered in detail here. We shall make most of the comparisons with the van der Waals one-fluid model but will consider the Kay rule in some cases because of its widespread use in chemical engineering.

B. Comparison of Different Values of the Combinatorial Free Energy Using the van der Waals One-Fluid Model

The exact form of the combinatorial free energy fortunately has a relatively small effect on the predicted critical properties except in a few extreme cases. The predicted critical temperature and pressure of the system OMCTS + cyclopentane using various values of *r* (the ideal combinatorial free energy is given by $r = 1$) are compared in Figure 4. It can be seen that an increase in *r* always predicts a decrease in critical temperature or pressure (the dependence of critical volume on *r* is more complicated). Unfortunately, it is not possible to choose unambiguously which value of *r* is the "best" to use. While often not appreciated this problem arises in any consideration of the free energy of mixing of liquids.

C. Comparison of Various Equations of State Using the van der Waals One-Fluid Model

While the critical temperatures predicted by various equations of state are usually very similar, the predicted critical pressures vary considerably for the different equations of state. We shall use r = ratio of molar volumes at 20° and the van der Waals one-fluid model and will consider the following possibilities for equations of state and solutions.

(1) The van der Waals equation of state and the first-order solution.

(2) The van der Waals equation of state and the general solution.

(3) The Redlich-Kwong equation of state and the general solution.

(4) The Davis and Rice equation of state written as a Taylor series in density and the general solution.

(5) The Bak and Bjerre equation of state and the general solution.

Method 1 is the simplest approach and has been used by the authors in several publications.[25,31] We have also used the first-order solution but with an experimental equation of state valid at the critical point with an appreciable gain in the accuracy of prediction.[39] A similar concept was used by Kreglewski.[119] The simplicity of this method is its great advantage, as it is the only method discussed here which can be solved comfortably without the aid of a computer. Method 2 corresponds to the approach used by Scott and van Konynenburg[49,122] except that in their work the criticality conditions were solved in a different way peculiar to the van der Waals equation of state. We have verified[115] that the two approaches give identical results for several types of system including those for which p^c and T^c are not continuous single valued functions of composition. Method 3 is similar to that used by Kay and Hissong,[53] Spear, *et al.*,[51] and Joffe and Zudkevitch.[50] We do not follow exactly the same solution of the criticality conditions of these workers, however, since we wish to compare the various equations of state under the same conditions. Method 4 has only been used by the authors[39,115] and is certainly the best theoretically based method available for the prediction of critical properties provided the reduced temperature and volume of the mixture are within the range of convergence of the Taylor series. Method 5 has also only been used by the authors[39,124] and is not expected to be as good as method 4 for mixtures for which the reduced critical temperature and volume are near unity. However, method 5 should be valid over a far wider range of reduced temperature and volume than method 4.

The five methods are compared with experiment for the systems $CH_4 + N_2$, OMCTS + cyclopentane, and *n*-butane + n-heptane in Figures 5-7. As expected methods 4 and 5 are superior to the other methods, particularly in predicting the critical pressures.

Method 3 gives very similar results to method 5 which might have been expected considering the similarity between the two equations of state. In the present context the fact that the critical compressibility, as given by the Redlich-Kwong equation, is considerably larger than the experimental value appears to be no great disadvantage provided the equation of state is used in its reduced form. Earlier several workers used the equation in an unreduced form and consequently found the critical volumes so calculated were grossly in error.

The critical temperatures predicted for the methane + nitrogen system are not a good test of the five methods since the maximum difference in the calculated critical temperature for any composition is only of the order of 1

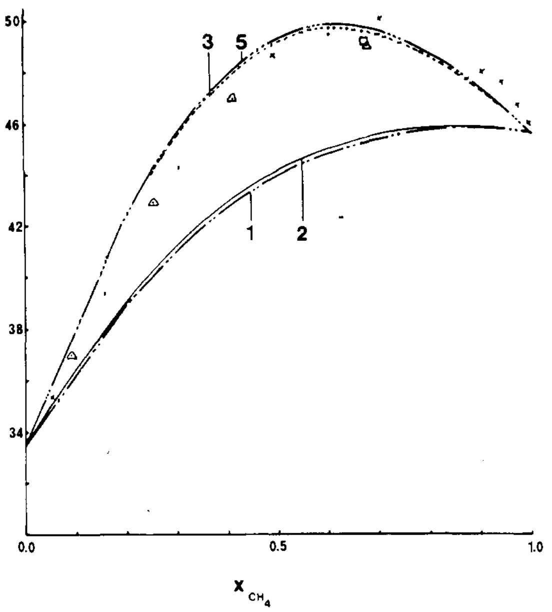

Figure 5. Comparison of the experimental critical pressures for the system methane and nitrogen with those predicted by various methods using the geometric mean rule. The numbers of the curves correspond to the numbering of the methods in the text. No results are given for method 4 since the iteration failed to find a solution: (×) exptl points of O. T. Bloomer and J. Parent, *Chem. Engr. Progr., Symp. Ser., No. 3,* **49**, 23 (1953); (□) exptl points of S. D. Chang and B. C.-Y. Lu, *ibid., No. 81,* **63**, 18 (1967); (△) exptl points of M. R. Cines, J. T. Roach, R. J. Hogan, and C. H. Roland + *ibid., No. 6,* **49**, 1 (1953).

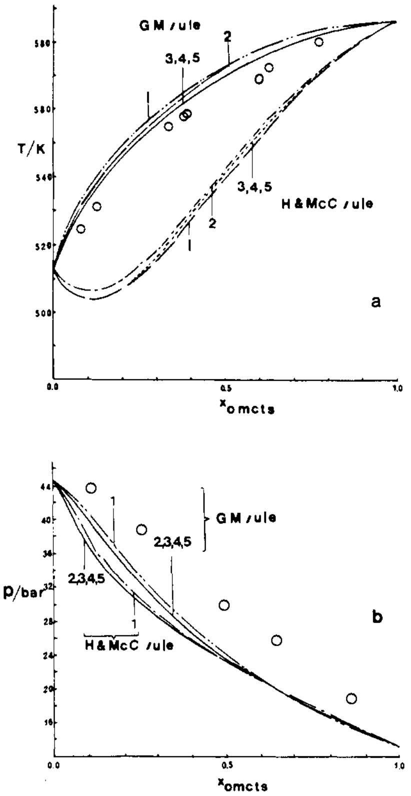

Figure 6. Comparison of experimental critical properties with those predicted by various methods using the geometric mean or the Hudson and McCoubrey combining rules for the system OMCTS and cyclopentane: (a) critical temperatures, (b) critical pressures. The numbers of the curves correspond to the numbering of the methods in the text.

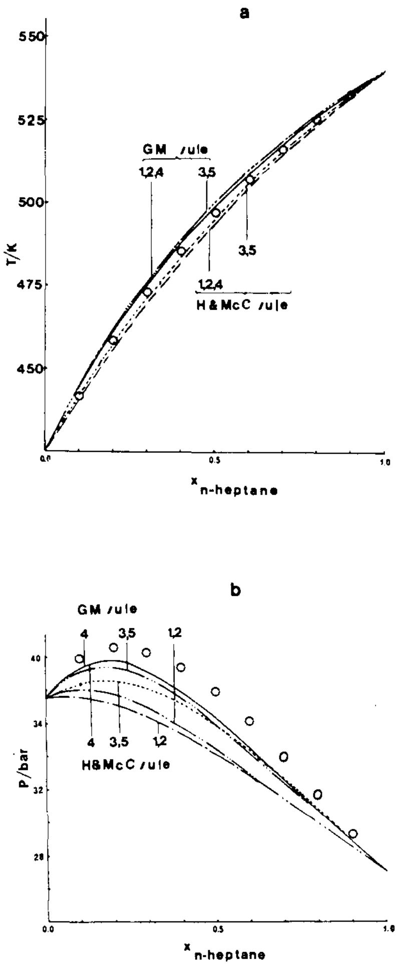

Figure 7. Comparison of experimental critical properties with those predicted by various methods using the geometric mean or Hudson and McCoubrey combining rules for the system *n*-butane and *n*-heptane: (a) critical temperatures, (b) critical pressures. The numbers of the curves correspond to the numbering of the methods in the text.

K. The difference between the predicted critical pressures using the geometric mean and the Hudson–McCoubrey combining rule is small for this system, and hence for the sake of clarity only the geometric mean rule values are shown.

D. Calculations for Binary Mixture Gas–Liquid Critical Points

In this section we shall discuss various types of mixtures, the critical properties of which have been compared with theory in the literature or in our own unpublished work. We shall only be concerned here with comparisons between theory and experiment for critical temperatures and critical pressures of binary mixtures. There are few, if any, mixtures for which the critical volumes are accurately known, and hence it is not profitable to compare experimental values with critical volumes predicted by the various methods.

1. Permanent Gas Mixtures

The critical temperatures of these mixtures have been compared with theory by Rowlinson and coworkers[67,68] and by the authors.[115] The equation of state used in the solution of the criticality conditions takes the place of a reference substance, and the mixtures which we would expect to follow most closely a particular equation of state are binaries of species which themselves are well described by the particular equation of state. In the case of the Davis and Rice Taylor series for the corresponding states fluid, the permanent gases, CH_4, N_2, A, Kr, O_2,

TABLE II. Standard Deviation, σ, between Calculated and Experimental Critical Temperatures[a]

Mixture	Method 1		Method 4		Method 5	
	GM	H-Mc	GM	H-Mc	GM	H-Mc
$CH_4 + O_2$	4.1	3.6	4.5	4.1	4.5	4.0
$CH_4 + Ar$	0.7	0.2	1.3	0.7	1.1	0.4
$CH_4 + CO$	0.5	0.5			1.0	0.9
$CH_4 + N_2$	1.0	0.8			2.1	1.8
$N_2 + O_2$	0.8	1.5			0.5	1.1
$N_2 + CO$	0.4	0.4	0.5	0.4	0.5	0.4
$Ar + O_2$	0.5	0.2	0.5	0.2	0.5	0.2
$Ar + CO$	0.3	0.4			0.4	0.3
$Ar + N_2$	0.6	0.7			0.3	0.5
$O_2 + CO$	0.2	0.4			0.3	0.2

[a] Assuming $r = 1$ except for the methane systems for which it was assumed $r = 1.15$.

CO, form a set of substances which should conform closely to this equation of state, and so binary mixtures formed from these should enable us to test the theory in general for the prediction of gas-liquid critical loci. It is unfortunate that only the critical temperatures of such mixtures have been widely studied since these, in general, provide no real test of the equation of state for simple mixtures. Critical volumes have not been measured for any of these systems, while the critical pressures have been measured for only three ($CH_4 + N_2$, $CH_4 + CO$, $N_2 + O_2$). The sources of the experimental data for mixtures which are discussed here will be found in Appendix A.

Standard deviations between the predicted and experimental critical temperature defined by

$$\sigma^2 = (\text{std dev})^2 = \sum_{i=1}^{k}(x_i^{\text{calcd}} - x_i^{\text{exptl}})^2/(k-1) \qquad (113)$$

are given in Table II. We compare the experimental values with those predicted by methods 1, 4, and 5, using the geometric mean (Berthelot) rule for f_{12} and the Lorentz rule for h_{12} together with r = unity. The standard deviations of the critical temperature for the three methods are similar, but the critical pressures are predicted more accurately by methods 4 and 5. The van der Waals prescription with method 4 or 5 together with the Lorentz-Berthelot combining rule predicts the known critical properties reasonably accurately for all the permanent gas mixtures except $CH_4 + O_2$. This particular binary would require f_{12} well below the geometric mean if agreement with experiment were to be improved by this means alone. We may separate these systems into two groups on the basis of the critical temperatures: (a) those which are predicted by f_{12} taken to be the geometric mean, *i.e.*

$$N_2 + Ar,\ N_2 + O_2, \text{ and } O_2 + CO$$

and (b) those which require f_{12} to be somewhat smaller than the geometric mean if all else remains unchanged, *i.e.*

$$\begin{array}{cccc} CH_4 + N_2 & Ar + CH_4 & O_2 + CH_4 & CO + CH_4 \\ N_2 + CO & Ar + O_2 & Ar + CO & \end{array}$$

This result agrees qualitatively with the work of Leland, Rowlinson, and Sather[67] who found that to fit the low-pressure excess (Gibbs) free energies of fluid mixtures of this type by a one-fluid model using the van der Waals prescription they required an f_{12} only 0.2% different from the geometric mean for $N_2 + Ar$ and $N_2 + O_2$. They also found f_{12} to be smaller than the geometric mean for the binaries $CH_4 + Ar$, CO_2; $N_2 + CO$; $Ar + O_2$, CO. The other two systems which they considered have not had their critical properties studied. Marsh, McGlashan, and Warr[70] have carried out a more detailed comparison than Rowlinson, *et al.*, but arrived at similar conclusions in respect of the interaction energies.

TABLE III. Comparison of ξ Obtained from the Experimental Data Interpolated to Equimolar Composition with Those Predicted by the Hudson and McCoubrey Combining Rule for *n*-Alkane + *n*-Alkane Mixtures

Mixture	Exptl	Calcd	Mixture	Exptl	Calcd
$C_2 + C_3$	1.009	0.992	$nC_5 + nC_6$	1.000	0.997
$+ nC_4$	0.990	0.975	$+ nC_7$	0.997	0.991
$+ nC_5$	0.988	0.954	$+ nC_8$	0.986	0.983
$+ nC_7$	0.892	0.908	$+ nC_9$	1.006	0.974
$+ nC_{10}$[a]	1.000	0.848	$+ nC_{10}$	1.012	0.964
			$+ nC_{11}$	1.014	0.954
$C_3 + nC_4$	1.000	0.995	$+ nC_{12}$	0.989	0.944
$+ nC_5$	0.982	0.984	$+ nC_{13}$	0.964	0.934
$+ nC_6$	0.988	0.969	$nC_6 + nC_7$	1.001	0.998
$+ nC_7$	0.968	0.951	$+ nC_8$	1.002	0.993
$+ nC_8$	0.963	0.934	$+ nC_{10}$	0.995	0.980
$+ nC_{10}$[a]	0.98	0.910	$+ nC_{14}$	1.001	0.956
			$+ nC_{16}$	1.008	0.948
$nC_4 + nC_5$	0.999	0.997	$nC_7 + nC_8$	1.001	0.999
$+ nC_6$	1.002	0.988	$nC_9 + nC_{14}$	1.006	0.990
$+ nC_7$	1.002	0.977	$nC_{10} + nC_{12}$	0.998	0.998
$+ nC_8$	1.003	0.965			
$+ nC_{10}$[a]	0.99	0.940			

[a] Experimental data only over a limited range of composition.

2. *n-Alkane + n-Alkane Mixtures (Excluding Methane Mixtures)*

These mixtures have been investigated experimentally by many workers and have been compared with theory by Kay and coworkers[48,53] and by the authors.[72,124] We have compared the experimental results with critical properties predicted by methods 1, 4, and 5 in previous publications,[72,124] and therefore we will only summarize the conclusions here. Using method 1 the agreement between predicted and experimental critical temperatures using the Lorentz-Berthelot combining rule was good except for mixtures in which the size differences were large. If the Berthelot (geometric mean) combining rule is replaced by the Hudson-McCoubrey rule, the agreement is, in general, no better. Similar behavior was observed by Knobler, *et al.*,[125] for the mixed second virial coefficients of *n*-alkane mixtures. The critical pressures are not all accurately predicted by method 1. Using methods 4 and 5 the agreement between experiment and theory for the critical temperatures is broadly similar to that obtained using method 1, but the critical pressures are predicted far more accurately by methods 4 and 5 than by method 1. The agreement for the critical temperature is fair for all the methods, while the general solution gives a more accurate prediction of critical pressures.

It is often useful to write a general form of eq 42:

$$f_{12} = \xi(f_{11}f_{22})^{1/2} \qquad (114)$$

where ξ is an adjustable parameter. Values of ξ for the *n*-alkane + *n*-alkane mixtures are given in Table III for method 1, the first-order solution.

Hicks[115] has attempted to predict critical properties of the *n*-alkane mixtures from a congruence prescription which enables the combining rules for f_{12} and h_{12} to be eliminated. The overall agreement with experiment is slightly poorer than by method 4. We have also compared the critical temperatures of *n*-alkane mixtures[126] with those predicted by the "segment" model.[127] The model is not as successful as the van der Waals one-fluid model.

3. *Branched Alkane + n-Alkane and Branched Alkane + Branched Alkane Mixtures*

Young[128] has discussed these mixtures in terms of methods 4 and 5. It appears that the critical properties of these mixtures are similar in behavior to those of the *n*-alkane + *n*-alkane mixtures.

4. *n-Alkane + Cycloalkane, n-Alkane + Benzene, and n-Alkane + Hexafluorobenzene Mixtures*

These mixtures have been discussed in some detail by the authors.[72,82,124] Similar comments to those given for the *n*-alkane + *n*-alkane mixtures apply to the cycloalkane + *n*-alkane mixtures. However, for the benzene + *n*-alkane mixtures the experimental critical temperatures agree best with those given by methods 1, 4, and 5 using the Hudson and McCoubrey combining rule instead of the Berthelot rule.[82,124] The critical pressures are predicted fairly accurately by all of the methods except for those of ethane + benzene which none of the methods discussed here predict at all accurately. The critical pressures of the systems propane + hexafluorobenzene and *n*-hexane + hexafluorobenzene have been measured,[40] but otherwise only the critical temperatures of hexafluorobenzene + *n*-alkane mixtures have been measured. A comparison of the critical temperatures of these mixtures with those predicted by methods 1, 4, and 5, indicates[82,15] that the interaction energy between unlike molecules must be weaker than either the Berthelot or Hudson and McCoubrey combining rule.

5. *Cycloalkane + Cycloalkane, Cycloalkane + Benzene, and Cycloalkane + Hexafluorobenzene Mixtures*

Only the critical temperatures of these mixtures have been studied in detail.[25,31] It appears that the unlike interaction energy parameters in these mixtures are similar to those in the corresponding *n*-alkane + cycloalkane, + benzene, and + hexafluorobenzene mixtures.

6. *Aliphatic Hydrocarbon + Aliphatic Fluorocarbon Mixtures*

The critical temperatures of such mixtures indicate a very weak interaction between unlike molecules in these systems.[31,34,40] The "best fit" values of ξ are given in Table IV for some of these mixtures together with the ξ predicted by the Hudson and McCoubrey rule. A study of the free energy, heats of mixing, and mixed second virial coefficients of such systems also indicates very weak interactions between unlike molecules.[129,130]

7. *Mixtures Containing Polydimethylsiloxanes*

The polydimethylsiloxanes have a much lower melting point than the straight-chain hydrocarbons with a similar number of carbon atoms. Even polydimethylsiloxanes with molecular weights of several hundred are stable enough for their critical properties to be studied provided certain simple precautions are taken.[131] The critical volumes of these substances are greater and the critical pressure far lower than those of most other substances stable at the critical point.

A fairly large number of mixtures containing octamethylcyclotetrasiloxane (OMCTS), a large quasi-spherical molecule, have been studied.[39,73,132] For OMCTS + hydrocarbon mixtures[73] the interaction energy between unlike molecules needed to fit the critical temperature is fairly close to that given by the van der Waals combining rule, *i.e.*, approximately half way between the geometric mean rule and the Hudson and McCoubrey combining rule. The unlike interactions in mixtures of OMCTS + hexafluorobenzene and OMCTS + perfluorocyclohexane appear to be very similar to those in hydrocarbon + hexafluorobenzene and hydrocarbon + perfluorocyclohexane mixtures.[130]

TABLE IV. Comparison of ξ Obtained from the Experimental Data Interpolated to Equimolar Composition with Those Predicted by the Hudson and McCoubrey Combining Rule for Hydrocarbon and Fluorocarbon Mixtures

Mixture		Exptl[a]	Calcd
Hexafluorobenzene	+ cyclohexane	0.95	0.999
	+ methylcyclohexane	0.96	0.999
	+ 1,4-dimethylcyclohexane	0.94_5	0.993
	+ benzene	0.96_5	0.994
	+ toluene	0.98	0.998
	+ *p*-xylene	0.97_5	0.999
	+ carbon tetrachloride	0.97_5	0.994
	+ perfluoromethylcyclohexane	0.97_5	0.964
	+ perfluoro-*n*-hexane	0.99_5	0.999
	+ *n*-pentane	0.94_5	0.999
	+ *n*-hexane	0.95_5	0.999
	+ *n*-heptane	0.95_5	0.994
	+ *n*-octane	0.95_5	0.988
	+ *n*-nonane	0.95	0.980
	+ *n*-decane	0.95	0.972
	+ *n*-dodecane	0.93_5	0.954
Perfluoro-*n*-hexane	+ *n*-hexane	0.90	0.962
	+ propane	0.86_5	0.891
Perfluoropropane	+ propane	0.89_5	0.971
Perfluoromethylcyclohexane	+ *n*-hexane	0.90_5	0.974
	+ 3-methylpentane	0.91_5	0.969
	+ 2-methylpentane	0.91	0.969
	+ 2,2-dimethylbutane	0.91_5	0.971
	+ 2,3-dimethylbutane	0.91	0.968
Perfluoro-*n*-heptane	+ ethane + propane	the approximate solution to criticality conditions is inadequate	
	+ *n*-butane	0.87	0.908
	+ *n*-pentane	0.88_5	0.934
	+ *n*-hexane	0.89_5	0.951
	+ *n*-heptane	0.90	0.962
	+ *n*-octane	0.92	0.969
	+ *n*-nonane	0.92_5	0.973
Perfluorocyclohexane[b]	+ cyclopentane	0.90	0.980
	+ cyclohexane	0.90	0.991
	+ cycloheptane	0.88	0.997
	+ cyclooctane	0.85	1.000
	+ cyclopentane	0.95	0.994
	+ cycloheptane	0.95	1.000

[a] Some of the ξ values differ slightly from those given in the original literature. This arises because (i) a value of $r = 1$ has been used here whereas in some publications r has been taken as the ratio of the molar volumes, and (ii) the interpolation to equimole fraction has been carried differently. [b] The ionization potential of perfluorocyclohexane is not known, and the ξ values have been estimated assuming both ionization potentials are equal. However, the effect is small and could not account for the major part of the estimated discrepancy between experimental and predicted values.

The critical pressures of OMCTS + hydrocarbon mixtures are not predicted accurately by any of the methods outlined in section V.C.

The critical temperatures of mixtures of linear polydi-

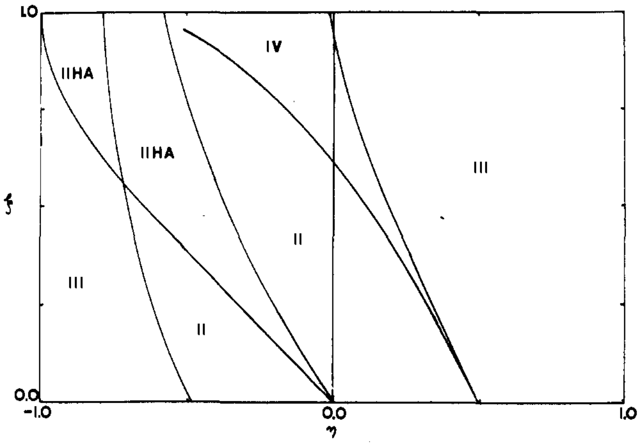

Figure 8. Types of phase behavior for mixtures obeying the van der Waals equation of state and eq 49.

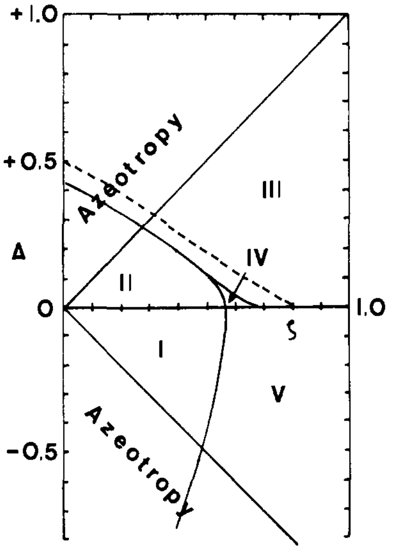

Figure 9. The critical lines of a binary van der Waals mixture of molecules of equal sizes. The five major regions of characteristics p,T phase diagrams are separated by the full lines. The area corresponding to type III has been subdivided into two regions depending on whether there is a minimum and maximum in one of the critical lines (type IIIa and type IIIb) or not (type IIIc and type IIId).

methylsiloxanes have been studied, and the results indicate that these mixtures are similar to n-alkane + n-alkane mixtures in their critical behavior as might be expected.

8. *n-Alkane + Acetone Mixtures*

Relatively little work has been undertaken on the interpretation of critical data of mixtures more complex than those mentioned above. One of the authors (C.L.Y.) has compared experimental values for the acetone + n-alkane mixtures with values predicted by the methods discussed above. In general, the values of ξ needed to fit the critical temperature data are less than the geometric mean or Hudson–McCoubrey rule. This almost certainly arises because of the dipolar nature of acetone.

VI. Concluding Remarks

A. Location of All Critical Points

The only published study of the location of other types of critical loci using the van der Waals one-fluid model is that given by Scott and van Konynenburg[5,49,122] which extended earlier work started by van der Waals but never completed satisfactorily. The major problem is basically one of finding solutions to equations in reasonable computer time. While Scott and van Konynenburg's work is only qualitative since it is based on the van der Waals equation of state, it will be discussed briefly here as it is useful in showing a relationship between various types of phase behavior exhibited by mixtures of nonpolar substances.

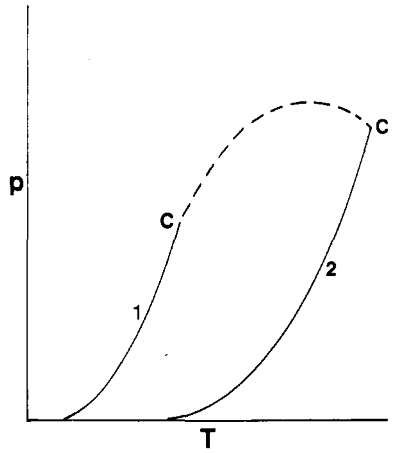

Figure 10. Type I phase behavior: 1, vapor pressure curve of component I; 2, vapor pressure curve of component II; ${}^{\mathrm{l}}\mathrm{c}$, critical point of pure component; - - - -, critical loci; ucep, upper critical end point; lcep, lower critical end point; L–L, liquid–liquid critical line; L–L–G, liquid–gas equilibrium line.

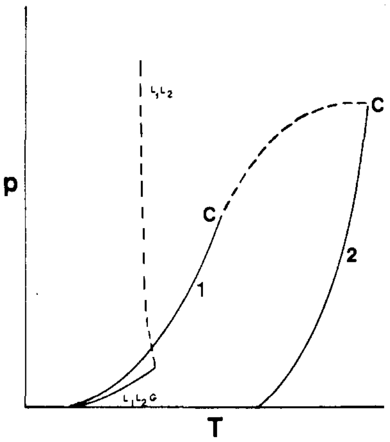

Figure 11. Type II phase behavior. Legend as for Figure 10.

van Konynenburg[122] was able to divide up all mixtures into five basic types which occurred for certain ranges of ξ, η, and λ defined by eq 110, 111, and 112. These five basic types can be further subdivided if azeotropes occur on the critical loci. Figure 8 gives the basic divisions of ξ, λ space for the case where $a_{12} = (a_{11}a_{22})^{1/2}$ (*i.e.*, eq 49 or 50), and Figure 9 gives the basic divisions of Δ, ζ space for mixtures of molecules of similar size where

$$\Delta = \frac{a_{11} + a_{22} - 2a_{12}}{a_{11} + a_{22}} \qquad (115)$$

$$\zeta = \frac{a_{22} - a_{11}}{a_{11} + a_{22}} \qquad (116)$$

It is convenient to discuss the projection of the p,T,x diagram on the p,T surface rather than the three-dimensional diagram. Figures 10–16 illustrate the five types of phase diagram corresponding to the various areas on Figure 9.

The various types are the following.

Type I. The phase diagram has a simple continuous gas–liquid p^{c},T^{c} locus with or without azeotropy. This

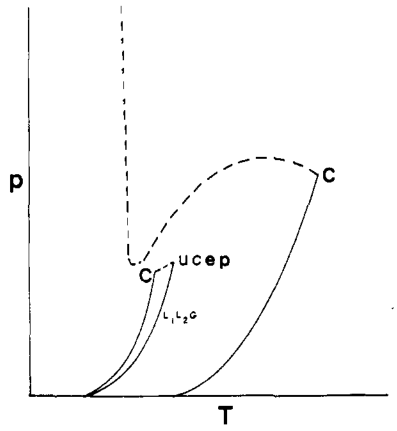

Figure 12. Type IIIa phase behavior. Legend as for Figure 10.

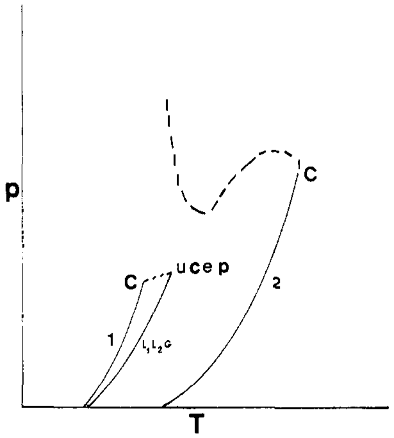

Figure 13. Type IIIb phase behavior. Legend as for Figure 10.

type of phase diagram can often be successfully treated by the theory outlined in sections III and IV together with fairly simple iterative techniques for solving the criticality conditions.

Type II. The phase diagram has a simple continuous gas–liquid p^c,T^c locus with or without azeotropy but with a liquid–liquid–gas line ending at an upper critical end point at a temperature lower than the critical point of either pure component. The liquid–liquid critical line starts from the UCEP and rapidly approaches high pressures. The gas–liquid critical locus of many of systems of this type can also be successfully treated by the theory outlined in sections III and IV together with fairly simple iterative techniques for solving the criticality conditions.

Type III. This phase diagram has two distinct critical lines, one starting at the critical point of the component with the higher critical temperature which goes to higher pressures and lower temperatures but never approaches the critical point of the other component. The other line starts at the critical point of the component with the lower critical temperatures and meets a liquid–liquid–gas line in an UCEP. Various different types of diagram are possible but all having the above features.

Type IV. This has three distinct critical loci, one which may be termed liquid–liquid line which starts at an UCEP on a liquid–liquid–gas line and rapidly moves to higher pressures for a small change in temperature. The second line starts at the critical point of the component with the lower critical temperature and ends at an UCEP on a liquid–liquid–gas line. The third line starts at the critical point of the component with the higher critical temperature and ends in a LCEP on a liquid–liquid–gas line.

Type V. This has two distinct critical lines and corresponds to type IV without the liquid–liquid critical line.

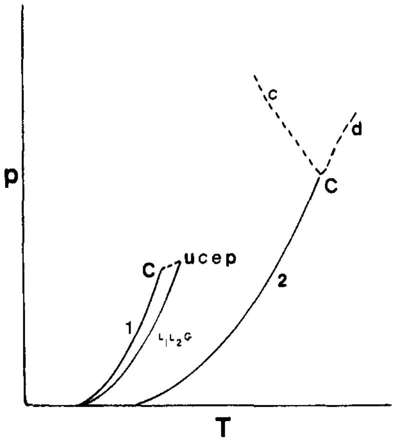

Figure 14. Types IIIc and IIId phase behavior. Legend as for Figure 10.

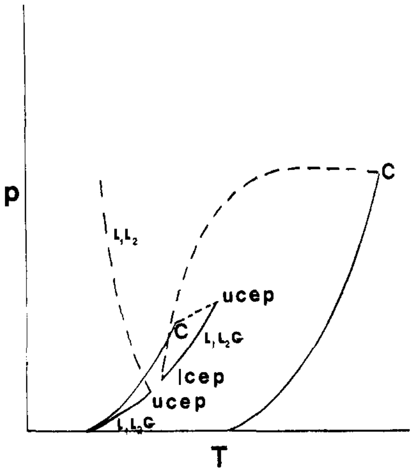

Figure 15. Type IV phase behavior. Legend as for Figure 10.

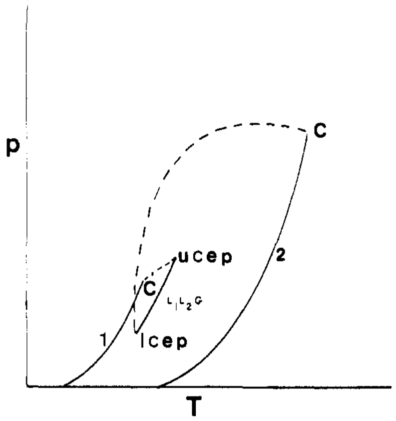

Figure 16. Type V phase behavior. Legend as for Figure 10.

Examples of systems showing these various types of behavior are given in Table V and the three-dimensional phase diagrams have been discussed by Rowlinson.[1]

Figure 9 corresponds only to the van der Waals one-fluid model together with the van der Waals equation of state for equal size molecules. van Konynenburg[122] also briefly studied mixtures for which the size ratio of the molecules was 1:2. No new types of critical lines appeared and the general shapes of the boundary lines are very similar although they are displaced. van Konynenburg concluded that the onset of the high-temperature LCST's depends primarily on the magnitude of the ratio of critical temperatures rather than the ratio of critical pressures (or volumes).

TABLE V. Examples of Mixtures Exhibiting the Five Types of Phase Behavior

Type	Subdivision of type	Example	Ref
I	No maximum or minimum in P^cT^c locus	$CO_2 + C_3H_8$	
	Maximum in P^c in P^cT^c locus	$C_2H_6 + n\text{-}C_7H_{16}$	41
	Minimum in P^c in P^cT^c locus	$SO_2 + CH_3Cl$	
	Maximum in T^c in P^cT^c locus	$HCl + (CH_3)_2O$	136
	Negative azeotropy		
	Minimum in T^c in P^cT^c locus	$CO_2 + C_2H_6$	137
	Positive azeotropy		
II	—	$n\text{-}C_8H_{18} + C_3F_8$	15
III	a	$CO_2 + n\text{-}C_{16}H_{34}$	
		$C_3F_8 + n\text{-}C_{10}H_{22}$	15
III	b	$CH_4 + CH_3\text{-c-}C_5H_9$	138
III	c	$N_2 + NH_3$	139, 140
III	d	$He + C_3H_8$	141
IV	—	$CH_4 +$ *n*-hex-1-ene	142
V	—	$C_2H_6 + C_2H_5OH$	143
		$CH_4 + n\text{-}C_6H_{14}$	144

Whether the above treatment could be profitably extended to other equations of states and give semiqualitative results is not completely clear. However, the success of the simple Bak and Bjerre equation of state in predicting type II phase behavior reasonably accurately is encouraging.

Some calculations have recently been made by the authors using both the Bak and Bjerre and Redlich–Kwong equations of state. While the results are fairly limited, it appears that for both of these equations of state the topography of the figures corresponding to Figure 9 are very similar to the van der Waals case but considerably compressed towards the $\zeta = 0$ axis.

Schneider[3] and Franck[145] have recently reviewed examples of the high-pressure phase behavior discussed above.

B. Conclusion and Summary

The gas–liquid properties of most nonpolar mixtures can be predicted with fair accuracy using the van der Waals one-fluid model provided the ratio of the critical volumes of the pure components is less than 1:2 and the ratio of the critical temperatures is less than 4:5. It appears that the major sources of discrepancies between theory and experiment are as follows.

(1) The van der Waals one-fluid model is probably not very accurate when the ratio of critical volumes exceeds 1:3.

(2) There is no closed equation of state that fits the p,v,T data even of the rare gases within 1% for reduced temperatures and volumes in the ranges 0.5 to 2, and 0.3 to 2, respectively.

(3) It is assumed that the two pure components of the mixture obey the same reduced equation of state, and this usually implies obeying the same two-parameter principle of corresponding states. It is well known that even simple hydrocarbons like ethane and propane[64] do not obey the same principle of corresponding states, as the inert gases and substances like cyclohexane,[65] the higher alkanes, and the fluorocarbons deviate considerably from the simple corresponding states principle of the inert gases.

(4) The Lorentz–Berthelot combining rules, although remarkably successful for hydrocarbon + hydrocarbon mixtures, cannot be expected to be very accurate in general. Although no detailed studies have been made on a wide range of mixtures of chemically different components, it appears that interactions between one molecule which has a large quadrupole, such as carbon dioxide and aliphatic fluorocarbons, and a nonquadrupolar molecule, deviate considerably from the Lorentz–Berthelot rule.

While it is impossible to accurately predict how the study of critical phenomenon in mixtures will develop, we might well see increasing interest in the following topics.

Rice and coworkers[146–148] have made several detailed studies on the shape of the composition-temperature coexistence curve in the region of liquid–liquid critical points. The nature of the critical point in mixtures has recently attracted considerable attention,[149–152] and comparisons between certain critical indexes (exponents) for pure components and mixtures have been made.[5,151]

There are many equations of states which have been proposed for many different purposes, but there is still a definite need for yet another equation of state which is fairly accurate over a wide range of reduced temperature and reduced volume. The lack of such an equation is probably now the major problem in predicting critical properties of mixtures, p,v,T,x data for reduced pressures greater than unity, and vapor–liquid equilibrium at high pressures.

The qualitative prediction of phase equilibria from theoretical considerations still remains unsolved, but no doubt owing to the industrial importance of such behavior this problem will attract increasing interest. Several workers[153,154] have attempted to predict the conditions necessary for "gas-gas" immiscibility (which as usually defined can occur in van Konynenburg's type III systems).

Rogers and Prausnitz[155] have developed a method of calculating high-pressure vapor–liquid equilibria using a perturbed hard-sphere equation of state. A spherical core-Kihara-type potential was used to fit pure fluid p,v,T data to perturbation theory. Comparison with experimental measurements, including the critical point, on mixtures was limited to the argon + neopentane system at 50° and the methane + neopentane system at 25° because of the large amount of computing time involved.

The approach looks to be very promising particularly if the computations can be simplified and the computer time drastically reduced. However, at the present it is difficult to assess the accuracy of this approach for the prediction of critical properties of mixtures in general.

The study of critical temperatures is probably the simplest method of obtaining information about interactions between unlike simple nonpolar molecules. At present, virtually nothing is known about such interactions for mixtures containing one component with a simple dipole or a large quadrupole (except carbon dioxide + hydrocarbon and fluorocarbon + hydrocarbon mixtures) or interactions between nonhydrocarbon molecules. The critical properties of many inorganic compounds are within experimentally convenient ranges of temperature and pressure.[156]

Accurate critical volumes of any mixtures and even the critical pressures of most of the permanent gas mixtures still have not been measured.

Acknowledgments. The interest of Professor R. H. Stokes and Dr. K. N. Marsh in this work was appreciated. Financial support from the Queen Elizabeth II Fellowship Committee to C. L. Young is gratefully acknowledged.

VII. List of Symbols

a, b	equation of state constants
f	ϵ/ϵ_{00} energy or temperature reducing ratio
g	σ/σ_{00} dimensional reducing ratio
h	g^3
ij	species identifiers
k	number of experimental determinations
n	chain-length parameter equal to number of carbon atoms for n-alkanes
p	pressure
r	size ratio parameter
s, t	general variables
u	intermolecular potential energy function
v	molar volume
x	mole fraction of species 2 unless otherwise subscripted
y	general variable
z	effective number of outer shell electrons (eq 47)
A	molar Helmhotz free energy
D	diamagnetic susceptibility
G	molar Gibbs free energy
I	first ionization potential (eq 44)
P	polarizability (eq 45), partial pressure of mercury (eq 5)
Q	A_{xv}/A_{2v}
R	molar gas constant
T	absolute temperature
U	molar energy
Z	compressibility factor, pv/RT
ϵ	characteristic energy for an intermolecular interaction
σ	characteristic distance for an intermolecular interaction (or standard deviation (eq 113) use confined to section 5)
ϕ	volume fraction
Ω	adjustable parameter (eq 103)
ρ	intermolecular distance, density
ξ,η,λ	parameters defined by eq 110, 111, and 112
ξ	adjustable parameter (eq 114) value determined from fit to experimental results
Δ	parameter defined by eq 115
ξ	parameter defined by eq 116

superscripts

c	critical point property
*	configurational property
†	molecular contribution to a property
~	reduced with respect to the equivalent substance critical properties

subscripts

x,v,f,h,T	partial derivatives with respect to x,v,f,h, and T
i, j	property of species i, j
ij	property for interaction between molecules of species i and j
0	reference substance property
00	property for interaction between molecules of the reference substance
cb	combinatorial contribution to a property
es	equivalent substance property
m	mixture property
r	reduced with respect to the critical properties of component 1

VIII. Appendix A. Compilation of Gas-Liquid Critical Data for Hydrocarbon Mixtures

Most of the data given in this section have been taken directly from tables in the literature and converted into appropriate units. However, a few results were read from graphs and are consequently less accurate.

The critical temperatures are quoted in kelvin, critical pressures in bars, and critical volumes in cm^3 mol^{-1}.

A. Methane + n-Alkanes

Methane(1) + Ethane(2)

(a) M. Ruhemann, *Proc. Roy. Soc., Ser. A*, **171**, 121 (1939).

$x(1)$	T^c	P^c
0.40	273.2	83.1

(b) O. T. Bloomer, D. C. Gami, and J. D. Parent, *Inst. Gas Tech. Res. Bull.*, No. 22 (July 1953).

$x(1)$	T^c	P^c
0.05	302.0	51.1
0.1498	295.0	55.5
0.3002	282.9	61.8
0.5002	263.1	67.6
0.7000	238.0	67.3
0.8516	218.0	60.9
0.9250	204.3	54.0
0.9746	195.4	49.1

(c) A. R. Price and R. Kobayashi, *J. Chem. Eng. Data*, **4**, 40 (1959).

$x(1)$	T^c	P^c
0.19	283.1	62.0
0.56	255.4	68.9
0.82	227.6	62.7
0.96	199.8	51.0

(d) I. Wichterle and R. Kobayashi, *J. Chem. Eng. Data*, **17,** 9 (1972).

$x(1)$	T^c	P^c
0.9520	199.92	51.57
0.9706	195.44	49.14
0.98214	193.92	48.13
0.99125	192.39	47.22

Methane(1) + Propane(2)

(a) A. R. Price and R. Kobayashi, *J. Chem. Eng. Data*, **4**, 40 (1959)

$x(1)$	T^c	P^c
0.67	283.1	96.5
0.82	255.4	91.7

(b) H. H. Reamer, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **42**, 534 (1950); correction, *ibid.*, **42**, 1258 (1950); also quoted in *J. Chem. Eng. Data*, **15**, 75, 82 (1970).

$x(1)$	T^c	P^c	V^c
0.1400	360.9	53.0	202
0.3228	344.3	70.3	159
0.4691	327.6	84.0	144
0.5882	310.9	93.2	130
0.6772	294.3	100.9	143
0.7459	277.6	101.6	102

(c) W. W. Akers, J. F. Burns, and W. R. Fairchild, *Ind. Eng. Chem.*, **46**, 2531 (1954).

$x(1)$	T^c	P^c
0.745	273.2	99.9
0.800	256.5	95.1
0.835	241.5	94.4
0.921	226.5	77.2
0.945	213.2	73.2
0.960	194.8	47.5

(d) 8. H. Sage, W. N. Lacey, and J. G. Schaafsma, *Ind. Eng. Chem.*, **26**, 214 (1934).

$x(1)$	T^c	P^c	V^c
0.100	364.2	52.8	178
0.200	354.4	61.4	166
0.300	344.1	70.2	153
0.400	332.5	79.8	142
0.500	319.5	89.1	130
0.600	304.3	97.0	119
0.700	283.6	101.2	108

(e) J. G. Roof and J. D. Baron, *J. Chem. Eng. Data*, **12**, 292 (1967).

x(1)	T^c	P^c
0.17	356.1	56.7
0.28	344.8	67.0
0.42	328.0	79.8
0.49	316.6	86.1
0.57	305.0	91.2

(f) I. Wichterle and R. Kobayashi, *J. Chem. Eng. Data*, **17**, 4 (1972).

x(1)	T^c	P^c
0.9469	213.71	65.10
0.9856	195.2	49.90
0.9926	192.3	47.47

Methane(1) + *n*-Butane(2)

(a) B. H. Sage, B. L. Hicks, and W. N. Lacey, *Ind. Eng. Chem.*, **32,** 1085 (1940).

x(1)	T^c	P^c	V^c
0.3602	394.2	87.1	168.8
0.4722	377.6	104.8	147.1
0.5503	360.9	117.1	132.3
0.6165	344.3	124.8	121.9
0.6718	327.6	129.3	112.9
0.7236	310.9	131.8	105.6
0.771	294.3	132.6	97.4

(b) L. R. Roberts, R. H. Wang, A. Azarnoosh, and J. J. McKetta, *J. Chem. Eng. Data*, **7,** 484 (1962).

x(1)	T^c	P^c
0.7953	277.6	132.0
0.8630	244.3	118.9
0.9214	210.9	71.7

(c) W. M. Rutherford, *Amer. Inst. Chem. Eng. J.*, **9,** 843 (1963).

x(1)	T^c
0.40	388.7
0.49	372.0

Methane(1) + n-Pentane(2)

(a) B. H. Sage, H. H. Reamer, R. H. Olds, and W. N. Lacey, *Ind. Eng. Chem.*, **34,** 1108 (1942).

x(1)	T^c	P^c	V^c
0.2950	444.3	70.7	229.7
0.5211	410.9	111.0	176.0
0.6705	377.6	143.5	141.0
0.7665	344.3	161.2	117.0
0.8236	310.9	169.3	96.9

Methane(1) + n-Hexane(2)

(a) J. Shim and J. P. Kohn, *J. Chem. Eng. Data*, **7,** 3 (1962).

x(1)	T^c	P^c	V^c
0.6250	423.15	121.6	
0.7466	298.15	196.2	81.38

(b) G. S. Stepanova, *Izv. Vyssh. Ucheb. Zaved., Neft Gaz.*, No. 3, 113 (1960); *Chem. Abstr.*, **54,** 17023h (1960).

x(1)	T^c	P^c
0.85	281.2	203.2

(c) G. S. Stepanova and Ya. I. Vybornova, *Tr. Vses. Nauchn-Issled. Inst. Priorochi, Gazov*, 203 (1962); *Chem. Abstr.*, **59,** 5853h (1963).

x(1)	T^c	P^c
0.80	332	208
0.90	263	190

Methane(1) + n-Heptane(2)

(a) H. H. Reamer, B. H. Sage, and W. W. Lacey, *J. Chem. Eng. Data*, **1,** 29 (1956).

(x)1	T^c	P^c
0.441	510.9	83.1
0.585	477.6	131.4
0.672	444.2	170.2
0.732	410.9	201.7
0.778	377.6	227.4
0.817	344.2	244.6
0.855	310.9	248.8
0.894	277.6	229.4

(b) K. E. Bett, B. Juren, and R. G. Reynolds, paper given at a Symposium on Physical Properties of Liquids and Gases for Plant and Process Design, Glasgow, March 1968.

x(1)	T^c	P^c	V^c
0.800	363	232	106.4
0.815	343	235	100.0
0.830	323	237	91.7
0.850	303	240	82.6

Methane(1) + n-Octane(2)

(a) J. P. Kohn and W. F. Bradish, *J. Chem. Eng. Data*, **9,** 5 (1964).

x(1)	T^c	P^c	V^c
0.787	323.15	273.4	86.1
0.798	298.15	266.5	81.5

Methane(1) + *n*-Nonane(2)

(a) L. M. Shipman and J. P. Kohn, *J. Chem. Eng. Data*, **11**, 176 (1966).

x(1)	T^c	P^c	V^c
0.860	348.15	317	88.0
0.872	323.15	322	79.5
0.880	298.15	322	73.4
0.885	273.15	323	68.6

Methane(1) + n-Decane(2)

(a) H. H. Reamer, R. H. Olds, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **34**, 1526 (1942).

x(1)	T^c	P^c	V^c
0.739	510.9	200.6	183.9
0.798	477.6	248.4	148.0
0.833	444.3	287.0	124.0
0.857	410.9	315.7	107.0
0.877	377.6	340.1	93.0
0.891	344.3	357.6	82.4
0.898	310.9	365.8	73.6

(b) K. E. Bett, B. Juren, and R. G. Reynolds, paper given at a Symposium on Physical Properties of Liquids and Gases for Plant and Process Design, Glasgow, March 1968.

x(1)	T^c	P^c	V^c
0.857	383	342	100.0
0.870	363	354	92.6
0.875	343	365	87.0
0.885	323	370	80.0

(c) H. C. Wiese, H. H. Reamer, and 8. H. Sage, *J. Chem. Eng. Data*, **15,** 75 (1970), data quoted in (a) plus.

x(1)	T^c	P^c	V^c
0.905	277.6	361.3	65.9

B. *n*-Alkanes + *n*-Alkanes

Ethane(1) + Propane(2)

(a) D. E. Matschke and G. Thodos, *J. Chem. Eng. Data*, **7**, 232 (1962); correction, *ibid.*, **7**, 433 (1962).

$x(1)$	T^c	P^c
0.0930	366.5	44.7
0.3215	355.4	50.7
0.5060	344.3	50.9
0.6685	333.1	51.9
0.8100	322.0	51.7
0.9350	310.9	50.5

Ethane(1) + n-Butane(2)

(a) W. B. Kay, *Ind. Eng. Chem.*, **32**, 353 (1940).

$x(1)$	T^c	P^c	V^c
0.1749	412.7	44.6	223.4
0.4510	387.3	53.8	188.2
0.6577	361.6	58.1	162.1
0.8218	337.4	57.0	148.8
0.9472	315.6	52.4	139.8

(b) V. S. Mehra and G. Thodos, *J. Chem. Eng. Data*, **10**, 307 (1965).

$x(1)$	T^c	P^c
0.382	394.3	51.7
0.625	366.5	57.7
0.810	338.7	57.8

(c) J. C. Herlihy and G. Thodos, *J. Chem. Eng. Data*, **7**, 348 (1962).

$x(1)$	T^c	P^c
0.813	338.7	57.1

(d) H. M. Cota and G. Thodos, *J. Chem. Eng. Data*, **7**, 62 (1962); the same binary data are also in J. C. Forman and G. Thodos, *Amer. Inst. Chem. Eng. J.*, **8**, 209 (1962).

$x(1)$	T^c	P^c
0.602	370.4	57.7
0.874	327.6	56.1

(e) V. S. Mehra and G. Thodos, *J. Chem. Eng. Data*, **13**, 155 (1968).

$x(1)$	T^c	P^c
0.075	422.0	40.7

Ethane(1) + n-Pentane(2)

(a) H. H. Reamer, B. H. Sage, and W. N. Lacey, *J. Chem. Eng. Data*, **5**, 44 (1960).

$x(1)$	T^c	P^c
0.481	422.0	62.3
0.652	394.3	67.8
0.764	366.5	67.6

(b) O. Ekiner and G. Thodos, *J. Chem. Eng. Data*, **11**, 154 (1966).

$x(1)$	T^c	P^c
0.562	408.1	62.7
0.766	371.2	66.5
0.888	339.8	58.4

(c) J. C. Herlihy and G. Thodos, *J. Chem. Eng. Data*, **7**, 348 (1962).

$x(1)$	T^c	P^c
0.865	338.7	62.7

Ethane(1) + n-Hexane(2)

(a) E. J. Zais and I. H. Silverberg, *J. Chem. Eng. Data*, **15**, 253 (1970).

$x(1)$	T^c	P^c
0.525	449.8	67.6
0.735	394.3	79.0
0.920	338.7	64.7

Ethane(1) + n-Heptane(2)

(a) W. B. Kay, *Ind. Eng. Chem.*, **30**, 459 (1938).

$x(1)$	T^c	P^c	V^c
0.2654	515.5	47.0	317.1
0.5871	463.1	76.2	221.2
0.7709	409.2	87.0	164.8
0.8871	360.9	78.0	139.4
0.9683	322.3	58.6	129.9

(b) O. Ekiner and G. Thodos, *Can. J. Chem. Eng.*, **43**, 205 (1965).

$x(1)$	T^c	P^c
0.6550	455.9	80.10
0.7104	439.5	85.34
0.8014	406.5	88.71
0.8760	372.9	83.74
0.9112	349.0	73.83

(c) V. S. Mehra and G. Thodos, *J. Chem. Eng. Data*, **10**, 211 (1965).

$x(1)$	T^c	P^c
0.681	449.8	84.0
0.760	422.0	87.8
0.825	394.3	86.1
0.883	366.5	80.4
0.939	338.7	68.3

Ethane(1) + n-Decane(2)

(a) H. H. Reamer and B. H. Sage, *J. Chem. Eng. Data*, **7**, 161 (1962).

$x(1)$	T^c	P^c	V^c
0.698	510.9	102.0	244.4
0.788	477.6	113.1	202.7
0.835	444.3	118.2	173.9
0.888	410.9	116.3	150.2
0.927	377.6	104.7	126.2
0.964	344.3	81.6	110.4
0.995	310.9	53.6	133.7

(b) H. H. Reamer, J. H. Lower, and B. H. Sage, *J. Chem. Eng. Data*, **9**, 54 (1964).

$x(1)$	T^c	P^c	V^c
0.977	310.9	53.6	142

Propane(1) + n-Butane(2)

(a) C. N. Nysewander, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **32**, 118 (1940).

$x(1)$	T^c	P^c	V^c
0.203	416.8	40.5	244
0.339	411.1	41.9	239
0.516	402.3	43.5	228
0.695	390.7	44.0	214
0.855	380.1	43.5	204

(b) R. B. Grieves and C. Thodos, *J. Appl. Chem.*, **13**, 466 (1963).

$x(1)$	T^c	P^c
0.456	404.3	43.0
0.700	390.4	43.6

(c) A. Kreglewski and W. B. Kay, *J. Phys. Chem.*, **73**, 3359 (1969); see also W. B. Kay, *J. Chem. Eng. Data*, **15**, 46 (1970).

$x(1)$	T^c	P^c	V^c
0.147	418.55	39.35	250
0.309	410.85	40.74	242
0.521	399.75	42.36	229
0.755	386.15	43.05	213
0.826	381.45	43.07	209
0.926	374.95	42.85	201

(d) H. C. Wiese, J. Jacobs, and B. H. Sage, *J. Chem. Eng. Data*, **15**, 82 (1970).

$x(1)$	T^c	P^c
0.8895	377.6	43.3

Propane(1) + *n*-Pentane(2)

(a) B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.*, **32,** 992 (1940).

x(1)	T^c	P^c	V^c
0.3498	443.8	41.9	272
0.5557	422.6	44.7	246
0.7921	397.5	46.2	214
0.8190	394.5	45.8	211

(b) A. Kreglewski and W. B. Kay, *J. Phys. Chem.*, **73,** 3359 (1969); see also W. B. Kay, *J. Chem. Eng. Data*, **15,** 46 (1970).

x(1)	T^c	P^c	V^c
0.147	460.15	37.13	282
0.387	439.95	42.33	251
0.616	417.85	45.34	228
0.786	399.25	45.64	213
0.878	387.45	44.94	205

Propane(1) + n-Hexane(2)

(a) A. Kreglewski and W. B. Kay, *J. Phys. Chem.*, **73,** 3359 (1969); see also W. B. Kay, *J. Chem. Eng. Data*, **16,** 137 (1971).

x(1)	T^c	P^c	V^c
0.220	490.65	37.06	355
0.460	466.25	44.96	290
0.649	440.15	49.10	250
0.760	422.15	49.90	229
0.813	411.45	49.51	219
0.918	390.05	46.89	199

(b) S. Chun, Ph.D. Thesis, Ohio State University, 1964.

x(1)	T^c	P^c	V^c
0.1435	496.30	35.27	335.4
0.4437	468.17	44.34	305.1
0.6996	431.26	49.75	244.1
0.8201	409.50	49.41	215.5
0.9218	387.55	46.55	200.9

Propane(1) + n-Heptane(2)

(a) A. Kreglewski and W. B. Kay, *J. Phys. Chem.*, **73,** 3359 (1969); see also W. B. Kay, *J. Chem. Eng. Data*, **16,** 137 (1971).

x(1)	T^c	P^c
0.214	521.15	36.06
0.519	482.85	48.71
0.715	448.15	53.88
0.851	417.25	53.36
0.909	400.65	51.09

Propane(1) + n-Octane(2)

(a) A. Kreglewski and W. B. Kay, *J. Phys. Chem.*, **73,** 3359 (1969).

x(1)	T^c	P^c	V^c
0.214	547.95	35.44	385
0.331	535.25	41.48	368
0.573	499.25	53.64	298
0.718	471.15	58.59	299
0.775	455.75	59.60	242
0.864	427.85	57.86	218
0.959	389.95	49.29	191

Propane(1) + n-Decane(2)

(a) H. H. Reamer and 8. H. Sage, *J. Chem. Eng. Data*, **11**, 17 (1966).

x(1)	T^c	P^c	V^c
0.7120	510.9	68.1	281
0.7993	477.6	70.8	236
0.8673	444.3	67.6	204
0.9283	410.9	60.2	201
0.9870	377.6	46.7	200

n-Butane(1) + *n*-Pentane(2)

(a) W. B. Kay, unpublished data.

x(1)	T^c	P^c
0.100	466.10	34.40
0.200	462.25	35.18
0.300	458.24	35.89
0.400	454.10	36.43
0.500	449.84	36.83
0.600	445.41	37.20
0.700	440.75	37.49
0.800	435.82	37.71
0.900	430.66	37.84

n-Butane(1) + n-Hexane(2)

(a) W. B. Kay, unpublished data.

x(1)	T^c	P^c
0.100	501.97	31.81
0.200	495.92	33.34
0.300	489.39	34.77
0.400	482.21	36.01
0.500	474.62	37.14
0.600	466.65	38.11
0.700	457.70	38.73
0.800	447.80	38.95
0.900	437.43	38.76

n-Butane(1) + n-Heptane(2)

(a) W. B. Kay, *Ind. Eng. Chem.*, **33**, 590 (1941), and unpublished data.

x(1)	T^c	P^c	V^c
0.1590	528.8	31.1	370.9
0.4249	504.8	37.1	314.5
0.6311	481.9	40.5	282.2
0.8010	459.8	41.1	262.9
0.9401	436.3	39.7	252.7
0.100	533.38	29.70	
0.200	525.43	32.11	
0.300	516.73	34.44	
0.400	507.27	36.59	
0.500	496.95	38.45	
0.600	485.61	39.92	
0.700	473.05	40.80	
0.800	458.65	41.09	
0.900	444.09	40.41	

n-Butane(1) + n-Octane(2)

(a) W. B. Kay, unpublished data.

x(1)	T^c	P^c
0.100	561.04	27.80
0.200	552.50	30.70
0.300	543.10	33.63
0.400	532.46	36.53
0.500	520.12	39.22
0.600	506.12	41.47
0.700	490.19	42.91
0.800	472.16	43.22
0.900	451.15	41.90

n-Butane(1) + n-Decane(2)

(a) H. H. Reamer and 8. H. Sage, *J. Chem. Eng. Data*, **9,** 24 (1964).

x(1)	T^c	P^c	V^c
0.739	510.9	49.2	310
0.865	477.6	47.8	263
0.956	444.3	42.5	250

n-Pentane(1) + n-Hexane(2)

(a) E. J. Partington, J. S. Rowlinson, and J. F. Weston, *Trans. Faraday Soc.*, **56**, 479 (1960).

$x(1)$	T^c
0.245	499.4
0.469	491.4
0.626	485.7
0.827	477.8
0.927	473.3

n-Pentane(1) + n-Heptane(2)

(a) L. W. T. Cummings, F. W. Stone, and M. A. Volante, *Ind. Eng. Chem.*, **25**, 728 (1933).

$x(1)$	T^c	P^c
0.255	526.2	30.60
0.558	506.2	33.0
0.747	492.2	33.2

n-Pentane(1) + n-Octane(2)

(a) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **66**, 1340 (1970).

$x(1)$	T^c	$x(1)$	T^c
0.159	558.9	0.536	524.7
0.349	544.0	0.709	507.2
0.376	541.2	0.870	487.2

n-Pentane(1) + n-Nonane(2)

(a) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **66**, 1340 (1970).

$x(1)$	T^c	$x(1)$	T^c
0.204	578.2	0.743	518.7
0.334	568.2	0.832	503.2
0.508	554.7	0.838	504.7

(b) D. Hissong and W. B. Kay, *Proc. Amer. Petr. Inst., Refining Div.*, **48**, 397 (1968).

$x(1)$	T^c	P^c
0.100	587.80	25.01
0.200	580.48	27.13
0.300	572.20	29.25
0.400	563.30	31.17
0.500	553.40	32.99
0.600	541.72	34.64
0.700	526.98	36.01
0.800	510.98	36.57
0.900	493.35	36.07

n-Pentane(1) + n-Decane(2)

(a) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **66**, 1340 (1970).

$x(1)$	T^c	$x(1)$	T^c
0.163	602.9	0.578	564.4
0.293	593.4	0.674	545.4
0.405	585.2	0.877	507.0
0.462	577.2		

n-Pentane(1) + n-Undecane(2)

(a) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **66**, 1340 (1970).

$x(1)$	T^c	$x(1)$	T^c
0.212	619.7	0.576	575.2
0.334	608.2	0.623	569.2
0.336	609.7	0.895	506.2
0.505	593.2		

n-Pentane(1) + n-Dodecane(2)

(a) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **66**, 1340 (1970).

$x(1)$	T^c	$x(1)$	T^c
0.201	639.2	0.709	566.2
0.336	620.8	0.793	541.4
0.542	601.7	0.898	507.4

n-Pentane(1) + n-Tridecane(2)

(a) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **66**, 1340 (1970).

$x(1)$	T^c
0.287	645.2
0.501	614.7
0.702	574.0
0.779	550.9
0.914	518.2

n-Hexane(1) + n-Heptane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47**, 653 (1967).

$x(1)$	T^c	P^c
0.100	537.5	27.96
0.200	534.7	28.30
0.300	531.7	28.64
0.400	528.6	28.99
0.500	525.5	29.34
0.600	522.1	29.63
0.700	518.6	29.87
0.800	515.0	30.08
0.900	511.4	30.30

n-Hexane(1) + n-Octane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47**, 653 (1967).

$x(1)$	T^c	P^c
0.100	564.5	25.95
0.200	559.8	26.71
0.300	554.9	27.46
0.400	549.4	28.20
0.500	543.4	28.92
0.600	537.1	29.50
0.700	530.5	29.94
0.800	523.5	30.30
0.900	515.8	30.52

n-Hexane(1) + n-Decane(2)

(a) S. C. Pak and W. B. Kay, *Ind. Eng. Chem. Fundam.*, **11**, 255 (1972).

$x(1)$	T^c	P^c
0.100	609.6	23.06
0.200	602.1	24.72
0.300	594.4	26.35
0.400	585.5	27.98
0.500	576.3	29.45
0.600	565.5	30.67
0.700	553.3	31.52
0.800	539.6	31.90
0.900	524.4	31.64

n-Hexane(1) + n-Tridecane(2)

(a) S. C. Pak and W. B. Kay, *Ind. Eng. Chem. Fundam.*, **11**, 255 (1972).

$x(1)$	T^c	P^c
0.100	666.2	19.90
0.200	657.2	22.63
0.300	647.3	25.30
0.400	637.0	27.92
0.500	624.3	30.42
0.600	609.3	32.78
0.700	591.5	34.44
0.800	570.0	35.16
0.900	542.2	34.42

n-Hexane(1) + *n*-Tetradecane(2)

(a) S. C. Pak and W. B. Kay, *Ind. Eng. Chem. Fundam.*, **11**, 255 (1972).

$x(1)$	T^c	P^c
0.100	689.2	17.57
0.200	680.8	20.77
0.300	670.3	23.96
0.400	657.9	27.16
0.500	643.2	30.22
0.600	626.5	33.09
0.700	606.0	35.44
0.800	580.8	36.68
0.900	548.2	35.68

n-Heptane(1) + n-Octane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47**, 653 (1967).

$x(1)$	T^c	P^c
0.100	566.4	25.46
0.200	563.9	25.78
0.300	561.3	26.07
0.400	558.6	26.34
0.500	555.7	26.61
0.600	552.8	26.84
0.700	549.8	27.06
0.800	546.7	27.26
0.900	543.5	27.44

n-Nonane(1) + n-Tridecane(2)

(a) S. C. Pak and W. B. Kay, *Ind. Eng. Chem. Fundam.*, **11**, 255 (1972).

$x(1)$	T^c	P^c
0.100	669.6	18.22
0.200	664.7	19.17
0.300	658.8	20.12
0.400	652.2	21.02
0.500	644.7	21.82
0.600	636.4	22.49
0.700	626.8	22.96
0.800	616.6	23.22
0.900	605.5	23.22

n-Decane(1) + n-Dodecane(2)

(a) S. C. Pak and W. B. Kay, *Ind. Eng. Chem. Fundam.*, **11**, 255 (1972).

$x(1)$	T^c	P^c
0.100	655.3	19.04
0.200	651.5	19.43
0.300	647.5	19.78
0.400	643.6	20.10
0.500	639.6	20.39
0.600	635.5	20.65
0.700	631.3	20.87
0.800	626.8	21.08
0.900	621.9	21.26

C. Cycloalkanes + *n*-Alkanes

Methane(1) + Cyclohexane(2)

(a) H. H. Reamer, B. H. Sage, and W. N. Lacey, *J. Chem. Eng. Data*, **3**, 241 (1958).

$x(1)$	T^c	P^c	V^c
0.608	444.3	200.6	126.0
0.667	410.9	230.9	109.1
0.711	377.6	254.3	94.8
0.737	344.3	267.4	84.5
0.758	310.9	278.4	74.9
0.765	294.3	281.9	69.9

Ethane(1) + Cyclohexane(2)

(a) W. B. Kay and R. E. Albert, *Ind. Eng. Chem.*, **48**, 422 (1956).

$x(1)$	T^c	P^c	V^c
0.1378	537.3	52.2	261.9
0.2893	515.5	65.6	226.5
0.4284	489.5	78.1	229.5
0.5020	473.8	84.0	185.1
0.5785	461.2	87.6	
0.7099	422.2	92.1	
0.7298	412.0	91.5	151.1
0.8617	362.7	78.8	133.0

n-Pentane(1) + Cyclopentane(2)

(a) D. Hissong and W. B. Kay, *Proc. Amer. Petr. Inst., Refining Div.*, **48**, 397 (1968).

$x(1)$	T^c	P^c
0.100	507.64	43.91
0.200	503.15	42.67
0.300	498.82	41.42
0.400	494.67	40.28
0.500	490.54	39.15
0.600	486.40	38.05
0.700	482.27	36.96
0.800	478.29	35.94
0.900	474.30	34.93

n-Pentane(1) + Cyclohexane(2)

(a) E. J. Partington, J. S. Rowlinson, and J. F. Weston, *Trans. Faraday Soc.*, **56**, 479 (1960).

$x(1)$	T^c
0.180	541.2
0.444	521.2
0.494	516.7
0.622	505.9
0.802	491.6

n-Hexane(1) + Cyclopentane(2)

(a) D. Hissong and W. B. Kay, *Proc. Amer. Petr. Inst., Refining Div.*, **48**, 397 (1968).

$x(1)$	T^c	P^c
0.100	511.60	43.28
0.200	511.14	41.52
0.300	510.54	39.85
0.400	510.03	38.30
0.500	509.63	36.83
0.600	509.28	35.43
0.700	508.97	34.11
0.800	508.70	32.81
0.900	508.38	31.59

n-Hexane(1) + Cyclohexane(2)

(a) E. J. Partington, J. S. Rowlinson, and J. F. Weston, *Trans. Faraday Soc.*, **56**, 479 (1960).

$x(1)$	T^c
0.319	538.0
0.610	524.5
0.834	514.5

(b) D. Hissong and W. B. Kay, *Proc. Amer. Petr. Inst., Refining Div.*, **48**, 397 (1968).

$x(1)$	T^c	P^c
0.100	549.12	39.61
0.200	544.15	38.40
0.300	539.25	37.31
0.400	534.50	36.28
0.500	529.83	35.28
0.600	525.40	34.24
0.700	520.95	33.17
0.800	516.59	32.17
0.900	512.37	31.28

n-Heptane(1) + Cyclopentane(2)

(a) D. Hissong and W. B. Kay, *Proc. Amer. Petr. Inst., Refining Div.*, **48**, 397 (1968).

$x(1)$	T^c	P^c
0.100	516.53	43.32
0.200	520.21	41.35
0.300	523.52	39.44
0.400	526.58	37.62
0.500	529.40	35.83
0.600	532.05	34.02
0.700	534.48	32.24
0.800	536.66	30.61
0.900	538.75	29.14

n-Heptane(1) + Cyclohexane(2)

(a) D. Hissong and W. B. Kay, *Proc. Amer. Petr. Inst., Refining Div.*, **48**, 397 (1968).

$x(1)$	T^c	P^c
0.100	552.45	39.07
0.200	550.86	37.48
0.300	549.34	36.02
0.400	547.90	34.60
0.500	546.54	33.23
0.600	545.25	31.95
0.700	544.01	30.77
0.800	542.86	29.73
0.900	541.77	28.65

n-Octane(1) + Cyclopentane(2)

(a) D. Hissong and W. B. Kay, *Proc. Amer. Petr. Inst., Refining Div.*, **48**, 397 (1968).

$x(1)$	T^c	P^c
0.100	521.88	43.75
0.200	529.86	41.92
0.300	536.95	39.80
0.400	543.30	37.60
0.500	548.87	35.42
0.600	553.82	33.25
0.700	558.23	31.13
0.800	562.27	29.01
0.900	565.92	27.00

n-Octane(1) + Cyclohexane(2)

(a) D. Hissong and W. B. Kay, *Proc. Amer. Petr. Inst., Refining Div.*, **48**, 397 (1968).

$x(1)$	T^c	P^c
0.100	556.48	39.03
0.200	558.46	37.28
0.300	560.22	35.52
0.400	561.84	33.79
0.500	563.38	32.13
0.600	564.79	30.67
0.700	566.11	29.24
0.800	567.33	27.82
0.900	568.34	26.39

n-Nonane(1) + Cyclopentane(2)

(a) D. Hissong and W. B. Kay, *Proc. Amer. Petr. Inst., Refining Div.*, **48**, 397 (1968).

$x(1)$	T^c	P^c
0.100	527.63	44.62
0.200	540.23	42.87
0.300	550.57	40.55
0.400	559.59	38.00
0.500	567.48	35.35
0.600	574.12	32.72
0.700	580.19	30.09
0.800	585.74	27.48
0.900	590.25	25.15

n-Nonane(1) + Cyclohexane(2)

(a) D. Hissong and W. B. Kay, *Proc. Amer. Petr. Inst., Refining Div.*, **48**, 397 (1968).

$x(1)$	T^c	P^c
0.100	560.86	39.19
0.200	566.42	37.39
0.300	571.37	35.47
0.400	575.80	33.39
0.500	579.75	31.43
0.600	583.25	29.64
0.700	586.55	27.88
0.800	589.48	26.14
0.900	592.04	24.44

n-Decane(1) + Cyclohexane(2)

(a) S. C. Pak and W. B. Kay, *Ind. Eng. Chem. Fundam.*, **11**, 255 (1972).

$x(1)$	T^c	P^c
0.100	565.1	39.77
0.200	574.9	38.01
0.300	583.2	35.72
0.400	590.6	33.41
0.500	597.0	31.15
0.600	602.3	28.96
0.700	606.8	26.90
0.800	610.8	24.98
0.900	614.3	23.14

n-Tridecane(1) + Cyclohexane(2)

(a) S. C. Pak and W. B. Kay, *Ind. Eng. Chem. Fundam.*, **11**, 255 (1972).

$x(1)$	T^c	P^c
0.100	581.6	42.13
0.200	602.7	40.49
0.300	618.6	37.60
0.400	631.6	34.36
0.500	642.5	31.15
0.600	651.6	28.02
0.700	659.2	25.06
0.800	665.7	22.35
0.900	670.6	19.78

D. Other Hydrocarbon + *n*-Alkane Mixtures

Methane(1) + 2-Methylpropane(2) (Isobutane)

(a) R. H. Olds, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **34,** 1008 (1942).

$x(1)$	T^c	P^c	V^c
0.337	377.6	71.0	190.3
0.558	344.3	100.4	140.5
0.690	310.9	115.7	116.1

Methane(1) + 2-Methylbutane(2) (Isopentane)

(a) E. H. Amick, W. B. Johnson, and B. F. Dodge, *Chem. Eng. Progr. Symp. Ser., No. 3*, **48**, 65 (1952).

$x(1)$	T^c	P^c
0.1500	449.2	50.02
0.3339	429.2	75.73

Methane(1) + Neopentane(2)

(a) B. L. Rogers and J. M. Prausnitz, *J. Chem. Thermodyn.*, **3**, 299 (1971).

$x(1)$	T^c	P^c	V^c
0.845	298.15	255	93.5

Methane(1) + Methylcyclohexane(2)

(a) H. L. Chang and R. Kobayashi, *J. Chem. Eng. Data*, **12**, 520 (1967).

x(1)	T^c	P^c
0.910	255.4	26.79
0.910	244.3	26.30
0.915	233.2	25.89
0.920	222.0	25.66
0.920	210.9	25.78
0.930	199.8	26.58

Methane(1) + Ethylene(2)

(a) M. Guter, D. M. Newitt, and M. Ruhermann, *Proc. Roy. Soc., Ser. A*, **176**, 140 (1940).

x(1)	T^c	P^c
0.11	273.2	67.4
0.59	231.2	75.0
0.85	195.2	51.7

Ethane(1) + Ethylene(2)

(a) J. L. McCurdy and D. L. Katz, *Ind. Eng. Chem.*, **36**, 674 (1944).

x(1)	T^c	P^c
0.285	290.0	52.0
0.440	292.5	51.9

Ethane(1) + Propene(2)

(a) H. Lu, D. M. Newitt, and M. Ruhemann, *Proc. Roy. Soc., Ser. A*, **178**, 506 (1941).

x(1)	T^c	P^c	V^c
0.0525	362.7	46.62	172.1
0.1031	360.0	47.07	191.9
0.3445	348.2	50.06	180.7
0.5285	337.6	51.18	191.2
0.8056	319.3	51.06	150.9
0.8989	311.9	49.87	122.1
0.9502	308.7	49.45	146.9

(b) R. A. McKay, H. H. Reamer, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **43**, 2112 (1951).

x(1)	T^c	P^c	V^c
0.350	344.3	48.6	160.6
0.930	310.9	49.8	142.9

Ethane(1) + Acetylene(2)

(a) J. P. Kuenen, *Phil. Mag.*, **44**, 174 (1897).

x(1)	T^c	P^c
0.27	297.0	56.98
0.41	294.30	55.72
0.51	293.11	55.37
0.61	293.92	54.11
0.68	296.90	52.75

Ethane(1) + Benzene(2)

(a) W. B. Kay and T. D. Nevens, *Chem. Eng. Progr. Symp., Ser. No. 3*, **48**, 108 (1952).

x(1)	T^c	P^c	V^c
0.0646	540.76	63.14	217.9
0.1990	499.05	84.89	212.3
0.2798	473.10	93.44	195.8
0.5012	406.82	95.22	166.6
0.6998	358.46	77.08	153.5
0.8756	326.08	59.90	143.2

Propane(1) + 2-Methylbutane(2) (Isopentane)

(a) W. E. Vaughan and F. C. Collins, *Ind. Eng. Chem.*, **34**, 885 (1942).

x(1)	T^c	P^c	V^c
0.101	454.3	36.43	284
0.393	433.5	42.33	236
0.588	415.6	44.98	216
0.794	394.6	45.70	201
0.899	382.5	44.73	197

Propane(1) + Acetylene(2)

(a) J. L. McCurdy and D. L. Katz, *Oil Gas J.*, (44) **43**, 102 (1945).

x(1)	T^c	P^c
0.166	313.7	63.0
0.237	319.8	63.8
0.297	322.6	64.1
0.433	333.1	64.2
0.514	338.7	63.7
0.546	343.1	62.4
0.860	364.8	53.8

Propane(1) + Benzene(2)

(a) J. W. Glanville, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **42**, 508 (1950).

x(1)	T^c	P^c
0.487	477.6	59.8
0.683	444.3	59.2
0.875	410.9	53.0
0.985	377.6	44.1

Propane(1) + 2,2-Dimethylbutane(2)

(a) S. Chun, Ph.D. Thesis, Ohio State University, 1964.

x(1)	T^c	P^c	V^c
0.1527	477.91	35.17	337.2
0.4490	450.81	43.10	281.6
0.6587	425.36	46.98	214.1
0.8205	401.93	46.98	214.6
0.9194	385.15	45.25	206.3

Propane(1) + 2,3-Dimethylbutane(2)

(a) S. Chun, Ph.D. Thesis, Ohio State University, 1964.

x(1)	T^c	P^c	V^c
0.1516	488.41	36.15	324.0
0.4522	459.36	44.49	288.2
0.6508	432.05	48.36	236.5
0.8257	404.31	48.24	212.2
0.9153	387.50	46.11	206.3

Propane(1) + 2-Methylpentane(2)

(a) S. Chun, Ph.D. Thesis, Ohio State University, 1964.

x(1)	T^c	P^c	V^c
0.1497	486.49	34.77	339.4
0.4446	458.19	43.68	277.1
0.6488	431.97	47.80	239.7
0.8196	405.45	48.00	211.7
0.9190	386.58	45.77	199.3

Propane(1) + 3-Methylpentane(2)

(a) S. Chun, Ph.D. Thesis, Ohio State University, 1964.

x(1)	T^c	P^c	V^c
0.1451	492.65	36.13	319.1
0.4453	462.68	45.22	268.5
0.6554	436.37	49.01	255.5
0.8336	404.92	48.64	213.7
0.8850	391.01	46.85	206.9

n-Pentane(1) + Neopentane(2)

(a) E. J. Partington, J. S. Rowlinson, and J. F. Weston, *Trans. Faraday Soc.*, **56**, 479 (1960).

x(1)	T^c
0.175	440.6
0.350	447.4
0.576	455.5
0.791	462.7

n-Pentane(1) + Benzene(2)

(a) E. J. Partington, J. S. Rowlinson, and J. F. Weston, *Trans. Faraday Soc.*, **56,** 479 (1960).

x(1)	T^c
0.378	528.4
0.469	515.2
0.565	504.8
0.697	490.1
0.856	474.4

n-Pentane(1) + Toluene(2)

(a) E. J. Partington, J. S. Rowlinson, and J. F. Weston, *Trans. Faraday Soc.*, **56,** 479 (1960).

x(1)	T^c
0.203	563.2
0.404	535.2
0.558	515.3
0.805	489.7

n-Pentane(1) + Ethylbenzene(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst. Refining Div.*, **49,** 13 (1969).

x(1)	T^c	P^c
0.100	605.73	37.74
0.200	594.00	39.06
0.300	581.75	40.05
0.400	568.57	40.68
0.500	554.17	40.90
0.600	538.78	40.59
0.700	522.83	39.72
0.800	506.05	38.35
0.900	488.72	36.35

n-Hexane(1) + Neopentane(2)

(a) E. J. Partington, J. S. Rowlinson, and J. F. Weston, *Trans. Faraday Soc.*, **56,** 479 (1960).

x(1)	T^c
0.154	446.9
0.320	460.6
0.514	475.8
0.721	490.8

n-Hexane(1) + Methylcyclopentane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47,** 653 (1967).

x(1)	T^c	P^c
0.100	530.5	37.07
0.200	527.7	36.25
0.300	525.0	35.47
0.400	522.5	34.69
0.500	520.0	33.90
0.600	523.4	36.12
0.700	518.8	34.46
0.800	514.4	33.08
0.900	511.0	31.70

n-Hexane(1) + 2,2-Dimethylbutane(2)

(a) C. L. Young, unpublished data.

x(1)	T^c
0.1009	491.0
0.2018	492.8
0.3586	495.7
0.6071	500.5
0.6173	500.9
0.8569	504.7

n-Hexane(1) + 2,3-Dimethylbutane(2)

(a) C. L. Young, unpublished data.

x(1)	T^c
0.3266	502.0
0.3275	501.7
0.5828	504.3
0.6151	504.1
0.7872	505.1

n-Hexane(1) + 3-Methylpentane(2)

(a) C. L. Young, unpublished data.

x(1)	T^c
0.1569	504.5
0.4358	505.6
0.6467	506.1
0.5311	505.9
0.8030	506.8

n-Hexane(1) + *cis*-Decalin(2)

(a) S. C. Pak and W. B. Kay, *Ind. Eng. Chem. Fundam.*, **11,** 255 (1972).

x(1)	T_c	P_c
0.100	691.7	34.60
0.200	676.8	36.78
0.300	660.5	38.49
0.400	642.7	39.71
0.500	623.2	40.27
0.600	601.9	40.13
0.700	579.3	39.28
0.800	556.2	37.48
0.900	532.0	34.36

n-Hexane(1) + Acetylene(2)

(a) V. S. Mislavskaya and S. M. Khodeeva, *Russ. J. Phys. Chem.*, **43,** 1062 (1969).

x(1)	T^c	P^c	V^c
0.335	413	104	170
0.405	433	93.7	190
0.485	453	78.7	215
0.625	473	62.3	255

n-Hexane(1) + Benzene(2)

(a) E. J. Partington, J. S. Rowlinson, and J. F. Weston, *Trans. Faraday Soc.*, **56,** 479 (1960).

x(1)	T^c
0.250	540.1
0.384	532.7
0.546	524.8
0.595	522.8
0.727	517.6
0.762	516.1

(b) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47,** 653 (1967).

x(1)	T^c	P^c
0.100	554.5	46.6
0.200	547.1	44.1
0.300	540.2	41.8
0.400	534.0	39.7
0.500	528.5	37.9
0.600	523.4	36.13
0.700	518.8	34.47
0.800	514.4	33.09
0.900	511.0	31.72

n-Hexane(1) + Toluene(2)

(a) E. J. Partington, J. S. Rowlinson, and J. F. Weston, *Trans. Faraday Soc.*, **56,** 479 (1960).

x(1)	T^c
0.269	567.6
0.611	538.1
0.781	523.5

(b) L. M. Watson and B. F. Dodge, *Chem. Eng. Progr. Symp. Ser., No. 3*, **48,** 73 (1952).

$x(1)$	T^c	P^c	V^c
0.366	560.8	39.51	319
0.505	547.6	37.99	325
0.700	530.4	35.37	338

n-Hexane(1) + Ethylbenzene(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **49,** 13 (1969).

$x(1)$	T^c	P^c
0.100	606.81	36.51
0.200	596.40	36.52
0.300	585.95	36.37
0.400	575.36	36.02
0.500	564.40	35.51
0.600	553.17	34.84
0.700	542.00	33.90
0.800	530.78	32.82
0.900	519.40	31.66

n-Heptane(1) + Ethylene(2)

(a) W. B. Kay, *Ind. Eng. Chem.*, **40,** 1459 (1948); correction, *ibid.*, **41,** 484 (1949).

$x(1)$	T^c	P^c	V^c
0.0301	301.5	64.2	117.7
0.1069	342.8	90.9	122.6
0.2199	396.1	104.5	147.1
0.3948	453.6	90.7	196.0
0.5275	483.6	74.5	237.0
0.7143	513.4	52.3	309.6
0.8154	525.1	42.3	344.0
0.9296	535.4	32.5	393.1

n-Heptane(1) + Benzene(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47,** 653 (1967).

$x(1)$	T^c	P^c
0.100	557.3	45.84
0.200	553.2	42.91
0.300	550.1	40.20
0.400	547.5	37.75
0.500	545.5	35.65
0.600	543.8	33.77
0.700	542.5	32.07
0.800	541.5	30.43
0.900	540.8	28.94

n-Heptane(1) + Ethylbenzene(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **49,** 13 (1969).

$x(1)$	T^c	P^c
0.100	608.23	35.61
0.200	599.95	34.80
0.300	591.83	33.91
0.400	583.95	33.01
0.500	576.35	32.08
0.600	568.73	31.13
0.700	561.38	30.19
0.800	554.25	29.31
0.900	547.30	28.45

n-Octane(1) + 2-Methylheptane(2)

(a) C. L. Young, unpublished data.

$x(1)$	T^c
0.1978	561.8
0.4075	563.5
0.5993	565.2
0.6518	565.4
0.7214	565.8

n-Octane(1) + Benzene(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47,** 653 (1967).

$x(1)$	T^c	P^c
0.100	561.1	45.51
0.200	561.0	42.28
0.300	561.4	39.43
0.400	562.1	36.83
0.500	563.1	34.48
0.600	564.2	32.36
0.700	565.4	30.43
0.800	566.6	28.57
0.900	567.8	26.79

(b) A. Kreglewski, *Rocz. Chem.*, **29,** 754 (1955).

$x(1)$	T^c
0.209	560.3
0.497	562.4
0.704	564.8

n-Octane(1) + Ethylbenzene(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **49**, 13 (1969).

$x(1)$	T^c	P^c
0.100	610.39	34.85
0.200	604.47	33.50
0.300	598.85	32.16
0.400	593.72	30.95
0.500	588.83	29.85
0.600	584.26	28.83
0.700	580.03	27.82
0.800	576.19	26.85
0.900	572.48	25.93

n-Nonane(1) + Benzene(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47**, 653 (1967).

$x(1)$	T^c	P^c
0.100	566.0	45.53
0.200	569.6	42.31
0.300	573.2	39.35
0.400	576.7	36.53
0.500	580.3	33.83
0.600	583.7	31.42
0.700	586.8	29.17
0.800	589.6	26.97
0.900	591.9	24.94

n-Decane(1) + Benzene(2)

(a) C. P. Hicks and C. L. Young, *J. Chem. Thermodyn.*, **3,** 899 (1971).

$x(1)$	T^c	$x(1)$	T^c
0.1266	570.2	0.4710	594.1
0.1791	575.0	0.4845	593.3
0.2995	583.6	0.5945	600.0
0.3755	587.8	0.7764	608.2

(b) S. C. Pak and W. B. Kay, *Ind. Eng. Chem. Fundam.*, **11**, 255 (1972).

$x(1)$	T^c	P^c
0.100	570.1	45.97
0.200	578.0	42.86
0.300	584.9	39.78
0.400	591.1	36.70
0.500	596.8	33.77
0.600	602.1	31.00
0.700	606.8	28.36
0.800	611.0	25.87
0.900	614.4	23.57

n-Tridecane(1) + Benzene(2)

(a) S. C. Pak and W. B. Kay, *Ind. Eng. Chem. Fundam.*, **11,** 255 (1972).

$x(1)$	T^c	P^c
0.100	586.2	48.53
0.200	605.9	46.53
0.300	621.9	42.21
0.400	634.7	37.15
0.500	644.9	33.04
0.600	653.5	29.35
0.700	660.5	25.95
0.800	666.2	22.75
0.900	671.0	19.86

n-Hexadecane(1) + Benzene(2)

(a) S. C. Pak and W. B. Kay, *Ind. Eng. Chem. Fundam.*, **11,** 255 (1972).

$x(1)$	T^c	P^c
0.100	604.6	52.57
0.200	655.7	48.69
0.300	657.4	43.57
0.400	672.9	38.66
0.500	685.4	33.91
0.600	695.8	29.49
0.700	704.8	25.22
0.800	712.3	21.39
0.900	718.4	17.92

E. Other Hydrocarbon + Hydrocarbon Mixtures

Cyclopentane(1) + Cyclohexane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47,** 653 (1967).

$x(1)$	T^c	P^c
0.100	550.5	41.54
0.200	546.8	42.16
0.300	543.1	42.78
0.400	539.2	43.35
0.500	535.2	43.86
0.600	531.0	44.27
0.700	526.6	44.59
0.800	522.1	44.86
0.900	517.4	45.05

(b) C. L. Young, *Aust. J. Chem.*, **25,** 1625 (1972).

$x(1)$	T^c
0.2942	541.6
0.4741	534.4
0.5511	530.7
0.7633	522.0

Cyclopentane(1) + Methylcyclopentane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47,** 653 (1967).

$x(1)$	T^c	P^c
0.100	531.4	38.72
0.200	529.5	39.46
0.300	527.6	40.19
0.400	525.6	40.94
0.500	523.6	41.70
0.600	521.4	42.45
0.700	519.3	43.19
0.800	517.0	43.92
0.900	514.7	44.59

Cyclopentane(1) + Methylcyclohexane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47,** 653 (1967).

$x(1)$	T^c	P^c
0.100	568.0	36.40
0.200	563.3	37.74
0.300	558.2	39.05
0.400	552.9	40.31
0.500	547.5	41.45
0.600	541.5	42.53
0.700	534.9	43.50
0.800	527.7	44.30
0.900	520.1	44.90

Cyclopentane(1) + Cycloheptane(2)

(a) C. L. Young, *Aust. J. Chem.*, **25,** 1625 (1972).

$x(1)$	T^c
0.2357	583.9
0.3571	574.6
0.3896	572.8
0.5192	562.0
0.5971	553.4
0.7648	557.4

Cyclopentane(1) + Cyclooctane(2)

(a) C. L. Young, *Aust. J. Chem.*, **25,** 1625 (1972).

$x(1)$	T^c	$x(1)$	T^c
0.2830	621.5		
0.3925	613.2	0.7509	559.3
0.4752	601.8	0.8372	540.0
0.6315	577.0	0.8626	536.1

Cyclohexane(1) + Neopentane(2)

(a) E. J. Partington, J. S. Rowlinson, and J. F. Weston, *Trans. Faraday Soc.*, **56,** 479 (1960).

$x(1)$	T^c
0.254	464.8
0.342	476.2
0.596	506.6
0.824	533.2

Cyclohexane(1) + Methylcyclopentane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47,** 653 (1967).

$x(1)$	T^c	P^c
0.100	535.5	38.28
0.200	537.6	38.57
0.300	539.6	38.85
0.400	541.7	39.12
0.500	543.7	39.40
0.600	545.8	39.70
0.700	547.9	40.00
0.800	550.0	40.31
0.900	552.1	40.62

Cyclohexane(1) + Methylcyclohexane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47,** 653 (1967).

$x(1)$	T^c	P^c
0.100	570.8	35.59
0.200	569.1	36.18
0.300	567.4	36.78
0.400	565.7	37.37
0.500	564.0	37.98
0.600	562.1	38.57
0.700	560.2	39.16
0.800	558.3	39.76
0.900	556.3	40.35

Cyclohexane(1) + Cycloheptane(2)

(a) C. L. Young, *Aust. J. Chem.*, **25,** 1625 (1972).

$x(1)$	T^c
0.2733	589.7
0.3618	586.0
0.5106	579.9
0.6124	573.3
0.7231	568.1
0.7517	565.7

Cyclohexane(1) + Cyclooctane(2)

(a) C. L. Young, *Aust. J. Chem.*, **25,** 1625 (1972).

$x(1)$	T^c	$x(1)$	T^c
0.1632	635.7	0.6929	586.0
0.3924	616.7	0.8290	573.0
0.4322	611.9	0.8660	566.3
0.6201	593.5	0.8677	566.9
0.6448	592.2		

Cyclohexane(1) + *cis*-Decalin(2)

(a) S. C. Pak and W. B. Kay, *Ind. Eng. Chem. Fundam.*, **11,** 255 (1972).

$x(1)$	T^c	P^c
0.1000	695.2	34.66
0.2000	684.6	37.17
0.3000	672.8	39.44
0.4000	660.3	41.41
0.5000	646.3	42.93
0.6000	630.8	43.99
0.7000	613.9	44.43
0.8000	595.8	44.22
0.9000	575.9	43.28

Cycloheptane(1) + Cyclooctane(2)

(a) C. L. Young, *Aust. J. Chem.*, **25,** 1625 (1972).

$x(1)$	T^c
0.2010	613.1
0.3591	620.8
0.4703	624.6
0.6109	630.1
0.7049	634.2
0.7603	637.2

Methylcyclopentane(1) + Methylcyclohexane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47,** 653 (1967).

$x(1)$	T^c	P^c
0.100	569.0	35.45
0.200	565.5	35.90
0.300	561.9	36.33
0.400	558.2	36.72
0.500	554.4	37.07
0.600	550.4	37.38
0.700	546.3	37.62
0.800	542.1	37.78
0.900	537.8	37.91

cis-Decalin(1) + Benzene(2)

(a) S. C. Pak and W. B. Kay, *Ind. Eng. Chem. Fundam.*, **11,** 255 (1972).

$x(1)$	T^c	P^c
0.100	582.1	50.63
0.200	601.6	51.03
0.300	619.5	50.44
0.400	635.6	49.03
0.500	650.1	46.94
0.600	663.2	44.44
0.700	674.8	41.65
0.800	685.7	38.65
0.900	695.8	35.47

cis-Decalin(1) + Ethylbenzene(2)

(a) S. C. Pak and W. B. Kay, *Ind. Eng. Chem. Fundam.*, **11,** 255 (1972).

$x(1)$	T^c	P^c
0.100	626.4	36.91
0.200	635.6	37.22
0.300	645.0	37.33
0.400	654.2	37.21
0.500	663.4	36.90
0.600	672.3	36.45
0.700	680.8	35.81
0.800	689.1	34.97
0.900	697.1	33.75

cis-Decalin(1) + o-Xylene(2)

(a) S. C. Pak and W. B. Kay, *Ind. Eng. Chem. Fundam.*, **11,** 255 (1972).

$x(1)$	T^c	P^c
0.100	637.4	37.76
0.200	645.4	37.82
0.300	653.3	37.72
0.400	661.0	37.47
0.500	668.7	37.03
0.600	676.2	36.39
0.700	683.6	35.55
0.800	690.9	34.61
0.900	698.0	33.46

2,2-Dimethylbutane(1) + 2,2-Dimethylpentane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **49,** 13 (1969).

$x(1)$	T^c	P^c
0.100	517.99	28.40
0.200	515.23	28.82
0.300	512.23	28.82
0.400	509.40	29.59
0.500	506.30	29.89
0.600	502.36	30.18
0.700	499.61	30.42
0.800	496.11	30.62
0.900	492.48	30.79

2,2-Dimethylbutane(1) + 2,2-Dimethylhexane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **49,** 13 (1969).

$x(1)$	T^c	P^c
0.100	545.50	26.44
0.200	540.77	27.29
0.300	535.86	28.13
0.400	530.50	28.86
0.500	524.61	29.52
0.600	518.43	30.09
0.700	511.81	30.57
0.800	504.78	30.90
0.900	497.00	31.06

2,2-Dimethylbutane(1) + 2,2-Dimethylheptane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **49,** 13 (1969).

$x(1)$	T^c	P^c
0.100	571.07	24.97
0.200	565.02	26.01
0.300	558.67	27.27
0.400	551.25	28.46
0.500	543.10	29.52
0.600	534.63	30.42
0.700	525.05	31.14
0.800	514.53	31.59
0.900	502.43	31.64

2,2-Dimethylpentane(1) + 2,2-Dimethylhexane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **49,** 13 (1969).

$x(1)$	T^c	P^c
0.100	547.43	25.88
0.200	544.81	26.19
0.300	542.15	26.49
0.400	539.36	26.77
0.500	536.48	27.04
0.600	533.51	27.30
0.700	530.39	27.54
0.800	527.29	27.77
0.900	524.02	27.92

2,2-Dimethylpentane(1) + 2,2-Dimethylheptane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **49,** 13 (1969).

x(1)	T^c	P^c
0.100	572.07	24.13
0.200	567.30	24.76
0.300	562.50	25.38
0.400	557.58	25.99
0.500	552.53	26.57
0.600	547.11	27.06
0.700	541.15	27.50
0.800	534.80	27.79
0.900	527.91	27.95

2,2-Dimethylhexane(1) + 2,2-Dimethylheptane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **49,** 13 (1969).

x(1)	T^c	P^c
0.100	574.29	23.74
0.200	571.89	23.99
0.300	569.35	24.24
0.400	566.37	24.48
0.500	564.37	24.71
0.600	561.65	24.95
0.700	558.90	25.17
0.800	556.12	25.36
0.900	553.18	25.51

2-Methylpentane(1) + 2-Methylhexane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **49,** 13 (1969).

x(1)	T^c	P^c
0.100	528.05	27.90
0.200	525.35	28.32
0.300	522.39	28.71
0.400	519.25	29.05
0.500	516.03	29.38
0.600	512.75	29.67
0.700	509.25	29.94
0.800	505.60	30.17
0.900	501.75	30.38

2-Methylpentane(1) + 2-Methylheptane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **49,** 13 (1969).

x(1)	T^c	P^c
0.100	555.25	26.01
0.200	550.25	27.07
0.300	544.95	27.99
0.400	539.50	28.81
0.500	533.85	29.52
0.600	527.95	30.07
0.700	521.45	30.48
0.800	514.35	30.73
0.900	506.65	30.68

2-Methylpentane(1) + 2-Methyloctane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **49,** 13 (1969).

x(1)	T^c	P^c
0.100	579.05	24.35
0.200	573.95	25.63
0.300	567.60	26.84
0.400	560.35	27.99
0.500	552.25	28.99
0.600	543.45	29.90
0.700	534.05	30.61
0.800	523.65	30.91
0.900	511.45	30.84

2-Methylhexane(1) + 2-Methylheptane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **49,** 13 (1969).

x(1)	T^c	P^c
0.100	557.90	25.39
0.200	555.54	25.76
0.300	552.88	26.08
0.400	550.09	26.37
0.500	547.20	26.64
0.600	544.27	26.89
0.700	541.20	27.12
0.800	538.10	27.31
0.900	534.85	27.46

2-Methylhexane(1) + 2-Methyloctane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **49,** 13 (1969).

x(1)	T^c	P^c
0.100	580.75	23.81
0.200	577.45	24.44
0.300	573.50	25.06
0.400	568.80	25.64
0.500	563.65	26.14
0.600	557.95	26.60
0.700	551.75	27.00
0.800	545.25	27.32
0.900	538.40	27.49

2-Methylheptane(1) + 2-Methyloctane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **49**, 13 (1969).

x(1)	T^c	P^c
0.100	581.10	23.43
0.200	579.25	23.75
0.300	577.35	24.04
0.400	575.35	24.30
0.500	573.25	24.55
0.600	571.10	24.76
0.700	568.68	24.94
0.800	565.98	25.06
0.900	563.05	25.10

Ethylene(1) + Propene(2)

(a) G. G. Haselden, F. A. Holland, M. B. King, and R. F. Strickland-Constable, *Proc. Roy. Soc., Ser. A*, **240,** 1 (1957).

x(1)	T^c	P^c	V^c
0.117	358.0	48.3	186.9
0.256	349.7	50.4	194.2
0.384	341.2	52.3	213.7
0.494	332.8	53.6	205.8
0.625	322.8	54.7	194.9
0.759	310.3	54.4	185.9
0.914	293.0	52.7	161.3

Ethylene(1) + Acetylene(2)

(a) J. L. McCurdy and D. L. Katz, *Ind. Eng. Chem.*, **36**, 674 (1944).

x(1)	T^c	P^c
0.54	288.7	56.70

(b) S. W. Churchill, W. G. Collamore, and D. L. Katz, *Oil Gas J.*, (13) **41**, 33 (1942).

x(1)	T^c	P^c
0.70	285.9	56.6
0.82	278.7	52.3

Propene(1) + n-But-1-ene(2)

(a) G. H. Goff, P. S. Farrington, and B. H. Sage, *Ind. Eng. Chem.*, **42,** 735 (1950).

x(1)	T^c	P^c	V^c
0.217	407.6	43.5	228.8
0.551	394.3	46.6	210.7
0.824	377.6	47.0	194.0

Propene(1) + Acetylene(2)

(a) J. L. McCurdy and D. L. Katz, *Oil Gas J.*, (44) **43,** 102 (1945).

$x(1)$	T^c	P^c
0.114	313.7	62.7
0.307	325.9	63.4
0.506	342.6	63.2
0.788	353.7	59.0
0.885	358.1	54.4

Benzene(1) + Neopentane(2)

(a) E. J. Partington, J. S. Rowlinson, and J. F. Weston, *Trans. Faraday Soc.*, **56,** 479 (1960).

$x(1)$	T^c
0.198	449.7
0.375	472.0
0.539	493.0
0.676	515.2

Benzene(1) + Cyclopentane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47,** 653 (1967).

$x(1)$	T^c	P^c
0.900	556.9	49.03
0.800	551.3	48.75
0.700	545.8	48.36
0.600	540.5	47.97
0.500	535.3	47.55
0.400	530.4	47.10
0.300	525.6	46.64
0.200	521.0	46.14
0.100	516.4	45.66

(b) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **67,** 1605 (1971).

$x(1)$	T^c	$x(1)$	T^c
0.136	518.0	0.690	546.0
0.305	526.1	0.720	545.7
0.503	536.2	0.822	552.6

Benzene(1) + Cyclohexane(2)

(a) E. J. Partington, J. S. Rowlinson, and J. F. Weston, *Trans. Faraday Soc.*, **56,** 479 (1960).

$x(1)$	T^c	$x(1)$	T^c
0.079	553.0	0.538	553.9
0.195	552.6	0.683	555.6
0.433	553.3	0.813	557.8

(b) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **67,** 1605 (1971).

$x(1)$	T^c	$x(1)$	T^c
0.164	553.2	0.602	554.7
0.349	553.1	0.670	555.6
0.469	553.9	0.821	557.7
0.561	554.6	0.856	558.7
0.589	554.7		

(c) D. Hissong and W. B. Kay, *Proc. Amer. Petr. Inst., Refining Div.*, **48,** 397 (1968).

$x(1)$	T^c	P^c
0.100	553.63	41.45
0.200	553.45	42.09
0.300	553.47	42.82
0.400	553.84	43.55
0.500	554.41	44.32
0.600	555.28	45.12
0.700	556.58	45.97
0.800	558.21	46.93
0.900	558.13	47.97

Benzene(1) + Methylcyclopentane(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47,** 653 (1967).

$x(1)$	T^c	P^c
0.100	534.9	38.79
0.200	536.7	39.69
0.300	538.7	40.63
0.400	541.0	41.59
0.500	543.7	42.62
0.600	546.7	43.71
0.700	550.2	44.91
0.800	554.0	46.24
0.900	558.0	47.65

Benzene(1) + Methylcyclohexane(2)

(a) D. Hissong and W. B. Kay, *Proc. Amer. Petr. Inst., Refining Div.*, **48,** 397 (1968).

$x(1)$	T^c	P^c
0.100	570.39	39.16
0.200	568.65	37.34
0.300	567.10	38.56
0.400	565.66	39.84
0.500	564.28	41.18
0.600	563.14	42.57
0.700	562.38	44.04
0.800	561.99	45.62
0.900	561.94	47.28

Benzene(1) + Ethylene(2)

(a) S. G. Lyubetski, *Zh. Prikl. Khim.*, **35,** 141 (1962).

$x(1)$	T^c	P^c	V^c
0.060	307.8	64.3	122
0.240	357.6	90.5	126
0.348	398.0	98.0	138
0.534	449.2	96.1	166
0.756	514.5	69.7	210

Benzene(1) + Toluene(2)

(a) E. J. Partington, J. S. Rowlinson, and J. F. Weston, *Trans. Faraday Soc.*, **56,** 479 (1960).

$x(1)$	T^c
0.186	587.4
0.362	581.9
0.692	572.3
0.838	567.3

(b) J. Harard, *Monatsh.*, **65,** 153 (1935).

(x)1	T^c	$x(1)$	T^c
0.02	593.7	0.50	579.2
0.04	593.0	0.60	576.3
0.06	591.4	0.70	573.4
0.10	590.1	0.80	569.5
0.20	587.9	0.90	567.7
0.30	585.3	0.94	566.1
0.40	583.2	0.96	565.6
		0.98	564.7

(c) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47,** 653 (1967).

$x(1)$	T^c	P^c
0.100	590.3	42.00
0.200	587.7	42.83
0.300	585.1	43.64
0.400	582.4	44.45
0.500	579.5	45.24
0.600	576.4	46.02
0.700	573.2	46.81
0.800	570.0	47.59
0.900	566.6	48.36

Benzene(1) + Ethylbenzene(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47,** 653 (1967).

$x(1)$	T^c	P^c
0.100	613.5	37.67
0.200	609.3	39.20
0.300	604.9	40.65
0.400	600.1	42.08
0.500	595.0	43.50
0.600	589.6	44.86
0.700	583.5	46.10
0.800	577.2	47.25
0.900	570.6	48.23

Benzene(1) + o-Xylene(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47,** 653 (1967).

$x(1)$	T^c	P^c
0.100	625.3	38.81
0.200	620.0	40.37
0.300	614.6	41.81
0.400	608.9	43.20
0.500	602.9	44.54
0.600	596.0	45.82
0.700	588.4	46.96
0.800	580.6	47.94
0.900	572.4	48.65

Benzene(1) + Naphthalene(2)

(a) D. C.-H. Cheng, *Chem. Eng. Sci.*, **18,** 715 (1963).

$x(1)$	T^c	V^c
0.318	705.1	346
0.527	670.6	307
0.542	667.2	302
0.758	621.9	272
0.826	606.1	282
0.857	597.9	271
0.321†	703.2	345
0.659†	641.2	298
0.680†	637.3	291
0.896†	587.6	257
0.901†	586.4	257

† Second sample of naphthalene.

Toluene(1) + Neopentane(2)

(a) E. J. Partington, J. S. Rowlinson, and J. F. Weston, *Trans. Faraday Soc.*, **56,** 479 (1960).

$x(1)$	T^c
0.321	481.7

Toluene(1) + Cyclohexane(2)

(a) E. J. Partington, J. S. Rowlinson, and J. F. Weston, *Trans. Faraday Soc.*, **56,** 479 (1960).

$x(1)$	T^c
0.234	561.0
0.378	566.3
0.672	578.2
0.834	585.0

Toluene(1) + Ethylbenzene(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47,** 653 (1967).

$x(1)$	T^c	P^c
0.100	615.5	36.66
0.200	613.3	37.19
0.300	611.0	37.75
0.400	608.7	38.32
0.500	606.2	38.86
0.600	603.7	39.37
0.700	601.2	39.83
0.800	598.7	40.26
0.900	596.0	40.70

Toluene(1) + o-Xylene(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47,** 653 (1967).

$x(1)$	T^c	P^c
0.100	627.0	37.72
0.200	623.7	38.26
0.300	620.2	38.75
0.400	616.7	39.20
0.500	613.0	39.63
0.600	609.0	40.02
0.700	605.1	40.39
0.800	601.1	40.72
0.900	597.0	41.02

o-Xylene(1) + Ethylbenzene(2)

(a) W. B. Kay and D. Hissong, *Proc. Amer. Petr. Inst., Refining Div.*, **47,** 653 (1967).

$x(1)$	T^c	P^c
0.100	618.8	36.26
0.200	620.1	36.37
0.300	621.4	36.47
0.400	622.7	36.58
0.500	624.0	36.68
0.600	625.2	36.78
0.700	626.2	36.88
0.800	627.4	36.97
0.900	628.7	37.06

Naphthalene(1) + Cyclohexane(2)

(a) D. C.-H. Cheng, *Chem. Eng. Sci.*, **18,** 715 (1963).

$x(1)$	T^c	V^c
0.215	604.2	303
0.245	610.3	323
0.308	624.7	316
0.414	646.9	349
0.540	671.1	345

Naphthalene(1) + Ethylene(2)

(a) G. S. A. van Welie and G. A. M. Diepen, *Recl. Trav. Chim. Pays-Bas*, **80,** 673, 693 (1961).

$x(1)$	T^c	P^c	V^c
0.170	325.25	176.3	77.0
0.170	332.10	183.3	
0.170	341.85	192.8	
0.170	352.00	202.0	
0.1851	404.2	236.1	93.0
0.2200	475.2	247.2	113.0
0.2886	540.2	230.0	134.5

Benzene(1) + Phenanthrene(2)

(a) D. C.-H. Cheng, *Chem. Eng. Sci.*, **18,** 715 (1963).

$x(1)$	T^c	V^c
0.709	711.7	289
0.734	706.2	284
0.849	645.7	256
0.893	623.7	269
0.894	621.2	247

Benzene(1) + Anthracene(2)

(a) D. C.-H. Cheng, *Chem. Eng. Sci.*, **18,** 715 (1963).

$x(1)$	T^c	V^c
0.897	621.7	254
0.913	614.2	256
0.936	597.7	260
0.952	589.7	245

F. Mixtures of Simple Molecules

Methane(1) + Argon(2)

(a) I. W. Jones and J. S. Rowlinson, *Trans. Faraday Soc.*, **59,** 1702 (1963).

x(1)	T^c
0.204	160.5
0.407	169.6
0.595	176.9
0.795	184.2

Methane(1) + Oxygen(2)

(a) I. W. Jones and J. S. Rowlinson, *Trans. Faraday Soc.*, **59,** 1702 (1963).

x(1)	T^c
0.201	159.1
0.401	168.1
0.598	175.7
0.797	183.2

Methane(1) + Carbon Monoxide(2)

(a) I. W. Jones and J. S. Rowlinson, *Trans. Faraday Soc.*, **59,** 1702 (1963).

x(1)	T^c
0.203	145.9
0.402	158.5
0.599	170.3
0.799	181.1

(b) A. Toyama, P. S. Chappelear, T. W. Leland, and R. Kobayashi, *Advan. Cryog. Eng.*, **7,** 125 (1961).

x(1)	T^c	P^c
0.107	185.9	48.13
0.363	172.0	49.64
0.59	158.1	46.54
0.82	144.2	39.99

Methane(1) + Carbon Dioxide(2)

(a) H. G. Donnelly and D. L. Katz, *Ind. Eng. Chem.*, **46,** 511 (1954).

x(1)	T^c	P^c
0.120	286.5	83.77
0.295	273.7	86.18
0.457	256.5	84.46
0.820	222.0	67.91

(b) G. Kaminishi and T. Toriumi, *Rev. Phys. Chem. Jap.*, **38,** 79 (1968).

x(1)	T^c	P^c
0.12	293.15	80.2
0.22	283.15	83.3

Methane(1) + Nitrogen(2)

(a) I. W. Jones and J. S. Rowlinson, *Trans. Faraday Soc.*, **59,** 1702 (1963).

x(1)	T^c
0.202	140.1
0.400	154.6
0.605	168.4
0.798	180.1

(b) S. D. Chang and B. C-Y. Lu, *Chem. Eng. Progr., Symp. Ser., No. 81,* **63,** 18 (1967).

x(1)	T^c	P^c
0.669	171.4	49.67

(c) M. R. Cines, J. T. Roach, R. J. Hogan, and C. H. Roland, *Chem. Eng. Progr., Symp. Ser., No. 6,* **49,** 1 (1953).

x(1)	T^c	P^c
0.09	133.1	37.44
0.25	144.3	43.44
0.41	155.4	47.57
0.67	172.0	49.64

(d) O. T. Bloomer and J. Parent, *Chem. Eng. Progr., Symp. Ser., No. 3,* **49,** 23 (1953).

x(1)	T^c	P^c
0.0485	129.6	35.78
0.1577	136.9	39.85
0.3030	146.9	44.82
0.4912	159.6	49.23
0.7121	174.2	50.68
0.8998	185.1	48.61
0.9389	187.2	48.16
0.9705	189.0	47.26
0.9858	189.8	46.54

Nitrogen(1) + Argon(2)

(a) I. W. Jones and J. S. Rowlinson, *Trans. Faraday Soc.*, **59,** 1702 (1963).

x(1)	T^c
0.201	131.0
0.401	135.9
0.599	141.0
0.800	146.1

Nitrogen(1) + Oxygen(2)

(a) I. W. Jones and J. S. Rowlinson, *Trans. Faraday Soc.*, **59,** 1702 (1963).

x(1)	T^c
0.202	149.4
0.401	143.8
0.599	138.0
0.798	132.0

(b) J. P. Kuenen, J. Verschoyle, and A. T. van Urk, *Commun. Phys. Lab. Leiden*, No. 161 (1922).

x(1)	T^c	P^c
0.25	147.49	46.50
0.50	140.43	42.46

(c) J. P. Kuenen and A. L. Clark, *Commun. Phys. Lab. Leiden*, No. 150b (1917).

x(1)	T^c	P^c
0.79 (Air)	132.36	37.74

Nitrogen(1) + Carbon Monoxide(2)

(a) I. W. Jones and J. S. Rowlinson, *Trans. Faraday Soc.*, **59,** 1702 (1963).

x(1)	T^c
0.203	131.4
0.402	130.0
0.598	128.5
0.796	127.3

Nitrogen(1) + Carbon Dioxide(2)

(a) N. K. Muirbrook and J. M. Prausnitz, *Amer. Inst. Chem. Eng. J.*, **11,** 1092 (1965).

x(1)	T^c	P^c	V^c
0.2926	273.15	120.0	77.5

(b) G. H. Zenner and L. I. Dana, *Chem. Eng. Progr., Symp. Ser., No. 44,* **59,** 36 (1963).

x(1)	T^c	P^c
0.302	273.15	118.6

(c) I. R. Krichevskii, N. E. Khazanova, L. S. Lesnevskaya, and L. Y. Scandalova, *Khim. Prom.*, 169 (1962); *cf. Chem. Abstr.*, **59,** 4566b (1963).

x(1)	T^c	P^c
0.14	293.15	98.6

Argon(1) + Oxygen(2)

(a) I. W. Jones and J. S. Rowlinson, *Trans. Faraday Soc.*, **59,** 1702 (1963).

$x(1)$	T^c
0.206	153.6
0.406	152.7
0.601	151.9
0.799	151.3

Argon(1) + Carbon Monoxide(2)

(a) I. W. Jones and J. S. Rowlinson, *Trans. Faraday Soc.*, **59,** 1702 (1963).

$x(1)$	T^c
0.203	135.8
0.406	139.4
0.596	142.9
0.798	147.1

Oxygen(1) + Carbon Monoxide(2)

(a) I. W. Jones and J. S. Rowlinson, *Trans. Faraday Soc.*, **59,** 1702 (1963).

$x(1)$	T^c
0.203	136.9
0.401	140.8
0.599	145.5
0.805	150.1

Oxygen(1) + Carbon Dioxide(2)

(a) N. K. Muirbrook and J. M. Prausnitz, *Amer. Inst. Chem. Eng. J.*, **11,** 1092 (1965).

$x(1)$	T^c	P^c	V^c
0.312	273.15	117.4	76.0

(b) H. S. Booth and J. M. Carter, *J. Phys. Chem.*, **34,** 2801 (1930).

$x(1)$	T^c	P^c
0.10	295.66	87.1
0.20	285.65	100.9
0.60	213.10	150.0
0.50	237.45	142.6

(c) W. H. Keesom, *Commun. Phys. Lab. Leiden*, No. 88 (1903).

$x(1)$	T^c	P^c
0.1047	295.14	87.75
0.1994	285.66	101.0

(d) G. H. Zenner and L. I. Dana, *Chem. Eng. Progr., Symp. Ser., No. 44*, **59,** 36 (1963).

$x(1)$	T^c	P^c
0.32	273.15	116
0.56	232.85	146
0.62	218.15	150

Helium(1) + Hydrogen(2)

(a) C. M. Sneed, R. E. Sonntag, and G. J. van Wyles, *J. Chem. Phys.*, **49,** 2410 (1968); W. B. Streett, R. E. Sonntag, and G. J. van Wylen, *ibid.*, **40,** 1390 (1964).

$x(1)$	T^c	P^c
0.076	32.50	176
0.134	31.90	214
0.171	31.50	243
0.214	31.00	285
0.239	30.60	324
0.281	29.80	410
0.320	29.00	527
0.363	28.45	667
0.385	28.20	816
0.404	28.14	1034

Helium(1) + Nitrogen(2)

(a) W. B. Streett, *Chem. Eng. Progr., Symp. Ser., No. 81*, **63,** 37 (1967).

$x(1)$	T^c	P^c
0.575	119.92	503
0.609	119.92	662
0.52	120.40	365
0.49	121.00	296
0.43	121.74	228

(b) W. B. Streett and J. L. E. Hill, *J. Chem. Phys.*, **52,** 1402 (1970).

$x(1)$	T^c	P^c
0.52	120.40	405
0.60	120.59	963
0.66	124.05	1611
0.67	126.81	2080
0.67	130.00	2690
0.68	134.00	3390
0.68	136.50	3850

Helium(1) + Argon(2)

(a) W. B. Streett, American Institute of Chemical Engineers, Symposia on Phase Equilibria and Related Properties, Nov 1967; and W. B. Streett, *Trans. Faraday Soc.*, **65,** 696 (1969).

$x(1)$	T^c	P^c
0.05	150	69
0.20	149	137
0.40	147.5	344
0.46	147.1	442

Hydrogen(1) + Nitrogen(2)

(a) T. T. H. Verschoyle, *Phil. Trans. Roy. Soc. London, Ser. A*, **230,** 189 (1931).

$x(1)$	T^c	P^c
0.53	88	140
0.58	78	193

Hydrogen(1) + Carbon Monoxide(2)

(a) T. T. H. Verschoyle, *Phil. Trans. Roy. Soc. London, Ser. A*, **230,** 189 (1931).

$x(1)$	T^c	P^c
0.58	88	189
0.60	82	231
0.64	73	329
0.66	68	384

Neon(1) + Argon(2)

(a) W. B. Streett, *J. Chem. Phys.*, **46,** 3282 (1967).

$x(1)$	T^c	P^c	V^c
0.39	129.93	155	
0.478	121.36	202	38.70
0.548	110.78	289	31.70
0.577	101.94	401	27.17
0.59	95.82	621	

Neon(1) + Nitrogen(2)

(a) W. B. Streett, *Cryogenics*, **5,** 27 (1965).

$x(1)$	T^c	P^c
0.175	120.64	58.6
0.267	117.61	68.9

(b) W. B. Streett, *Cryogenics*, **8,** 88 (1968).

$x(1)$	T^c	P^c
0.33	114.34	81
0.41	108.91	93
0.53	100.78	116
0.62	90.65	142
0.64	86.19	150
0.66	77.35	166
0.67	66.13	228

Neon(1) + Oxygen(2)

(a) W. B. Streett and C. H. Jones, *Advan. Cryog. Eng.*, **11**, 356 (1965).

x(1)	T^c	P^c
0.09	110.39	58.6
0.22	120.03	96.5
0.43	130.00	172
0.50	146.36	238
0.55	152.29	310

G. Mixtures Containing Perfluorocarbons

Propane(1) + Perfluoropropane(2)

(a) A. E. H. N. Mousa, W. B. Kay, and A. Kreglewski, *J. Chem. Thermodyn.*, **4**, 301 (1972).

x(1)	T^c	P^c
0.1162	341.73	27.72
0.3233	337.77	29.33
0.4263	337.38	30.25
0.5235	338.37	31.33
0.7060	345.28	34.54
0.9074	360.40	39.94

Propane(1) + n-Perfluorohexane(2)

(a) A. E. H. N. Mousa, W. B. Kay, and A. Kreglewski, *J. Chem. Thermodyn.*, **4**, 301 (1972).

x(1)	T^c	P^c
0.1225	443.20	22.07
0.3287	430.19	28.26
0.5781	405.50	35.63
0.7345	388.50	37.87
0.8695	375.67	38.84
0.9088	372.57	39.46

Propane(1) + Hexafluorobenzene(2)

(a) A. E. H. N. Mousa, W. B. Kay, and A. Kreglewski, *J. Chem. Thermodyn.*, **4**, 301 (1972).

x(1)	T^c	P^c
0.1008	508.13	36.78
0.3027	488.66	43.66
0.5319	454.53	50.72
0.7314	420.39	51.54
0.9083	387.08	46.43

Propane(1) + Perfluoroacetone(2)

(a) A. E. H. N. Mousa, W. B. Kay, and A. Kreglewski, *J. Chem. Thermodyn.*, **4**, 301 (1972).

x(1)	T^c	P^c
0.1240	353.57	29.69
0.3194	349.05	31.21
0.4437	346.90	32.14
0.7047	351.38	35.75
0.8573	359.48	39.10

Propane(1) + Perfluoroacetonitrile(2)

(a) A. E. H. N. Mousa, W. B. Kay, and A. Kreglewski, *J. Chem. Thermodyn.*, **4**, 301 (1972).

x(1)	T^c	P^c
0.1182	311.94	36.14
0.3340	318.59	36.30
0.5504	332.53	40.69
0.7130	345.00	42.51
0.8435	357.17	43.14

n-Hexane(1) + n-Perfluorohexane(2)

(a) A. E. H. N. Mousa, W. B. Kay, and A. Kreglewski, *J. Chem. Thermodyn.*, **4**, 301 (1972).

x(1)	T^c	P^c
0.1012	447.16	18.88
0.3352	446.66	20.24
0.5018	451.68	21.97
0.6242	461.49	23.98
0.9020	492.57	29.16

Perfluoromethylcyclohexane(1) + n-Hexane(2)

(a) J. Barber, Ph.D. Dissertation, Ohio State University, 1968.

x(1)	T^c	P^c
0.8172	478.20	21.56
0.6604	473.95	22.18
0.4830	473.58	23.31
0.3342	478.31	24.81
0.1732	489.94	27.55

Perfluoromethylcyclohexane(1) + 2-Methylpentane(2)

(a) J. Barber, Ph.D. Dissertation, Ohio State University, 1968.

x(1)	T^c	P^c
0.7980	476.53	21.70
0.6087	471.13	22.72
0.4104	471.00	24.26
0.3077	474.00	25.25
0.2059	479.12	26.52
0.0913	487.75	28.64

Perfluoromethylcyclohexane(1) + 3-Methylpentane(2)

(a) J. Barber, Ph.D. Dissertation, Ohio State University, 1968.

x(1)	T^c	P^c
0.7951	477.24	21.78
0.5869	472.82	23.16
0.4045	474.64	24.76
0.2952	478.75	25.93
0.2062	484.52	27.49
0.0855	495.16	29.64

Perfluoromethylcyclohexane(1) + 2,3-Dimethylbutane(2)

(a) J. Barber, Ph.D. Dissertation, Ohio State University (1968).

x(1)	T^c	P^c
0.8173	477.95	21.82
0.5930	472.22	23.21
0.4417	471.89	24.32
0.2875	476.00	26.10
0.2030	481.53	27.65
0.1078	488.96	29.61

Perfluoromethylcyclohexane(1) + 2,2-Dimethylbutane(2)

(a) J. Barber, Ph.D. Dissertation, Ohio State University, 1968.

x(1)	T^c	P^c
0.8330	477.70	21.69
0.6353	470.25	23.00
0.4025	467.85	24.71
0.2943	469.74	25.85
0.2056	473.27	27.17
0.0848	481.64	29.30

Perfluoromethylcyclohexane(1) + Methylcyclohexane(2)

(a) D. E. L. Dyke, J. S. Rowlinson, and R. Thacker, *Trans. Faraday Soc.*, **55**, 903 (1959).

x(1)	T^c
0.19	541
0.40	511
0.49	501
0.65	489
0.81	484

Perfluorocyclohexane(1) + Cyclopentane(2)

(a) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **67**, 1605 (1971).

x(1)	T^c
0.1280	490.2
0.1895	485.5
0.3130	472.0
0.3760	463.2
0.5310	455.0
0.6560	453.2

Perfluorocyclohexane(1) + Cyclohexane(2)

(a) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **67**, 1605 (1971).

$x(1)$	T^c
0.0210	550.0
0.2420	513.5
0.3470	494.7
0.6280	464.8
0.8460	459.5

Perfluorocyclohexane(1) + Cycloheptane(2)

(a) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **67**, 1605 (1971).

$x(1)$	T^c
0.0530	592.5
0.1700	558.8
0.3130	527.5
0.6850	474.3
0.7700	466.5

Perfluorocyclohexane(1) + Cyclooctane(2)

(a) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **67**, 1605 (1971).

$x(1)$	T^c
0.0680	627.5
0.3020	569.2
0.4510	529.8
0.7140	472.5
0.8990	446.0

Perfluorocyclohexane(1) + Octamethylcyclotetrasiloxane(2)

(a) C. L. Young, *J. Chem. Soc., Faraday Trans. 2*, **68**, 452 (1972).

$x(1)$	T^c
0.1690	559.4
0.4622	532.1
0.6519	491.6
0.7023	486.5
0.7919	475.5
0.8248	472.7
0.8255	471.7
0.9006	465.6

Hexafluorobenzene(1) + *n*-Perfluorohexane(2)

(a) M. L. Orton, Ph.D. Thesis, University of Birmingham, U.K., 1968; M. L. Orton and C. R. Patrick, *J. Chem. Soc.*, to be published.

$x(1)$	T^c
0.196	459.10
0.333	466.30
0.369	468.95
0.433	472.40
0.446	473.70
0.594	483.25
0.576	482.05
0.696	490.35
0.854	504.05

Hexafluorobenzene(1) + Perfluoromethylcyclohexane(2)

(a) M. L. Orton, Ph.D. Thesis, University of Birmingham, U.K., 1968; M. L. Orton and C. R. Patrick, *J. Chem. Soc.*, to be published.

$x(1)$	T^c
0.227	489.20
0.400	492.30
0.401	492.25
0.538	495.85
0.557	496.60
0.699	501.75
0.721	502.35
0.727	502.65
0.737	503.05
0.866	509.25

Hexafluorobenzene(1) + Carbon Tetrachloride(2)

(a) M. L. Orton, Ph.D. Thesis, University of Birmingham, U.K., 1968; M. L. Orton and C. R. Patrick, *J. Chem. Soc.*, to be published.

$x(1)$	T^c
0.098	550.3
0.103	548.95
0.107	548.95
0.292	538.65
0.304	538.4
0.403	532.45
0.415	532.3
0.590	526.1
0.599	525.85
0.787	520.8
0.802	520.55

(b) C. L. Young, unpublished results.

$x(1)$	T^c
0.1704	545.5
0.2603	540.1
0.4446	530.5
0.5513	527.0
0.6938	522.3
0.7380	521.4
0.8795	516.8

Hexafluorobenzene(1) + n-Pentane(2)

(a) C. P. Hicks and C. L. Young, *J. Chem. Thermodyn.*, **3**, 899 (1971).

$x(1)$	T^c
0.2143	471.2
0.3202	472.8
0.3672	475.6
0.4192	477.2
0.6576	489.0
0.7146	496.0
0.8145	504.6
0.8317	505.4
0.9099	510.6

Hexafluorobenzene(1) + n-Hexane(2)

(a) C. P. Hicks and C. L. Young, *J. Chem. Thermodyn.*, **3**, 899 (1971).

$x(1)$	T^c
0.2337	502.3
0.4654	500.4
0.5743	502.3
0.8166	507.5
0.8958	511.5

(b) A. E. H. N. Mousa, W. B. Kay, and A. Kreglewski, *J. Chem. Thermodyn.*, **4**, 301 (1972).

$x(1)$	T^c	P^c
0.9187	513.79	32.50
0.7039	506.65	31.49
0.4929	502.80	30.89
0.3459	502.31	30.59
0.1125	505.00	30.50

Hexafluorobenzene(1) + n-Heptane(2)

(a) C. P. Hicks and C. L. Young, *J. Chem. Thermodyn.*, **3**, 899 (1971).

$x(1)$	T^c
0.2213	530.2
0.3569	522.6
0.4669	521.1
0.5837	516.2
0.6228	515.6
0.8623	516.9
0.9505	516.7

Hexafluorobenzene(1) + n-Octane(2)

(a) C. P. Hicks and C. L. Young, *J. Chem. Thermodyn.*, **3,** 899 (1971).

$x(1)$	T^c
0.2384	555.2
0.2973	550.0
0.4277	540.2
0.5396	533.7
0.7228	524.1
0.7734	521.2
0.7859	521.2
0.8851	519.8

Hexafluorobenzene(1) + n-Nonane(2)

(a) C. P. Hicks and C. L. Young, *J. Chem. Thermodyn.*, **3,** 899 (1971).

$x(1)$	T^c
0.2540	576.5
0.3408	567.7
0.5074	551.2
0.5912	544.0
0.7968	528.2
0.8500	524.5
0.8711	521.8

Hexafluorobenzene(1) + n-Decane(2)

(a) C. P. Hicks and C. L. Young, *J. Chem. Thermodyn.*, **3,** 899 (1971).

$x(1)$	T^c
0.3027	590.2
0.3729	583.5
0.4050	580.4
0.5433	567.5
0.6574	555.5
0.6961	545.6
0.7208	544.0
0.8260	530.5
0.8754	527.5
0.9044	526.5

Hexafluorobenzene(1) + n-Dodecane(2)

(a) C. P. Hicks and C. L. Young, *J. Chem. Thermodyn.*, **3,** 899 (1971).

$x(1)$	T^c
0.2244	634.2
0.4888	602.0
0.5819	586.4
0.7074	566.5
0.7243	564.7
0.7952	551.5
0.9538	524.8

Hexafluorobenzene(1) + Cyclopentane(2)

(a) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **67,** 1598 (1971).

$x(1)$	T^c
0.065	508.2
0.180	503.2
0.280	502.7
0.470	500.7
0.640	505.2
0.801	510.4

Hexafluorobenzene(1) + Cyclohexane(2)

(a) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **67,** 1598 (1971).

$x(1)$	T^c	$x(1)$	T^c
0.1595	540.3	0.6071	516.8
0.2049	535.8	0.6488	516.2
0.2519	534.2	0.6732	515.5
0.3723	526.4	0.8002	514.7
0.5366	520.4	0.8669	515.5
0.5495	518.5		

Hexafluorobenzene(1) + Cycloheptane(2)

(a) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **67,** 1598 (1971).

$x(1)$	T^c
0.140	589.4
0.252	577.7
0.257	577.4
0.452	554.7
0.531	546.0
0.692	531.7
0.813	524.7

Hexafluorobenzene(1) + Methylcyclohexane(2)

(a) R. J. Powell, F. L. Swinton, and C. L. Young, *J. Chem. Thermodyn.*, **2,** 105 (1970).

$x(1)$	T^c
0.1455	562.7
0.3083	550.3
0.5435	533.7
0.6258	528.7
0.6731	525.2
0.8035	520.7
0.9218	518.7

Hexafluorobenzene(1) + *trans*-1,4-Dimethylcyclohexane(2)

(a) R. J. Powell, F. L. Swinton, and C. L. Young, *J. Chem. Thermodyn.*, **2,** 105 (1970).

$x(1)$	T^c
0.2126	569.0
0.3036	561.4
0.4674	547.4
0.6270	535.4
0.7531	527.4
0.8565	522.8

Hexafluorobenzene(1) + 1,*trans*-3,5-Trimethylcyclohexane(2)

(a) R. J. Powell, F. L. Swinton, and C. L. Young, *J. Chem. Thermodyn.*, **2,** 105 (1970).

$x(1)$	T^c
0.2112	581.3
0.3359	568.2
0.5320	552.3
0.7071	538.2
0.7945	531.0

Hexafluorobenzene(1) + Benzene(2)

(a) R. J. Powell, F. L. Swinton, and C. L. Young, *J. Chem. Thermodyn.*, **2,** 105 (1970).

$x(1)$	T^c
0.2229	542.7
0.4055	532.7
0.4815	528.9
0.5971	525.7
0.6686	523.5
0.7743	520.6
0.7932	520.5
0.8814	518.3

Hexafluorobenzene(1) + Toluene(2)

(a) R. J. Powell, F. L. Swinton, and C. L. Young, *J. Chem. Thermodyn.*, **2,** 105 (1970).

$x(1)$	T^c
0.1095	580.7
0.1145	579.9
0.2533	568.9
0.3583	599.7
0.5671	543.2
0.7820	529.0
0.8398	525.7

Hexafluorobenzene(1) + *p*-Xylene(2)

(a) R. J. Powell, F. L. Swinton, and C. L. Young, *J. Chem. Thermodyn.*, **2**, 105 (1970).

$x(1)$	T^c
0.1046	605.7
0.2516	590.7
0.4120	573.5
0.5481	558.9
0.5820	554.6
0.5849	554.2
0.7968	533.7

Hexafluorobenzene(1) + Mesitylene(2)

(a) R. J. Powell, F. L. Swinton, and C. L. Young, *J. Chem. Thermodyn.*, **2**, 105 (1970).

$x(1)$	T^c
0.1408	620.8
0.2715	605.9
0.4322	586.4
0.5730	569.8
0.6774	556.7

Hexafluorobenzene(1) + Octamethylcyclotetrasiloxane(2)

(a) C. L. Young, *J. Chem. Soc., Faraday Trans. 2*, **68**, 580 (1972).

$x(1)$	T^c
0.2381	575.7
0.3349	570.1
0.3689	567.0
0.5212	556.6
0.6052	549.5
0.7588	536.5
0.7815	533.5
0.8050	531.5
0.9180	522.9

Hexafluorobenzene(1) + Octafluorotoluene(2)

(a) C. L. Young, unpublished results.

$x(1)$	T^c
0.2400	531.9
0.3971	528.7
0.4152	528.2
0.6032	524.4
0.7245	520.5
0.8102	519.6

n-Perfluoroheptane(1) + Ethane(2)

(a) L. W. Jordan and W. B. Kay, *Chem. Eng. Progr., Symp. Ser., No. 44*, **59**, 46 (1963).

$x(1)$	T^c	P^c	V^c
0.1090	338.89	61.69	165
0.2860	389.01	65.91	215
0.4790	420.33	55.46	280
0.7390	457.26	31.78	449
0.8970	468.94	22.03	580

n-Perfluoroheptane(1) + Propane(2)

(a) L. W. Jordan and W. B. Kay, *Chem. Eng. Progr., Symp. Ser., No. 44*, **59**, 46 (1963).

$x(1)$	T^c	P^c	V^c
0.0920	468.09	21.98	548
0.1910	394.23	41.23	265
0.2800	404.62	41.03	293
0.4850	430.91	36.55	366
0.6880	450.41	30.25	436
0.9060	468.09	21.98	548

n-Perfluoroheptane(1) + n-Butane(2)

(a) L. W. Jordan and W. B. Kay, *Chem. Eng. Progr., Symp. Ser., No. 44*, **59**, 46 (1963).

$x(1)$	T^c	P^c	V^c
0.0840	420.80	33.56	278
0.3230	428.26	29.87	347
0.5380	444.21	26.74	411
0.6910	455.57	23.86	464
0.8700	467.26	19.74	531

n-Perfluoroheptane(1) + n-Pentane(2)

(a) L. W. Jordan and W. B. Kay, *Chem. Eng. Progr., Symp. Ser., No. 44*, **59**, 46 (1963).

$x(1)$	T^c	P^c	V^c
0.0870	459.54	30.35	348
0.2230	452.09	28.08	386
0.3900	449.42	25.11	440
0.4650	451.36	24.54	463
0.7090	460.29	21.61	541

n-Perfluoroheptane(1) + *n*-Hexane(2)

(a) L. W. Jordan and W. B. Kay, *Chem. Eng. Progr., Symp. Ser., No. 44*, **59**, 46 (1963).

$x(1)$	T^c	P^c	V^c
0.0960	493.42	27.87	396
0.1660	486.98	26.93	410
0.3380	472.67	23.29	455
0.4740	467.03	21.83	480
0.6210	464.74	19.71	505
0.7060	464.80	19.59	531
0.8700	467.28	18.99	576

n-Perfluoroheptane(1) + n-Heptane(2)

(a) L. W. Jordan and W. B. Kay, *Chem. Eng. Progr., Symp. Ser., No. 44*, **59**, 46 (1963).

$x(1)$	T^c	P^c	V^c
0.0960	522.07	26.30	449
0.5300	478.50	19.69	545
0.6380	474.92	18.77	576
0.7680	472.93	18.31	594
0.8220	471.87	18.06	610
0.8570	471.68	17.75	632
0.9000	471.82	17.46	635

n-Perfluoroheptane(1) + n-Octane(2)

(a) L. W. Jordan and W. B. Kay, *Chem. Eng. Progr., Symp. Ser., No. 44*, **59**, 46 (1963).

$x(1)$	T^c	P^c	V^c
0.0990	548.83	24.98	
0.4240	503.37	20.86	
0.4700	501.10	20.75	
0.5250	493.50	19.75	527
0.7240	482.28	18.32	617
0.9460	475.79	17.50	656

n-Perfluoroheptane(1) + n-Nonane(2)

(a) L. W. Jordan and W. B. Kay, *Chem. Eng. Progr., Symp. Ser., No. 44*, **59**, 46 (1963).

$x(1)$	T^c	P^c	V^c
0.1570	564.66	24.28	558
0.2630	538.89	23.79	576
0.4710	516.42	21.55	597
0.6520	502.12	19.78	615
0.8680	484.32	17.56	644

Perfluoromethane(1) + Trifluoromethane(2)

(a) A. Piacentini and F. P. Stein, *Chem. Eng. Progr., Symp. Ser., No. 81*, **63**, 28 (1967).

$x(1)$	T^c	P^c
0.21	283.2	50
0.51	255.4	48

H. Mixtures Containing Silicon Compounds

Tetraethylsilane(1) + Cyclopentane(2)

(a) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **67,** 1598 (1971).

x(1)	T^c	x(1)	T^c
0.125	530.7	0.637	585.5
0.153	535.7	0.640	585.0
0.301	551.4	0.690	589.5
0.386	563.7	0.708	593.0
0.391	564.1	0.752	594.0
0.538	580.0	0.830	599.6

Tetraethylsilane(1) + Cyclohexane(2)

(a) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **67,** 1598 (1971).

x(1)	T^c	x(1)	T^c
0.110	561.5	0.657	598.1
0.182	567.5	0.711	597.5
0.312	575.5	0.766	598.7
0.411	583.5	0.894	603.0
0.471	587.5		

Tetraethylsilane(1) + Cycloheptane(2)

(a) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **67,** 1598 (1971).

x(1)	T^c	x(1)	T^c
0.064	605.6	0.588	608.4
0.151	606.7	0.610	608.5
0.290	608.2	0.685	609.2
0.486	608.4	0.765	609.1

Tetraethylsilane(1) + Cyclooctane(2)

(a) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **67,** 1598 (1971).

x(1)	T^c	x(1)	T^c
0.265	634.1	0.714	619.0
0.277	633.8	0.737	618.5
0.451	625.2	0.779	614.7
0.578	622.2	0.823	612.0
0.592	621.2		

Octamethylcyclotetrasiloxane(1) + Cyclopentane(2)

(a) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **67,** 1598 (1971).

x(1)	T^c	x(1)	T^c
0.0798	524.7	0.3899	558.4
0.1229	531.5	0.5918	569.3
0.3319	555.0	0.6279	572.5
0.3850	557.8	0.7706	580.2

(b) C. P. Hicks and C. L. Young, unpublished work.

x(1)	T^c	P^c
0.865	583.7	19.09
0.645	573.8	25.90
0.490	565.8	30.16
0.255	547.4	38.77
0.115	529.8	43.86

Octamethylcyclotetrasiloxane(1) + Cyclohexane(2)

(a) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **67,** 1598 (1971).

x(1)	T^c	x(1)	T^c
0.1109	560.5	0.4604	575.5
0.1431	564.2	0.4937	576.3
0.3517	571.5	0.6587	580.0
0.4172	573.8		

Octamethylcyclotetrasiloxane(1) + Cycloheptane(2)

(a) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **67,** 1598 (1971).

x(1)	T^c	x(1)	T^c
0.1337	600.5	0.6457	592.5
0.1738	599.5	0.6668	592.3
0.3260	597.0	0.7195	590.8
0.5309	593.9		

Octamethylcyclotetrasiloxane(1) + Cyclooctane(2)

(a) C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, **67,** 1598 (1971).

x(1)	T^c	x(1)	T^c
0.0526	639.0	0.4787	608.5
0.2021	626.5	0.5920	601.4
0.4242	612.0	0.6960	599.5
0.4431	611.5	0.7606	597.8

Octamethylcyclotetrasiloxane(1) + 2,3-Dimethylbutane(2)

(a) C. L. Young, *J. Chem. Soc., Faraday Trans. 2*, **68,** 452 (1972).

x(1)	T^c	x(1)	T^c
0.1285	520.0	0.6149	567.9
0.1877	528.0	0.6470	570.5
0.3648	548.8	0.7920	577.6
0.4546	556.7		

(b) C. P. Hicks and C. L. Young, unpublished results.

x(1)	T^c	P^c
0.925	583.6	16.45
0.415	555.0	26.73
0.325	545.9	28.69
0.215	532.2	31.14
0.160	524.6	32.51

Octamethylcyclotetrasiloxane(1) + *trans*-1,4-Dimethylcyclohexane(2)

(a) C. L. Young, *J. Chem. Soc., Faraday Trans. 2*, **68,** 452 (1972).

x(1)	T^c	x(1)	T^c
0.2143	586.3	0.5744	587.0
0.2551	586.0	0.6938	586.6
0.3674	586.3	0.7406	586.6

Octamethylcyclotetrasiloxane(1) + Tetramethylsilane(2)

(a) C. P. Hicks and C. L. Young, unpublished results.

x(1)	T^c	P^c
0.0929	475.8	
0.1982	498.0	
0.2335	506.9	
0.4029	535.1	
0.4450	537.8	
0.5430	548.6	
0.6934	568.0	
0.8299	575.9	
0.950	585.0	15.13
0.555	551.2	25.16
0.395	533.7	28.69
0.342	527.5	29.76
0.282	518.1	31.18
0.145	488.1	33.49

Octamethylcyclotetrasiloxane(1) + Benzene(2)

(a) C. L. Young, *J. Chem. Soc., Faraday Trans. 2*, **68,** 452 (1972).

x(1)	T^c	x(1)	T^c
0.0521	565.2	0.6130	581.5
0.1282	568.0	0.6210	582.0
0.1563	569.5	0.6306	581.5
0.3130	573.6	0.6458	581.8
0.4626	577.2	0.7452	584.0
0.4913	578.3	0.8501	586.0

Octamethylcyclotetrasiloxane(1) + Carbon Tetrachloride(2)

(a) C. L. Young, *J. Chem. Soc., Faraday Trans. 2*, **68**, 452 (1972).

x(1)	T^c	x(1)	T^c
0.1839	567.2	0.3637	574.1
0.1995	567.5	0.5603	580.7
0.3009	571.9	0.7749	584.7

Octamethylcyclotetrasiloxane(1) + Neopentane(2)

(a) C. L. Young, *J. Chem. Soc., Faraday Trans. 2*, **68**, 452 (1972).

x(1)	T^c	x(1)	T^c
0.0951	470.1	0.6017	557.3
0.2588	509.5	0.6539	563.5
0.2945	523.2	0.7881	573.5
0.3898	538.5	0.8240	576.8
0.4913	546.5	0.8823	581.8
0.5051	549.2		

(b) C. P. Hicks and C. L. Young, unpublished results.

x(1)	T^c	P^c
0.955	585.3	14.66
0.320	526.5	33.19
0.245	509.7	35.87
0.210	501.8	36.96
0.198	497.7	37.16
0.170	490.5	37.31

Hexamethyldisiloxane(1) + Cyclopentane(2)

(a) C. L. Young, *J. Chem. Soc., Faraday Trans. 2*, **68**, 452 (1972).

x(1)	T^c	x(1)	T^c
0.3063	512.4	0.6931	515.5
0.4826	514.5	0.7215	515.5
0.4942	514.5	0.8372	516.3

Hexamethyldisiloxane(1) + Hexafluorobenzene(2)

(a) C. L. Young, *J. Chem. Soc., Faraday Trans. 2*, **68**, 452 (1972).

x(1)	T^c	x(1)	T^c
0.0980	511.6	0.6597	512.7
0.1807	510.5	0.6893	512.8
0.3202	508.7	0.7926	514.2
0.5093	510.2	0.8863	515.7
0.5690	511.0		

Octamethyltrisiloxane(1) + Hexamethyldisiloxane(2)

(a) C. L. Young, *J. Chem. Soc., Faraday Trans. 2*, **68**, 452 (1972).

x(1)	T^c
0.1395	526.6
0.3191	535.2
0.5194	546.0
0.8441	559.4

Decamethyltetrasiloxane(1) + Hexamethyldisiloxane(2)

(a) C. L. Young, *J. Chem. Soc., Faraday Trans. 2*, **68**, 580 (1972).

x(1)	T^c	x(1)	T^c
0.0596	524.7	0.5793	576.0
0.1885	539.5	0.6012	577.3
0.2473	546.3	0.6645	581.0
0.3135	553.5	0.7059	583.5
0.3456	556.7	0.9078	595.2

Decamethyltetrasiloxane(1) + Octamethyltrisiloxane(2)

(a) C. L. Young, *J. Chem. Soc., Faraday Trans. 2*, **68**, 580 (1972).

x(1)	T^c	x(1)	T^c
0.1424	570.3	0.5191	583.6
0.1762	571.0	0.5705	586.7
0.2430	574.1	0.7046	591.1

Dodecamethylpentasiloxane(1) + Hexamethyldisiloxane(2)

(a) C. L. Young, *J. Chem. Soc., Faraday Trans. 2*, **68**, 580 (1972).

x(1)	T^c	x(1)	T^c
0.0596	528.9	0.4458	583.9
0.1339	542.0	0.5791	596.0
0.1455	546.4	0.6757	605.6
0.1991	554.5	0.7217	607.2
0.2176	559.2	0.7934	612.7

Dodecamethylpentasiloxane(1) + Decamethyltetrasiloxane(2)

(a) C. L. Young, *J. Chem. Soc., Faraday Trans. 2*, **68**, 580 (1972).

x(1)	T^c	x(1)	T^c
0.1994	606.0	0.4584	613.5
0.2045	606.2	0.6628	619.6
0.4032	612.0	0.7446	622.0

Tetradecamethylhexasiloxane(1) + Hexamethyldisiloxane(2)

(a) C. L. Young, *J. Chem. Soc., Faraday Trans. 2*, **68**, 580 (1972).

x(1)	T^c	x(1)	T^c
0.1218	546.9	0.5912	617.3
0.2279	575.0	0.7155	629.0
0.4858	608.2	0.7784	636.1
0.5012	610.0		

Tetradecamethylhexasiloxane(1) + Octamethyltrisiloxane(2)

(a) C. L. Young, *J. Chem. Soc., Faraday Trans. 2*, **68**, 580 (1972).

x(1)	T^c	x(1)	T^c
0.1276	581.2	0.5367	619.9
0.2493	594.5	0.6550	629.9
0.3206	600.4	0.7165	632.8
0.4745	614.5	0.7825	637.9

Tetradecamethylhexasiloxane(1) + Decamethyltetrasiloxane(2)

(a) C. L. Young, *J. Chem. Soc., Faraday Trans. 2*, **68**, 580 (1972).

x(1)	T^c	x(1)	T^c
0.1040	606.8	0.6736	639.1
0.1735	611.7	0.7426	641.7
0.4687	628.5		

Hexadecamethylheptasiloxane(1) + Hexamethyldisiloxane(2)

(a) C. L. Young, *J. Chem. Soc., Faraday Trans. 2*, **68**, 580 (1972).

x(1)	T^c	x(1)	T^c
0.1055	554.6	0.4320	617.8
0.1110	556.7	0.5159	636.2
0.3557	598.3	0.6901	652.3
0.3896	606.4	0.8235	662.9
0.4315	617.1		

Octadecamethyloctasiloxane(1) + Hexamethyldisiloxane(2)

(a) C. L. Young, *J. Chem. Soc., Faraday Trans. 2*, **68**, 580 (1972).

x(1)	T^c	x(1)	T^c
0.1532	571.5	0.5180	641.8
0.2092	581.0	0.5928	653.2
0.2280	590.3	0.6878	665.7
0.3807	617.2		

Octadecamethyloctasiloxane(1) + Octamethyltrisiloxane(2)

(a) C. L. Young, *J. Chem. Soc., Faraday Trans. 2*, **68**, 580 (1972).

x(1)	T^c
0.1815	586.1
0.2359	615.4
0.2731	622.5
0.4588	645.3
0.7082	665.2

I. Mixtures of Nitrogen, Hydrogen, Hydrogen Sulfide, Carbon Monoxide, Carbon Dioxide, or Nitrous Oxide and *n*-Alkanes

Methane(1) + Hydrogen Sulfide(2)

(a) H. H. Reamer, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **43**, 976 (1951).

$x(1)$	T^c	P^c	V^c
0.1	361.1	101.6	
0.2	345.7	113.6	
0.209	344.3	114.5	80.8
0.3	327.6	124.9	
0.388	310.9	131.5	74.0
0.4	308.6	132.0	
0.5	288.1	134.7	
0.550	277.6	134.4	68.3
0.6	267.1	133.5	

(b) J. P. Kohn and F. Kurata, *Amer. Inst. Chem. Eng. J.*, **4**, 211 (1958).

$x(1)$	T^c	P^c
0.067	364.1	99.8
0.229	336.6	120.1
0.948	198.7	51.7
0.965	193.2	48.3

Ethane(1) + Nitrogen(2)

(a) B. E. Eakin, R. T. Ellington, and D. C. Gami, *Inst. Gas Tech. Res. Bull.*, No. 26 (July, 1955).

$x(1)$	T^c	P^c
0.0198	131.5	39.6
0.6831	273.97	91.04
0.7507	282.65	80.40
0.8499	292.59	66.86
0.9502	301.46	54.34

Ethane(1) + Hydrogen Sulfide(2)

(a) W. B. Kay and D. B. Brice, *Ind. Eng. Chem.*, **45**, 615 (1953).

$x(1)$	T^c	P^c	V^c
0.1103	360.39	83.93	100.5
0.2890	341.48	73.94	105.4
0.4999	323.77	63.13	115.0
0.6694	313.90	56.61	124.3
0.7779	309.54	53.48	130.2
0.8901	306.62	50.86	134.2

Ethane(1) + Carbon Dioxide(2)

(a) J. P. Kuenen, *Phil. Mag.*, **44**, 174 (1897).

$x(1)$	T^c
0.15	296.1
0.30	291.8
0.43	290.7
0.50	290.8

(b) N. E. Khazanova and L. S. Lesnevskaya, *Khim. Prom.*, **42**, 364 (1966).

$x(1)$	T^c	P^c	V^c
0.421			117.5
0.427	290.77	58.3	122

Ethane(1) + Nitrous Oxide(2)

(a) J. P. Kuenen, *Phil. Mag.*, **40**, 173 (1895).

$x(1)$	T^c	P^c
0.18	302.95	66.19
0.25	301.30	64.20
0.43	299.20	59.19
0.55	299.15	56.86
0.76	301.00	53.25

Propane(1) + Nitrogen(2)

(a) J. G. Roof and J. D. Baron, *J. Chem. Eng. Data*, **12**, 292 (1967).

$x(1)$	T^c	P^c
0.49	311.6	147.7
0.60	327.1	122.5
	344.3	90.5
0.94	365.2	51.6

(b) D. L. Schindler, G. W. Swift, and F. Kurata, *Hydrocarbon Process.*, **45** (11), 205 (1966).

$x(1)$	T^c	P^c
0.58	323	131
0.70	343	91.7

Propane(1) + Hydrogen(2)

(a) W. L. Buriss, N. T. Hsu, H. H. Reamer, and B. H. Sage, *Ind. Eng. Chem.*, **45**, 210 (1953).

$x(1)$	T^c	P^c
0.334	310.9	543
0.523	344.3	236
0.756	361.0	109

Propane(1) + Hydrogen Sulfide(2)

(a) W. B. Kay and G. M. Ramboseck, *Ind. Eng. Chem.*, **45**, 221 (1953).

$x(1)$	T^c	P^c	V^c
0.1016	365.89	79.94	107.4
0.2183	360.62	71.72	119.5
0.3245	358.04	65.93	130.9
0.4359	357.74	61.20	142.4
0.5658	358.89	56.65	155.5
0.7014	361.68	52.34	167.2
0.8367	365.18	47.92	179.7

(b) J. Brewer, N. Rodewald, and F. Kurata, *Amer. Inst. Chem. Eng. J.*, **7**, 13 (1961).

$x(1)$	T^c	P^c
0.783	363.7	49.5

Propane(1) + Carbon Monoxide(2)

(a) L. C. Widdoes and D. L. Katz, *Ind. Eng. Chem.*, **40**, 1742 (1948).

$x(1)$	T^c	P^c
0.3790	297.6	150
0.5244	327.6	114
0.5787	335.9	101
0.7341	354.8	71.0
0.796	359.8	62.1

Propane(1) + Carbon Dioxide(2)

(a) J. G. Roof and J. D. Baron, *J. Chem. Eng. Data*, **12**, 292 (1967).

$x(1)$	T^c	P^c
0.08	305.0	69.29
0.11	305.9	68.95
0.17	308.2	68.19
0.45	327.8	66.19
0.65	345.2	59.78
0.87	361.3	50.20

(b) F. H. Poettman and D. L. Katz, *Ind. Eng. Chem.*, **37**, 847 (1945).

$x(1)$	T^c	P^c
0.0607	304.4	70.46
0.2127	311.7	69.09
0.4935	337.0	67.98
0.6401	347.6	66.67
0.8481	366.2	54.47

(c) H. H. Reamer, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **43,** 2515 (1951).

x(1)	T^c	P^c	V^c
0.205	310.9	69.12	106.6
0.412	327.6	68.40	129.4
0.593	344.3	67.29	141.7

n-Butane(1) + Nitrogen(2)

(a) W. W. Akers, L. L. Attwell, and J. A. Robinson, *Ind. Eng. Chem.*, **46,** 2539 (1954).

x(1)	T^c	P^c
0.30	310.9	290
0.38	366.5	220
0.42	399.8	145
0.52	422.0	84

(b) W. R. Lehigh and J. J. McKetta, *J. Chem. Eng. Data*, **11,** 180 (1966).

x(1)	T^c	P^c
0.368	310.9	288.1

(c) L. R. Roberts and J. J. McKetta, *Amer. Inst. Chem. Eng. J.*, **7,** 173 (1961).

x(1)	T^c	P^c
0.44	344.3	213
0.59	377.6	148
0.80	410.9	76

n-Butane(1) + Hydrogen Sulfide(2)

(a) D. B. Robinson, R. E. Hughes, and J. A. W. Sandercock, *Can. J. Chem. Eng.*, **42,** 143 (1964).

x(1)	T^c	P^c
0.19	380.4	73.8
0.43	394.3	64.8
0.65	408.2	55.1

n-Butane(1) + Carbon Dioxide(2)

(a) F. H. Poettman and D. L. Katz, *Ind. Eng. Chem.*, **37,** 847 (1945).

x(1)	T^c	P^c
0.1391	321.8	77.36
0.2898	349.3	81.42
0.3927	368.2	78.60
0.5449	385.1	74.26
0.6239	396.5	64.81
0.8607	415.9	48.88

(b) R. H. Olds, H. H. Reamer, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **41,** 475 (1949).

x(1)	T^c	P^c	V^c
0.1694	325.93	79.08	105.0
0.3334	351.71	81.71	132
0.4984	377.21	75.37	162
0.6740	398.76	62.81	193
0.8273	412.26	51.10	217

n-Pentane(1) + Hydrogen Sulfide(2)

(a) H. H. Reamer, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **45,** 1805 (1953).

x(1)	T^c	P^c	V^c
0.034	377.6	89.77	102
0.1	385.8	89.15	112
0.2	398.7	87.70	129
0.274	410.9	85.84	144
0.3	415.8	85.01	150
0.4	434.0	80.81	174
0.454	444.3	77.22	187
0.5	449.4	74.95	200
0.6	460.4	67.50	225
0.7	466.4	59.36	243
0.8	468.8	50.81	262
0.9	469.6	42.26	275

n-Pentane(1) + Carbon Dioxide(2)

(a) F. H. Poettman and D. L. Katz, *Ind. Eng. Chem.*, **37,** 847 (1945).

x(1)	T^c	P^c
0.0489	314.9	79.16
0.1033	325.7	84.67
0.2062	368.5	99.35
0.3313	404.9	93.22

(b) E. H. Buchner, *Z. Phys. Chem.*, **54,** 665 (1906).

x(1)	T^c
0.429	358
0.597	373
0.868	433

n-Hexane(1) + Nitrogen(2)

(a) R. S. Poston and J. J. McKetta, *J. Chem. Eng. Data*, **11,** 364 (1966).

x(1)	T^c	P^c
0.30	411.0	295.7
0.55	444.3	203.3

n-Hexane(1) + Hydrogen(2)

(a) W. B. Nichols, H. H. Reamer, and B. H. Sage, *Amer. Inst. Chem. Eng. J.*, **3,** 262 (1957).

x(1)	T^c	P^c	V^c
0.2	409.3		
0.232	444.3	634	83.2
0.3	475.4	434	
0.312	477.6	408	116.7
0.4	488.2	279	
0.5	495.4	192	
0.6	499.3	138	
0.7	502.6	98.6	
0.8	504.8	68.9	
0.9	506.5	47.6	

n-Heptane(1) + Nitrogen(2)

(a) S. Peter and H. F. Eicke, *Ber. Bunsenges. Phys. Chem.*, **74,** 190 (1970).

x(1)	T^c	P^c
0.16	376.4	613
0.23	413.2	412
0.26	453.0	309

(b) W. W. Akers, D. M. Kehn, and C. H. Kilgore, *Ind. Eng. Chem.*, **46,** 2536 (1954).

x(1)	T^c	P^c
0.21	455.4	310.3

n-Heptane(1) + Hydrogen(2)

(a) S. Peter and K. Reinhartz, *Z. Phys. Chem. (Frankfurt am Main)*, **24,** 103 (1960).

x(1)	T^c	P^c
0.19	471.7	726
0.30	498.9	392

n-Decane(1) + Hydrogen Sulfide(2)

(a) H. H. Reamer, F. T. Selleck, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **45,** 1810 (1953).

x(1)	T^c	P^c	V^c
0.006	377.6	93.0	70.5
0.051	410.9	116.9	90.5
0.100	444.3	133.4	112.0

n-Decane(1) + Carbon Dioxide(2)

(a) H. H. Reamer and B. H. Sage, *J. Chem. Eng. Data*, **8**, 508 (1963).

x(1)	T^c	P^c	V^c
0.0054	310.9	80.0	94.0
0.0523	344.3	128.2	96.0
0.0954	377.6	164.9	105.2
0.1295	410.9	185.6	116.4
0.1570	444.3	188.4	133.5
0.1950	477.6	178.4	158.8
0.2720	510.9	153.3	197.9

J. Mixtures Containing an Alcohol, Ketone, or Ether

Ethylene(1) + Ethanol(2)

(a) D. S. Tsiklis and A. N. Kofman, *Russ. J. Phys. Chem.*, **35**, 549 (1961).

x(1)	T^c	P^c	V^c
0.175	493.15	82	135
0.30	473.15	99	130
0.35	463.15	106	125
0.44	443.15	120	115
0.575	423.15	129	110

Benzene(1) + Methanol(2)

(a) J. M. Skaates and W. B. Kay, *Chem. Eng. Sci.*, **19**, 431 (1964).

x(1)	T^c	P^c	V^c
0.1064	511.09	78.83	115
0.3056	515.59	75.50	153
0.4946	525.74	72.74	186
0.6894	539.75	66.22	212
0.8894	554.14	56.10	

(b) P. G. McCracken, T. S. Storvick, and J. M. Smith, *J. Chem. Eng. Data*, **5**, 130 (1960).

x(1)	T^c	P^c
0.25	515.4	76.5
0.50	517.6	62.6
0.75	522.0	46.9

(c) I. G. Makhanko and V. F. Nozdrev, *Akust. Zh.*, **10**, 249 (1964).

x(1)	T^c
0.0436	511.28
0.0760	511.2
0.2147	512.7
0.3809	517.90
0.6213	532.2

(d) I. R. Krichevskii, N. E. Khazanova, and L. R. Linshits, *Zh. Fiz. Khim.*, **31**, 2711 (1957).

x(1)	T^c	P^c	V^c
0.0436	512.15	78	123
0.1203	511.15	77	133
0.2909	514.65	74	153
0.5104	525.65	74	180
0.7869	545.65	71	226

(e) V. F. Nozdrev and V. I. Ghechkin, *Akust. Zh.*, **9**, 379 (1963).

x(1)	T^c	P^c
0.0941	511.2	73.0
0.2147	513.2	69.9
0.3809	519.6	64.3
0.6213	533.8	53.7

Benzene(1) + Ethanol(2)

(a) J. M. Skaates and W. B. Kay, *Chem. Eng. Sci.*, **19**, 431 (1964).

x(1)	T^c	P^c	V^c
0.0140	514.03	61.16	160
0.0590	514.31	60.94	174
0.1100	514.86	60.74	176
0.3068	519.55	59.93	192
0.5046	528.71	58.83	209
0.6975	540.46	56.49	229
0.8750	553.13	52.73	250

(b) P. G. McCracken, T. S. Storvick, and J. M. Smith, *J. Chem. Eng. Data*, **5**, 130 (1960).

x(1)	T^c	P^c
0.25	521.5	62.5
0.50	520.9	52.1
0.75	534.3	47.8

(c) M. T. Ratzsch and G. Strauch, *Z. Phys. Chem.*, **249**, 243 (1972).

x(1)	T^c
0.4990	531.4
0.4997	531.4
0.5005	531.4

(d) A. Z. Golik and S. D. Ravikovich, *Dopov. Akad. Nauk Ukr. RSR*, 101 (1950).

x(1)	T^c
0.25	523
0.50	533
0.75	547

Benzene(1) + Propan-1-ol(2)

(a) J. M. Skaates and W. B. Kay, *Chem. Eng. Sci.*, **19**, 431 (1964).

x(1)	T^c	P^c	V^c
0.0152	536.62	51.61	228
0.0619	536.57	51.69	223
0.1106	536.60	51.57	225
0.3088	537.90	51.39	235
0.5037	541.79	51.10	236
0.7016	548.07	50.72	245
0.8990	556.71	49.86	260

(b) E. C. Costa and J. M. Smith, *J. Chem. Eng. Data*, **8**, 289 (1963).

x(1)	T^c	P^c
0.25	477.6	21.1
0.48	477.0	20.0

Benzene(1) + Propan-2-ol(2)

(a) A. Kreglewski, *Rocz. Chem.*, **29**, 754 (1955).

x(1)	T^c
0.049	509.85
0.187	514.05
0.376	522.15
0.698	540.65

Benzene(1) + Butan-1-ol(2)

(a) J. M. Skaates and W. B. Kay, *Chem. Eng. Sci.*, **19**, 431 (1964).

x(1)	T^c	P^c	V^c
0.1123	560.79	45.01	267
0.3081	558.22	45.85	270
0.5046	556.89	46.63	266
0.5729	556.79	46.95	268
0.7019	557.29	47.55	267
0.8986	559.92	48.55	255

Benzene(1) + Butan-2-ol(2)

(a) A. Kreglewski, *Rocz. Chem.*, **29**, 754 (1955).

x(1)	T^c
0.065	549.15
0.205	548.45
0.359	548.45
0.792	555.00
0.928	559.60

Benzene(1) + Pentan-2-ol(2)

(a) A. Kreglewski, *Rocz. Chem.*, **29**, 754 (1955).

x(1)	T^c
0.258	572.85
0.399	568.85
0.638	563.80
0.771	562.15
0.862	560.95
0.972	561.10

n-Pentane(1) + Ethanol(2)

(a) P. G. McCracken, T. S. Storvick, and J. M. Smith, *J. Chem.Eng. Data*, **5**, 130 (1960).

x(1)	T^c	P^c,
0.25	495.37	57.0
0.50	472.04	45.3
0.75	465.37	40.1

n-Pentane(1) + Propan-2-ol(2)

(a) G. P. Sprague and C. L. Young, unpublished work.

x(1)	T^c
0.159	493.9
0.301	486.2
0.535	473.0
0.609	471.0
0.676	469.0
0.784	467.6
0.837	467.8
0.927	468.7

n-Pentane(1) + Butan-1-ol(2)

(a) G. P. Sprague and C. L. Young, unpublished work.

x(1)	T^c
0.207	542.9
0.362	525.2
0.474	516.6
0.696	493.8
0.866	477.9

n-Hexane(1) + Propan-1-ol(2)

(a) K. M. Bone and C. L. Young, unpublished work.

x(1)	T^c
0.0950	527.95
0.1503	523.95
0.2614	516.85
0.4230	507.95
0.5582	503.65
0.6652	502.15
0.7986	503.05
0.8940	504.65

n-Hexane(1) + Propan-2-ol(2)

(a) K. M. Bone and C. L. Young, unpublished work.

x(1)	T^c
0.0882	503.3
0.1451	500.2
0.2220	497.1
0.3711	493.1
0.5332	493.2
0.6273	494.8
0.6968	496.2
0.8092	499.4
0.8470	501.1

n-Hexane(1) + Butan-1-ol(2)

(a) K. M. Bone and C. L. Young, unpublished work.

x(1)	T^c
0.1865	547.7
0.2681	540.4
0.3784	533.3
0.5393	519.6
0.6429	515.3
0.7524	511.3
0.8406	508.8
0.9313	508.1

n-Heptane(1) + Butan-1-ol(2)

(a) K. M. Bone and C. L. Young, unpublished work.

x(1)	T^c
0.1885	550.2
0.2632	546.7
0.4494	538.9
0.5240	537.0
0.6395	535.4
0.7614	535.7
0.8749	537.1
0.9613	538.9

n-Octane(1) + Propan-1-ol(2)

(a) K. M. Bone and C. L. Young, unpublished work.

x(1)	T^c
0.0863	533.1
0.1463	532.4
0.2630	533.1
0.3738	536.3
0.5148	542.9
0.5899	546.2
0.6980	552.8
0.8527	561.1

n-Octane(1) + Butan-1-ol(2)

(a) K. M. Bone and C. L. Young, unpublished work.

x(1)	T^c
0.1544	555.5
0.1982	554.6
0.2056	554.4
0.3620	552.8
0.4109	552.8
0.5635	554.8
0.6817	557.8
0.7966	561.3
0.8597	563.0

n-Octane(1) + Propan-2-ol(2)

(a) A. Kreglewski, *Rocz. Chem.*, **29**, 754 (1955).

x(1)	T^c
0.035	508.55
0.105	509.35
0.149	511.20
0.367	522.40

n-Octane(1) + Butan-2-ol(2)

(a) A. Kreglewski, *Rocz. Chem.*, **29**, 754 (1955).

x(1)	T^c
0.055	547.60
0.129	546.05
0.145	545.90
0.258	545.45
0.333	545.90
0.496	549.50

n-Octane(1) + Pentan-2-ol(2)

(a) A. Kreglewski, *Rocz. Chem.*, **29**, 754 (1958).

x(1)	T^c
0.129	571.90
0.312	565.45
0.486	563.20
0.523	563.10
0.616	563.00
0.766	564.35
0.776	564.55

Cyclohexane(1) + Ethanol(2)

(a) M. T. Ratzsch and G. Strauch, *Z. Phys. Chem.*, **249,** 243 (1972).

x(1)	T^c
0.1375	512.0
0.3020	509.9
0.3980	511.5
0.4955	515.2
0.5653	519.6
0.8000	534.5

Toluene(1) + Ethanol(2)

(a) M. T. Ratzsch and G. Strauch, *Z. Phys. Chem.*, **249,** 243 (1972).

x(1)	T^c
0.4720	548.8
0.4925	551.0
0.5033	550.0
0.5062	549.8

Ethylbenzene(1) + Ethanol(2)

(a) M. T. Ratzsch and G. Strauch, *Z. Phys. Chem.*, **249,** 243 (1972).

x(1)	T^c
0.4955	567.5
0.4957	567.4
0.4980	565.6

Methanol(1) + Butan-1-ol(2)

(a) W. B. Kay and W. E. Donham, *Chem. Eng. Sci.*, **4,** 1 (1955).

x(1)	T^c	P^c	V^c
0.2381	554.11	54.46	237
0.5307	540.42	68.13	188
0.6993	531.37	74.29	162
0.8334	522.99	78.125	142

Butan-1-ol(1) + Butan-2-ol(2)

(a) W. B. Kay and W. E. Donham, *Chem. Eng. Sci.*, **4,** 1 (1955).

x(1)	T^c	P^c	V^c
0.2214	551.26	43.22	276
0.5103	555.63	43.59	277
0.7640	559.40	43.89	277

Butan-1-ol(1) + Diethyl Ether(2)

(a) W. B. Kay and W. E. Donham, *Chem. Eng. Sci.*, **4,** 1 (1955).

x(1)	T^c	P^c	V^c
0.2561	492.64	40.18	253
0.5235	521.09	43.11	261
0.7288	539.19	44.09	268
0.8690	551.72	44.29	273

Methanol(1) + Water(2)

(a) J. Griswold and S. Y. Wong, *Chem. Eng. Progr., Symp. Ser., No. 3,* **48,** 18 (1952).

x(1)	T^c	P^c
0.773	523	84.1

Ethanol(1) + Water(2)

(a) F. 8arr-David and 8. F. Dodge, *J. Chem. Eng. Data,* **4,** 107 (1959).

x(1)	T^c	P^c
0.330	573	125.5
0.490	548	98.6

(b) J. F. White, *Trans. Amer. Inst. Chem. Eng.*, **38,** 435 (1942).

x(1)	T^c
0.281	576
0.540	538
0.750	521

(c) J. Griswold, J. D. Haney, and V. A. Klein, *Ind. Eng. Chem.*, **35,** 701 (1943).

x(1)	T^c	x(1)	T^c
0.083	618.1	0.380	561.6
0.110	613.0	0.415	557.6
0.126	608.0	0.468	550.5
0.179	598.9	0.528	543.5
0.206	590.8	0.594	537.4
0.244	584.8	0.673	532.4
0.278	580.7	0.755	526.3
0.324	569.7	0.861	521.2

x(1)	P^c	x(1)	P^c
0.071	195.1	0.409	111.6
0.149	168.2	0.610	84.1
0.250	142.0	0.715	75.8

Propan-2-ol(1) + Water(2)

(a) F. Barr-David and B. F. Dodge, *J. Chem. Eng. Data,* **4,** 107 (1959).

x(1)	T^c	P^c
0.27	673	124
0.40	648	93
0.63	623	66

Ethane(1) + Acetone(2)

(a) W. B. Kay, *J. Phys. Chem.*, **68,** 827 (1964).

x(1)	T^c	P^c
0.265	478.0	69.8
0.499	436.5	89.0
0.661	396.1	92.1
0.788	361.3	81.1
0.827	348.2	80.9

Propane(1) + Acetone(2)

(a) W. B. Kay, *J. Phys. Chem.*, **68,** 827 (1964).

x(1)	T^c	P^c
0.138	491.5	52.6
0.339	464.4	58.1
0.507	438.1	58.3
0.666	413.0	54.3
0.779	396.1	49.9

n-Butane(1) + Acetone(2)

(a) W. B. Kay, *J. Phys. Chem.*, **68,** 827 (1964).

x(1)	T^c	P^c
0.254	482.0	48.2
0.403	465.9	46.8
0.626	446.2	43.6
0.771	434.5	40.9

n-Pentane(1) + Acetone(2)

(a) W. B. Kay, *J. Phys. Chem.*, **68,** 327 (1964).

x(1)	T^c	P^c
0.071	500.0	46.2
0.315	483.7	43.3
0.539	472.3	39.6
0.626	468.7	37.7
0.799	467.7	35.8

n-Hexane(1) + Acetone(2)

(a) W. B. Kay, *J. Phys. Chem.*, **68,** 827 (1964).

x(1)	T^c	P^c
0.072	503.8	45.6
0.161	498.7	43.6
0.359	493.6	40.3
0.441	493.1	38.1
0.696	496.4	35.8
0.889	502.6	33.1

(b) M. T. Ratzsch and G. Strauch, *Z. Phys. Chem.*, **249,** 243 (1972).

$x(1)$	T^c
0.4819	493.6
0.4969	493.4
0.4969	493.1
0.4972	493.3

n-Heptane(1) + Acetone(2)

(a) W. B. Kay, *J. Phys. Chem.*, **68,** 327 (1964).

$x(1)$	T^c	P^c
0.0606	506.6	45.9
0.200	505.8	43.0
0.367	508.7	40.4
0.575	517.3	37.4

n-Octane(1) + Acetone(2)

(a) W. B. Kay, *J. Phys. Chem.*, **68,** 827 (1964).

$x(1)$	T^c	P^c
0.0187	507.9	46.6
0.041	508.1	46.0
0.151	511.0	44.0
0.286	518.1	41.9
0.514	535.1	38.4
0.614	543.2	36.4
0.772	554.9	32.2

n-Decane(1) + Acetone(2)

(a) W. B. Kay, *J. Phys. Chem.*, **68,** 827 (1964).

$x(1)$	T^c	P^c
0.025	513.3	46.3
0.057	515.1	46.3
0.111	515.5	46.4
0.162	521.3	46.5
0.206	533.1	46.3
0.318	542.9	45.9
0.365	550.7	45.0

n-Tridecane(1) + Acetone(2)

(a) W. B. Kay, *J. Phys. Chem.*, **68,** 827 (1964).

$x(1)$	T^c	P^c
0.055	520.7	49.8
0.108	536.5	51.8
0.185	563.9	54.2

Acetone(1) + Benzene(2)

(a) A. N. Campbell and R. M. Chatterjee, *Can. J. Chem.*, **48,** 277 (1970).

$x(1)$	T^c
0.0925	557.10
0.1580	552.85
0.2160	549.90
0.3290	543.35
0.4410	537.15
0.5440	532.05
0.6530	526.10
0.7640	520.50
0.8250	517.25
0.8690	514.70
0.9370	511.35

(b) M. Ratzsch, *Z. Phys. Chem.*, **243,** 212 (1970).

$x(1)$	T^c
0.2650	548.2
0.4710	536.8
0.6500	527.4
0.8315	517.0

Acetone(1) + Cyclohexane(2)

(a) M. Ratzsch, *Z. Phys. Chem.*, **243,** 212 (1970).

$x(1)$	T^c
0.4961	521.2
0.4985	521.0
0.4995	520.8
0.5043	520.7
0.5065	520.6

Acetone(1) + Chloroform(2)

(a) M. Ratzsch, *Z. Phys. Chem.*, **243,** 212 (1970).

$x(1)$	T^c
0.1961	533.8
0.3993	528.1
0.5960	522.9
0.8034	515.6

(b) A. N. Campbell and G. M. Musbally, *Can. J. Chem.*, **48,** 3173 (1970).

$x(1)$	T^c
0.0771	534.20
0.2250	530.65
0.3985	527.30
0.5300	522.90
0.6057	521.30
0.7060	518.15
0.7694	516.20
0.8650	512.85
0.9598	509.65

Acetone(1) + Carbon Tetrachloride(2)

(a) A. N. Campbell and G. M. Musbally, *Can. J. Chem.* **48,** 3173 (1970).

$x(1)$	T^c
0.0650	552.65
0.1250	549.55
0.2090	544.85
0.2760	541.55
0.3950	535.65
0.5290	528.75
0.6450	523.05
0.7820	516.70
0.9525	509.80

Acetone(1) + Diethyl Ether(2)

(a) M. Ratzsch, *Z. Phys. Chem.*, **243**, 212 (1970).

$x(1)$	T^c
0.247	472.8
0.465	481.5
0.656	489.5
0.838	499.9

Acetone(1) + Water(2)

(a) J. Griswold and S. Y. Wong, *Chem. Eng. Progr., Symp. Ser., No. 3,* **48,** 18 (1952).

$x(1)$	T^c	P^c
0.555	523	67.6

2-Butanone(1) + *n*-Hexane(2)

(a) A. Kreglewski and W. B. Kay, *J. Phys. Chem.*, **73,** 3359 (1969).

$x(1)$	T^c	P^c
0.1	506.05	31.65
0.3	505.75	33.99
0.5	509.65	36.27
0.7	517.70	38.61
0.9	529.15	40.69

2-Butanone(1) + Diethylamine(2)

(a) A. Kreglewski and W. B. Kay, *J. Phys. Chem.*, **73,** 3359 (1969).

x(1)	T^c	P^c
0.1	501.27	38.04
0.3	505.90	38.96
0.5	512.15	39.78
0.7	519.90	40.58
0.9	529.65	41.33

Diethyl Ether(1) + Benzene(2)

(a) M. Ratzsch, *Z. Phys. Chem.*, **243,** 212 (1970).

x(1)	T^c
0.1955	544.0
0.4035	524.0
0.6117	504.4
0.8179	484.3

Diethyl Ether(1) + Chloroform(2)

(a) M. Ratzsch, *Z. Phys. Chem.*, **243,** 212 (1970).

x(1)	T^c
0.203	526.4
0.399	511.3
0.605	497.3
0.800	482.9

Diethyl Ether(1) + Water(2)

(a) F. E. C. Scheffer, *Z. Phys. Chem.*, **84,** 728 (1913).

x(1)	T^c	P^c
0.024	467.2	37.8
0.051	467.3	39.1
0.118	468.0	42.5
0.1925	469.6	45.9
0.226	470.8	47.7
0.260	472.5	49.5
0.275	473.3	50.3
0.298	474.0	51.1
0.300	474.2	51.32
0.316	475.1	52.23

Sulfur Dioxide(1) + Dimethyl Ether(2)

(a) A. C. Zawisza and S. Glowka, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **18,** 549 (1970).

x(1)	T^c	P^c	V^c
0.2232	415.03	56.80	157
0.3861	422.05	60.40	145
0.4964	426.06	63.22	140
0.5986	428.20	66.90	139

Sulfur Dioxide(1) + Methyl Ethyl Ether(2)

(a) A. C. Zawisza and S. Glowka, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **18,** 555 (1970).

x(1)	T^c	P^c	V^c
0.2148	440.11	49.41	202
0.3740	440.62	54.19	186
0.4934	441.37	58.36	169
0.5932	439.53	61.82	161
0.7279	437.50	66.71	149

Sulfur Dioxide(1) + Diethyl Ether(2)

(a) A. C. Zawisza, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **15,** 291 (1967).

x(1)	T^c	P^c	V^c
0.2419	460.52	45.19	247.4
0.4781	452.66	54.97	208.1
0.5896	448.70	59.58	185.2
0.7471	441.75	66.37	162.6

K. Miscellaneous Mixtures

Ethane(1) + Hydrogen Chloride(2)

(a) N. Quint, *Proc. Acad. Sci. Amsterdam*, **2,** 40 (1899).

x(1)	T^c	P^c
0.1388	350.66	43.7
0.4035	338.57	30.9
0.6107	332.45	27.6
0.7141	329.99	27.7

Ethane(1) + Water(2)

(a) A. Danneil, K. Toedheide, and E. U. Franck, *Chem.-Ing.-Tech.*, **39,** 816 (1967).

x(1)	T^c	P^c
0.175	629	500
0.225	623	680
0.240	623	760
0.295	629	1205
0.315	643	1680
0.320	651	1990
0.325	658	2190
0.340	673	3215

Propane(1) + Hydrogen Chloride(2)

(a) G. Glocker, D. L. Fuller, and C. P. Roe, *J. Chem. Phys.*, **1,** 714 (1933).

x(1)	T^c	P^c
0.084	324.2	77.7
0.154	326.1	75.3
0.241	329.4	73
0.383	336	70
0.478	340	68
0.551	347	64
0.636	351	61
0.705	355	58
0.830	361	52
0.910	364.8	48

Propane(1) + Sulfur Hexafluoride(2)

(a) H. P. Clegg and J. S. Rowlinson, *Trans. Faraday Soc.*, **51,** 1333 (1955).

x(1)	T^c	P^c	V^c
0.1230	317.44	36.92	200.4
0.1851	317.37	36.91	200.4
0.3113	319.74	37.25	205.3
0.5007	328.18	39.10	214.6
0.6711	340.04	41.38	217.4
0.8368	354.47	42.85	214.1

n-Butane(1) + Helium(2)

(a) A. E. Jones and W. B. Kay, *Amer. Inst. Chem. Eng. J.*, **13,** 717 (1967).

x(1)	T^c	P^c	V^c
0.8958	425.70	65.61	225.7
0.9497	425.37	50.37	242.5
0.9811	425.18	42.56	249.8

n-Butane(1) + Ammonia(2)

(a) W. B. Kay and H. A. Frisch, *Amer. Inst. Chem. Eng. J.*, **4,** 293 (1958).

x(1)	T^c	P^c	V^c
0.0507	396.45	102.35	76.6
0.1218	387.88	90.58	90.9
0.1960	383.06	82.74	108.1
0.3984	386.07	74.01	145.0
0.6011	399.70	66.46	173.3
0.8424	416.20	50.03	218.4

n-Butane(1) + Water(2)

(a) D. S. Tsiklis and V. Ya. Maslennikova, *Dokl. Akad. Nauk SSSR*, **157,** 426 (1964).

$x(1)$	T^c	P^c
0.16	673	700
0.26	683	1000
0.37	703	2400

(b) A. Danneil, K. Todheide, and E. U. Franck, *Chem.-Ing.-Tech.*, **39,** 816 (1967).

$x(1)$	T^c	P^c
0.09	628	600
0.15	628	490
0.17	637	640

n-Pentane(1) + Water(2)

(a) J. F. Connolly, *J. Chem. Eng. Data*, **11,** 13 (1966).

$x(1)$	T^c	P^c
0.08	625	375

n-Hexane(1) + Chloroform(2)

(a) M. T. Ratzsch and G. Strauch, *Z. Phys. Chem.*, **249,** 243 (1972).

$x(1)$	T^c
0.4894	516.0
0.4960	515.8
0.4983	516.0

n-Hexane(1) + Diethylamine(2)

(a) A. Kreglewski and W. B. Kay, *J. Phys. Chem.*, **73,** 3359 (1969).

$x(1)$	T^c	P^c
0.1	496.65	36.49
0.3	497.85	34.98
0.5	500.03	33.76
0.7	502.35	32.58
0.9	505.65	31.13

n-Hexane(1) + Acetic Acid(2)

(a) A. Kreglewski, *Rocz. Chem.*, **31,** 1001 (1957).

$x(1)$	T^c
0.522	514.2
0.654	507.7
0.756	505.4
0.784	505.3
0.856	506.0

n-Heptane(1) + Water(2)

(a) J. F. Connolly, *J. Chem. Eng. Data*, **11,** 13 (1966).

$x(1)$	T^c	P^c
0.04	628	250
0.06	628	300

n-Octane(1) + Acetic Acid(2)

(a) A. Kreglewski, *Rocz. Chem.*, **31,** 1001 (1957).

$x(1)$	T^c
0.131	567.7
0.266	553.6
0.431	548.5
0.622	552.1
0.768	557.1

n-Octane(1) + Pyridine(2)

(a) A. Kreglewski, *Rocz. Chem.*, **31,** 1001 (1957).

$x(1)$	T^c
0.280	589.6
0.491	577.3
0.559	574.5
0.701	570.8

n-Decane(1) + Acetic Acid(2)

(a) A. Kreglewski, *Rocz. Chem.*, **31,** 1001 (1957).

$x(1)$	T^c
0.086	578.3
0.135	574.3
0.185	572.2
0.284	572.6
0.403	577.4

n-Decane(1) + Pyridine(2)

(a) A. Kreglewski, *Rocz. Chem.*, **31,** 1001 (1957).

$x(1)$	T^c
0.317	605.1
0.426	605.7
0.663	609.8
0.708	610.6

n-Dodecane(1) + Acetic Acid(2)

(a) A. Kreglewski, *Rocz. Chem.*, **31,** 1001 (1957).

$x(1)$	T^c
0.032	589.1
0.075	584.6
0.111	583.9
0.162	586.3
0.202	589.5

n-Dodecane(1) + Pyridine(2)

(a) A. Kreglewski, *Rocz. Chem.*, **31,** 1001 (1957).

$x(1)$	T^c
0.034	617.3
0.049	617.2
0.079	617.3
0.167	619.6

Isobutane(1) + Carbon Dioxide(2)

(a) G. J. Besserer and D. B. Robinson, *J. Chem. Eng. Data*, **18,** 298 (1973).

$x(1)$	T^c	P^c
0.09	310.9	75
0.32	344.3	75
0.62	377.6	63
0.80	394.3	50

Neopentane(1) + Argon(2)

(a) B. L. Rogers and J. M. Prausnitz, *J. Chem. Thermodyn.*, **3,** 211 (1971).

$x(1)$	T^c	P^c	V^c
0.265	323.15	255	88.5

2-Methylpentane(1) + Water(2)

(a) J. F. Connolly, *J. Chem. Eng. Data*, **11,** 13 (1966).

$x(1)$	T^c	P^c
0.08	628	380

Cyclohexane(1) + Carbon Dioxide(2)

(a) I. R. Krichevskii and G. A. Sorina, *Russ. J. Phys. Chem.*, **34,** 679 (1960).

$x(1)$	T^c	P^c	V^c
0.157	373.15	140	98
0.280	423.15	150	120
0.430	473.15	127	158
0.513	493.15	119	178
0.625	513.15	96	204
0.660	518.15	90	209
0.800	535.15	67	234

Cyclohexane(1) + Water(2)

(a) K. Brollos, K. Peter, and G. M. Schneider, *Ber. Bunsenges. Phys. Chem.*, **74,** 682 (1970).

$x(1)$	T^c	P^c
0.045	623	225
0.125	623	390
0.134	633	550
0.149	643	700
0.171	663	1000
0.176	673	1200
0.188	683	1480

2,2,4-Trimethylpentane(1) + Hydrogen(2)

(a) S. Peter and K. Reinhartz, *Z. Phys. Chem. (Frankfurt am Main)*, **24,** 103 (1960).

$x(1)$	T^c	P^c
0.184	471.7	711
0.271	499.4	387

2,2,4-Trimethylpentane(1) + Nitrogen(2)

(a) S. Peter and H. F. Eicke, *Ber. Bunsenges. Phys. Chem.*, **74,** 190 (1970).

$x(1)$	T^c	P^c
0.17	376.5	623
0.22	413.2	422
0.26	453.0	309

2,2,4-Trimethylpentane(1) + Ammonia(2)

(a) W. B. Kay and F. M. Warzel, *Amer. Inst. Chem. Eng. J.*, **4,** 296 (1958).

$x(1)$	T^c	P^c	V^c
0.0217	403.55	107.39	85.7
0.0503	404.58	104.44	92.1
0.1000	412.32	106.89	106.2
0.1497	424.33	112.29	119.6
0.2004	438.18	115.84	136.8
0.2599	454.84	115.16	157.5
0.3016	464.01	112.42	168.1
0.5696	512.03	72.76	284.3
0.7118	525.93	54.05	345.1
0.8469	535.63	39.33	401.8
0.9510	541.56	29.70	447.6

Methylcyclohexane(1) + Hydrogen(2)

(a) S. Peter and K. Reinhartz, *Z. Phys. Chem. (Frankfurt am Main)*, **24,** 103 (1960).

$x(1)$	T^c	P^c
0.21	498.7	961

Methylcyclohexane(1) + Nitrogen(2)

(a) S. Peter and H. F. Eicke, *Ber. Bunsenges. Phys. Chem.*, **74,** 190 (1970).

$x(1)$	T^c	P^c
0.16	453.0	691

Ethylene(1) + Carbon Dioxide(2)

(a) J. S. Rowlinson, J. R. Sutton, and F. Weston, *Proc. Joint Conf. Therm. Trans. Prop.*, 10 (1958).

$x(1)$	T^c	P^c
0.2	294.95	68.6
0.4	288.55	61.5
0.6	284.75	57.3
0.8	283.15	54.1

Ethylene(1) + Nitrous Oxide(2)

(a) J. S. Rowlinson, J. R. Sutton, and F. Weston, *Proc. Joint Conf. Therm. Trans. Prop.*, 10 (1958).

$x(1)$	T^c	P^c
0.2	301.25	66.3
0.4	294.75	60.2
0.6	289.75	56.3
0.8	285.55	53.3

Ethylene(1) + Chloroform(2)

(a) J. Shim and J. P. Kohn, *J. Chem. Eng. Data*, **9,** 1 (1964).

$x(1)$	T^c	P^c	V^c
0.797	373.2	102.2	103.0
0.830	348.2	92.1	88.3
0.894	323.2	77.8	86.7
0.969	298.2	61.0	133.3

Ethylene(1) + Monochloroethylene(2)

(a) F. I. Duntov, V. S. Zernov, and S. G. Lyubetski, *Zh. Prikl. Khim.*, **40,** 599 (1967).

$x(1)$	T^c	P^c
0.70	358	82.4

Ethylene(1) + 1,1,1,3-Tetrachloropropane(2)

(a) G. D. Efremova and R. F. Kovpakova, *Zh. Fiz. Khim.*, **32,** 1231 (1958).

$x(1)$	T^c	P^c
0.890	348.2	127
0.910	323.2	100
0.981	298.2	68

Ethylene(1) + 1,1,1,5-Tetrachloropentane(2)

(a) G. D. Efremova and R. F. Kovpakova, *Zh. Fiz. Khim.*, **32,** 1231 (1958).

$x(1)$	T^c	P^c
0.892	298.2	118

Ethylene(1) + 1,1,1,7-Tetrachloroheptane(2)

(a) G. D. Efremova and R. F. Kovpakova, *Zh. Fiz. Khim.*, **32,** 1231 (1958).

$x(1)$	T^c	P^c
0.907	298.2	156

Ethylene(1) + 1,1,1,9-Tetrachlorononane(2)

(a) G. D. Efremova and R. F. Kovpakova, *Zh. Fiz. Khim.*, **32,** 1231 (1958).

$x(1)$	T^c	P^c
0.910	298.2	184

Acetylene(1) + Carbon Dioxide(2)

(a) J. P. Kuenen, *Phil. Mag.*, **44,** 174 (1897).

$x(1)$	T^c	P^c
0.5	305.70	67.40

Acetylene(1) + Ammonia(2)

(a) E. S. Lebedeva and S. M. Khodeeva, *Russ. J. Phys. Chem.*, **35,** 1285 (1961).

$x(1)$	T^c	V^c
0.2	387.7	80.1
0.4	370.5	88.0
0.6	352.7	94.9
0.8	330.7	106.5

Benzene(1) + Carbon Dioxide(2)

(a) S. W. Wan and B. F. Dodge, *Ind. Eng. Chem.*, **32,** 95 (1940).

$x(1)$	T^c	P^c
0.04	313	76
0.05	323	85.5
0.06	333	98

Benzene(1) + Chloroform(2)

(a) M. Ratzsch, *Z. Phys. Chem.*, **243,** 212 (1970).

$x(1)$	T^c
0.1995	544.4
0.3960	549.5
0.6020	554.9
0.7941	559.3

Benzene(1) + Carbon Tetrachloride(2)

(a) A. N. Campbell and G. M. Musbally, *Can. J. Chem.*, **48,** 3173 (1970).

$x(1)$	T^c
0.0958	556.65
0.2350	557.05
0.4400	558.15
0.5267	558.45
0.6178	558.85
0.7360	559.65
0.8375	560.05
0.9410	560.55

Benzene(1) + Water(2)

(a) C. J. Rebert and W. B. Kay, *Amer. Inst. Chem. Eng. J.*, **5,** 285 (1959).

$x(1)$	T^c	P^c
0.030	638.3	214.5
0.061	623.2	201.1
0.090	609.3	187.0
0.400	541.5	93.86
0.489	541.0	93.38
0.690	542.9	83.24
0.799	545.4	77.70

(b) Z. Alwani and G. Schneider, *Ber. Bunsenges. Phys. Chem.*, **71,** 633 (1967).

$x(1)$	T^c	P^c
0.143	573	480
0.148	583	850
0.153	593	1250
0.159	603	1600
0.164	613	2100

(c) J. F. Connolly, *J. Chem. Eng. Data*, **11,** 13 (1966).

$x(1)$	T^c	P^c
0.13	573	167
0.16	573	476

Toluene(1) + Water(2)

(a) J. F. Connolly, *J. Chem. Eng. Data*, **11,** 13 (1966).

$x(1)$	T^c	P^c
0.12	583	260

Naphthalene(1) + Carbon Dioxide(2)

(a) Yu. V. Tsekhanskaya, *Russ. J. Phys. Chem.*, **45,** 744 (1971).

$x(1)$	T^c	V^c
0.003	307.7	95.2

Dichloromethane(1) + Monochloropentafluoroethane(2)

(a) W. H. Mears, J. V. Sinka, P. F. Malbrunot, P. A. Meunier, A. G. Dedit, and G. M. Scatena, *J. Chem. Eng. Data*, **13,** 344 (1968).

$x(1)$	T^c	P^c	V^c
0.735	339.3	48.9	153
0.735	339.6		

Monochlorotrifluoromethane(1) + Trifluoromethane(2)

(a) J. V. Sinka, E. Rosenthal, and R. P. Dixon, *J. Chem. Eng. Data*, **15,** 73 (1970).

$x(1)$	T^c	P^c	V^c
0.50	292.6	43.57	155

Dichlorodifluoromethane(1) + 1,1-Difluoroethane(2)

(a) J. V. Sinka and K. P. Murphy, *J. Chem. Eng. Data*, **12,** 315 (1967).

$x(1)$	T^c	P^c	V^c
0.606	378.7	44.3	200.0
0.606	378.2	43.5	199.5

Monochloromonofluoromethane(1) + Dichlorotetrafluoroethane(2)

(a) J. V. Sinka, *J. Chem. Eng. Data*, **15,** 71 (1970).

$x(1)$	T^c	P^c	V^c
0.753	415.2	51.6	174

Monochlorotetrafluoroethane(1) + Perfluorocyclobutane(2)

(a) E. A. Stolyarov, V. S. Bamikov, and V. I. Mashendzhinov, *Tr. Gos. Inst. Prikl. Khim.*, No. 49, 283 (1962).

$x(1)$	T^c	P^c	V^c
0.77	380.2	29.42	280

Helium(1) + Dichlorodifluoromethane(2)

(a) D. S. Tsiklis, V. Ya. Maslennikova, and N. P. Goryunova, *Russ. J. Phys. Chem.*, **41,** 965 (1967).

$x(1)$	T^c	P^c
0.10	388	51
0.25	391	106
0.52	395	319

Helium(1) + Monochlorodifluoromethane(2)

(a) V. Ya. Maslennikova, N. P. Goryunova, and D. S. Tsiklis, *Dokl. Akad. Nauk SSSR*, **178,** 886 (1968).

$x(1)$	T^c	P^c
0.20	373	98
0.37	377	226

Helium(1) + Dibromotetrafluoroethane(2)

(a) V. Ya. Maslennikova, N. P. Goryunova, and D. S. Tsiklis, *Dokl. Akad. Nauk SSSR*, **178,** 886 (1968).

$x(1)$	T^c	P^c
0.25	489.7	74
0.37	493	118
0.50	496	201

Nitrogen(1) + Dichlorodifluoromethane(2)

(a) V. Ya. Maslennikova, N. P. Goryunova, and D. S. Tsiklis, *Russ. J. Phys. Chem.*, **41,** 383 (1967).

$x(1)$	T^c	P^c
0.45	348	130
0.55	323	157
0.61	295	178

Nitrogen(1) + Monochlorodifluoromethane(2)

(a) V. Ya. Maslennikova, N. P. Goryunova, and D. S. Tsiklis, *Russ. J. Phys. Chem.*, **41,** 383 (1967).

$x(1)$	T^c	P^c
0.435	333	129
0.515	313	162
0.570	295	195

Nitrogen(1) + Ammonia(2)

(a) R. Wiebe and V. L. Gaddy, *J. Amer. Chem. Soc.*, **59,** 1984 (1937).

$x(1)$	T^c	P^c
—	363	608
—	373	379

(b) A. E. Lindroos and B. F. Dodge, *Chem. Eng. Progr., Symp. Ser., No. 3,* **48,** 10 (1952).

$x(1)$	T^c	P^c
0.38	359.7	1013
0.42	361.7	1520
0.44	363.2	1814
0.49	373.2	2057
0.50	383.2	3040

Nitrogen(1) + Water(2)

(a) V. M. Prokhorov and D. S. Tsiklis, *Russ. J. Phys. Chem.*, **44,** 1173 (1970).

$x(1)$	T^c	P^c
0.13	638	700
0.17	637	750
0.23	638	800
0.48	658	2200

Argon(1) + Water(2)

(a) H. Lentz and E. U. Franck, *Ber. Bunsenges. Phys. Chem.*, **73,** 28 (1969).

$x(1)$	T^c	P^c	V^c
0.01	648.2	230	57.0
0.05	653.2	290	55.4
0.17	658.2	530	48.5
0.26	663.2	2270	28.5
0.275	668.2	2780	26.5
0.28	673.2	3100	25.5

Krypton(1) + Hydrogen Chloride(2)

(a) G. Glocker, D. L. Fuller, and C. P. Roe, *J. Chem. Phys.*, **1,** 709 (1933).

$x(1)$	T^c	P^c
0.038	320	86
0.121	312	91
0.248	296	96
0.366	281	97
0.511	263	94

Carbon Dioxide(1) + Hydrogen Sulfide(2)

(a) J. A. Bierlein and W. B. Kay, *Ind. Eng. Chem.*, **45,** 618 (1953).

$x(1)$	T^c	P^c	V^c
0.0630	366.65	89.97	95.4
0.1614	357.31	89.77	94.2
0.2608	347.63	88.52	93.6
0.3759	337.89	85.86	93.1
0.4728	330.13	83.21	93.0
0.6659	316.87	77.85	93.1
0.8292	309.11	74.83	93.5
0.9009	306.68	74.16	93.8

(b) D. P. Sobocinski and F. Kurata, *Amer. Inst. Chem. Eng. J.*, **5,** 545 (1959).

$x(1)$	T^c	P^c
0.1649	357	90
0.2347	349	89
0.3813	338	86
0.4475	333	84
0.500	329	83
0.6271	321	80
0.8346	309	75
0.9095	306	74

Carbon Dioxide(1) + Nitrous Oxide(2)

(a) F. Caubet, *Z. Phys. Chem.*, **49,** 101 (1904).

$x(1)$	T^c	P^c
0.0809	308.4	75.49
0.1894	307.6	76.80
0.4840	306.2	77.82
0.7868	304.4	76.80
0.9258	303.9	75.69
0.9592	303.9	75.49
0.9780	304.0	75.28

(b) D. Cook, *Proc. Roy. Soc., Ser. A*, **219,** 245 (1953).

$x(1)$	T^c	P^c	V^c
0.258	307.59	72.54	95.1
0.500	306.05	72.72	93.9
0.617	305.46	72.99	
0.742	304.94	73.22	93.8
0.881	304.45	73.33	93.5

(c) J. S. Rowlinson, J. R. Sutton, and F. Weston, *Proc. Joint Conf. Trans. Therm. Prop.*, 10 (1958).

$x(1)$	T^c	P^c
0.2	307.95	72.2
0.4	306.55	72.5
0.6	305.45	73.0
0.8	304.85	73.3

Carbon Dioxide(1) + Water(2)

(a) K. Todheide and E. U. Franck, *Z. Phys. Chem. (Frankfort am Main)*, **37,** 387 (1963).

$x(1)$	T^c	P^c
0.025	643.2	235
0.075	633.2	279
0.125	623.2	333
0.155	613.2	373
0.190	603.2	427
0.220	593.2	485
0.242	583.2	539
0.267	573.2	608
0.295	563.2	716
0.330	553.2	917
0.347	548.2	1080
0.367	543.2	1370
0.375	542.2	1470
0.385	541.2	1620
0.395	540.2	1890
0.415	539.2	2450
0.430	540.2	3140
0.435	541.2	3600
0.997	304.65	74

(b) S. Takenouchi and G. C. Kennedy, *Amer. J. Sci.*, **262,** 1055 (1964).

$x(1)$	T^c	P^c
0.105	623.2	325
0.180	598.2	430
0.236	573.0	575
0.270	548.2	885
0.288	543.2	1230
0.308	538.2	1850
0.312	538.2	2260

Carbon Dioxide(1) + Ammonia(2)

(a) S. M. Lenkowitz, J. Goedegebuur, and P. J. van den Berg, *J. Appl. Chem. Biotech.*, **21**, 229 (1971).

x(1)	T^c	P^c
0.023	429.1	147.7
0.030	436.9	161.3

Carbon Dioxide(1) + Sulfur Hexafluoride(2)

(a) I. R. Krichevskii, *Russ. J. Phys. Chem.*, **41**, 1332 (1967).

x(1)	T^c	P^c
0.00976	318.368	37.999
0.01010	318.373	38.018
0.01070	318.330	38.027

Carbon Dioxide(1) + Sulfur Dioxide(2)

(a) F. Caubet, *Z. Phys. Chem.*, **40**, 257 (1902).

x(1)	T^c	P^c
0.0891	418.6	83
0.1862	405.2	88
0.2907	392.7	93
0.4003	379.7	95
0.5290	359.2	94
0.6676	341.2	90
0.8432	321.5	81
0.8965	312.2	76

Ammonia(1) + Water(2)

(a) D. S. Tsiklis, L. R. Linshits, and N. P. Goryunova, *Russ. J. Phys. Chem.*, **39**, 1590 (1966).

x(1)	T^c	P^c
0.13	623.3	218
0.29	593.2	213
0.38	573.2	208
0.61	523.2	193
0.79	473.2	167
0.88	448.2	150
0.96	420.2	127

Sulfur Trioxide(1) + Water(2)

(a) J. E. Stuckey and C. H. Secoy, *J. Chem. Eng. Data*, **8**, 387 (1963).

x(1)	T^c	V^c
0.0193	677.4	45.9
0.0419	720.6	45.7
0.0654	756.0	48.5
0.0938	799.3	52.3
0.1251	835.2	55.9
0.1643	865.4	57.7
0.2084	894.2	63.0
0.2664	920.0	70.4
0.3368	938.6	77.4
0.4353	939.6	87.8
0.5591	910.4	89.2

IX. Appendix B. Calculation Procedure for the General Solution to the Criticality Conditions

The criticality conditions are set out and discussed in section IV. They were solved by defining: (i) $\alpha(\tilde{v},\tilde{T})$ equal to the left-hand side of eq 79 divided by RT, (ii) $\beta(\tilde{v},\tilde{T})$ equal to the left-hand side of eq 80 divided by RT, so that the criticality conditions could be written in the form

$$\alpha(\tilde{v},\tilde{T}) = 0$$
$$\beta(\tilde{v},\tilde{T}) = 0$$

The actual calculation procedure used can be separated into the steps detailed below.

Step 1. We computed f_{12} and h_{12} according to the assumed combining rules.

Step 2. We used the critical properties of the components of the mixture, together with f_{12}, h_{12}, and the composition of the mixture to calculate $T_{\rm es}{}^{\rm c}$, $f_{\rm x}/f_{\rm es}$, $f_{2\rm x}/f_{\rm es}$, $f_{3\rm x}/f_{\rm es}$, $v_{\rm es}{}^{\rm c}$, $h_{\rm x}/h_{\rm es}$, $h_{2\rm x}/h_{\rm es}$, and $h_{3\rm x}/h_{\rm es}$ according to the assumed prescription.

Step 3. We calculated the values of $(\partial^2 A_{\rm cb}/\partial x^2)/RT$ and $(\partial^3 A_{\rm cb}/\partial x^3)/RT$ using an assumed form for $A_{\rm cb}$. This required the size ratio, r, in some calculations. r was estimated as the ratio of molar volumes of the components of the mixture under specified conditions (usually 20°C).

Step 4. In this step we obtained an approximate solution, $\tilde{v}$, $\tilde{T}$, to the criticality conditions. Usually the first-order approximation to the general solution discussed in section IV was employed.

Step 5. We iteratively refined the approximate solution by the Newton–Raphson method until it gave the solution to the criticality conditions for the assumed reduced equation of state. This involves, given the approximate solution, $\tilde{v}$, $\tilde{T}$, and the reduced equation of state:

(a) Computing the quantities set out in Table I, and using them to calculate $(\partial^2 A_{\rm es}/\partial x^2)_{v,T}/RT$ and $(\partial^3 A_{\rm es}/\partial x^3)_{v,T}/RT$.

(b) Computing the remaining quantities in eq 79 and 80 (all divided by RT).

(c) Calculating the $\alpha(\tilde{v},\tilde{T})$ and $\beta(\tilde{v},\tilde{T})$ defined above.

(d) In a similar manner to (a)–(c) calculating the first derivatives of α and β with respect to $\tilde{v}$ and $\tilde{T}$.

(e) Using the values calculated in (c) and (d) to obtain an improved solution to the criticality conditions by means of a Newton–Raphson step.

(f) Repeating (a)–(e) until successive values of $\tilde{v},\tilde{T}$ given by (e) differed insignificantly. $\tilde{p}$ for the $\tilde{v},\tilde{T}$ is generated during calculation steps (a)–(e) by the reduced equation of state.

Step 6. $v_{\rm m}{}^{\rm c}$ and $T_{\rm m}{}^{\rm c}$ were obtained directly from $\tilde{v},\tilde{T}$ by the relations

$$v_{\rm m}{}^{\rm c} = v_{\rm es}{}^{\rm c}\tilde{v}$$
$$T_{\rm m}{}^{\rm c} = T_{\rm es}{}^{\rm c}\tilde{T}$$

We generally calculated $p_{\rm m}{}^{\rm c}$ from $\tilde{p}$ by the following steps which result in $p_{\rm m}{}^{\rm c}$ passing smoothly from $p_{11}{}^{\rm c}$ to $p_{22}{}^{\rm c}$

$$Z_{\rm es}{}^{\rm c} = x_1 Z_{11}{}^{\rm c} + x_2 Z_{22}{}^{\rm c}$$
$$p_{\rm es}{}^{\rm c} = Z_{\rm es}{}^{\rm c} R T_{\rm es}{}^{\rm c}/v_{\rm es}{}^{\rm c}$$
$$p_{\rm m}{}^{\rm c} = p_{\rm es}{}^{\rm c}\tilde{p}$$

X. Addendum to Compilation

Since completion of the compilation, the following papers containing data on gas–liquid critical points have been published or brought to our attention: hydrocarbon mixtures, references 158–164; mixtures of simple molecules, references 165–176; miscellaneous mixtures, references 177–188.

The following systems were studied in papers included in the compilation but were accidentally omitted during preparation of the manuscript: perfluorocyclobutane + pent-1-ene, reference 189; benzene + *n*-heptane, benzene + cyclohexane, reference 190.

XI. References

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