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LOW TEMPERATURE VAPOR-LIQUID EQUILIBRIUM
IN LIGHT HYDROCARBON MIXTURES:
METHANE-ETHANE-PROPANE SYSTEM

by

A. Roy Price

A THESIS
SUBMITTED TO THE FACULTY
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY IN CHEMICAL ENGINEERING

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Approved: Ruki Koyayashi

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NOMENCLATURE FOR FIGURES 1-6

A	Ascarite drier
AB	Alcohol bath
AC	Auxiliary cooling coil
B ₁ , B ₂ , B ₃	Calibrated volumetric bulbs
C	Visual equilibrium cell
CH	Charge
CP	Centrifugal pump
CT	Copper tube with slits for bath circulation
D	Drierite drier
D ₁ , D ₂	Stainless steel drying tubes
DF	Dewar flask
E	Equilibrium section
F	Calibrated glass mixing flask
G ₁ , G ₂ , G ₃ G ₄ , G ₅	Pressure gages
H	Mercury reservoir
M	Mercury pump
MN	Manometer
N	Needle valve
NB	Liquid nitrogen bath
NF	Liquid nitrogen flask
P	Magnetic pump
PB	Primary bath
PG	Pressure generator
PV	Pressure vessel
R	Visual cell for retrograde condensation

NOMENCLATURE FOR FIGURES 1-6 (Continued)

RC	Recycle coil
RD	Rupture disk
RG	Low pressure regulator
RT	Gas rotameter
S	Air powered stirrer
S_1 & S_2	Sample containers
SG	Silica gel driers
TC	Thermocouple well
TK	Surge tank
V	Variable volume cell
Vac.	Vacuum
VC	Vaporization coil
W	Water bath
1 & 2	Special charge cylinders
X	Needle valve
⊗	Glass stopcock

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NOMENCLATURE FOR EQUATIONS

a	Activity, empirical constant in BWR equation of state, parameter in Dieterici equation of state
A	Area, Liquid factor in MABP correlation, empirical constant in BWR equation of state
A_0	Empirical constant in BWR equation of state
b	Empirical constant in BWR equation of state, parameter in Dieterici equation of state
B	Vapor factor in MABP correlation, empirical constant in BWR equation of state
B_0	Empirical constant in BWR equation of state
$B(T)$	Second virial coefficient
c	Slope of emf. vs. thermal conductivity curve, empirical constant in BWR equation of state
C	Number of independent components (Gibbs Phase Rule)
C_0	Empirical constant in BWR equation of state
e	Base of natural logarithms
E	Emf
$\bar{E}$	Molal intermolecular potential energy
f	Fugacity
F	Number of degrees of freedom (Gibbs Phase Rule)
G	Free energy
H	Enthalpy
k	Vaporization equilibrium constant $\left(\frac{f_L^0}{f_V^0} \right)$
k_H	Henry's constant
K	K-Value (y/x)
m	Mol fraction
M	Moles
MABP	Molal average boiling point $\left(\sum_{i=1}^n m_i T_{B,i} \right)$

NOMENCLATURE FOR EQUATIONS (Continued)

n	Number of components, moles
N	Avogadro's number
p	Partial pressure
P	Total pressure
P°	Vapor pressure
Q	Flow rate
r	Distance, radius
R	Universal gas constant
t	Time
T	Temperature (absolute)
U	Internal energy
U_r	Intermolecular potential energy
$v, \bar{V}$	Molal volume
V	Volume
x	Mol fraction in liquid
y	Mol fraction in vapor
z, Z	Compressibility factor

Greek Letters

α	Empirical constant in BWR equation of state, abbreviation defined on p. 88
β	Abbreviation defined on p. 88
γ	Activity coefficient, empirical constant in BWR equation of state
Δ	Experimental correction term (p. 99)
ϵ	An energy parameter
μ	Chemical potential

NOMENCLATURE FOR EQUATIONS (Continued)

π	3.14159
ρ	Density
σ	A length parameter
Φ	Abbreviation defined on p. 96
Ψ	Abbreviation defined on p. 97
Θ	Abbreviation defined on p. 96

Subscripts

B	Boiling point
BWR	Benedict-Webb-Rubin equation of state
c	Pure component or critical
g	Solute
G	Gaseous (or vapor)
H	Referring to hydrocarbon
i	Component designation
j	Component designation
L	Liquid phase
m	Mixture
R	Reference
S	Solvent, sample, or smoothed
T	Total
V	Vapor (or gaseous)
1,2,----	Component designation
1,2	Initial and final
I, II	Phase designations

NOMENCLATURE FOR EQUATIONS (Continued)

Superscripts

$^{\circ}, *$	Standard state
$^{\circ}$	Vapor pressure
$'$	Pseudo properties (mixtures)

ABSTRACT

Experimental equilibrium data have been determined for 175 mixtures of methane, ethane, and propane. The investigation included temperatures from 50°F to -200°F and pressures up to the critical. A vapor recycle apparatus was used to establish equilibrium. Phase samples were analyzed by infrared spectrophotometer and gas-liquid partition chromatography.

The Benedict-Webb-Rubin equation of state was programmed for an automatic electronic computer to enable calculation of equilibrium data. These were compared with the corresponding experimental results. Methane K-values are predicted reasonably well, however ethane and propane show serious deviation at low temperatures.

A correlation is presented based on the experimental data of this study. Molal average boiling point of each phase is used as the correlation composition variable in the manner of De Priester's modification of the Kellogg Equilibrium Charts. Comparisons with published data show good correlation for methane, ethane, and propane in mixtures with paraffinic and olefinic hydrocarbons of molecular weight lower than n-heptane.

A correlation based on the law of corresponding states is also given. Methods for calculating the pseudocritical properties of simple mixtures are proposed. Thermodynamic properties obtained from generalized tables were

ABSTRACT (Continued)

used to calculate K-values. Empirical correction factors were evaluated for light hydrocarbon systems and correlated with composition variables.

INTRODUCTION

The first investigations concerning the liquefaction of gaseous mixtures were stimulated by Caillettet's unexpected observations in 1880 (16). While compressing a mixture of carbon dioxide and air at constant temperature, he observed the appearance of a liquid phase as expected. Additional increase of pressure, however, eventually caused the liquid to disappear. Van der Waals (74), Andrews (3), Kuenen (39)(40), and Duhem (22) made similar observations of this phenomenon, to which Kuenen applied the name retrograde condensation. Both Kuenen and Duhem explored the general phase behavior of binary mixtures in considerable detail.

Whereas these investigators were mainly interested in the conditions defining the liquid-vapor region, the compositions of the separating phases are of extreme importance. The distribution of components between such equilibrium phases forms the basis for distillation and related operations.

In a heterogeneous system at equilibrium, the chemical potential (μ) of any component must be equal in every phase in which it appears. If the system is restricted to constant temperature, fugacity (f) may be used in place of μ ; i.e.

$$(f_i)_I = (f_i)_{II} = (f_i)_{III} = \text{-----} \quad 1$$

where $(f_i)_I, (f_i)_{II}, \dots$ = fugacities of component i in phases I, II, ----

But $f_i = a_i f_i^0 \quad 2$

where a_i = activity of component i in the mixture

f_i° = fugacity of component i in the standard state

Therefore

$$(a_i)_I (f_i^\circ)_I = (a_i)_{II} (f_i^\circ)_{II} = (a_i)_{III} (f_i^\circ)_{III} = \dots \quad 3$$

In the case of two phases, liquid and vapor, equation 3 may be written:

$$(a_i)_L (f_i^\circ)_L = (a_i)_V (f_i^\circ)_V \quad 4$$

or

$$\frac{(a_i)_V}{(a_i)_L} = \frac{(f_i^\circ)_L}{(f_i^\circ)_V} = k_i \quad 5$$

This equation defines the vaporization equilibrium constant (k) of component i in the manner of Gamson and Watson (24).

The standard states for components in the vapor phase are customarily chosen as the pure gases at the temperature and pressure of the system. Those for the liquid phase are similarly taken as the pure liquids at system conditions. From this, it is evident that the vaporization equilibrium constant (k) is a function of temperature, pressure, and the nature of the component (but not composition).

Activities may be related to concentrations by means of activity coefficients:

$$(a_i)_V = (\gamma_i)_V y_i \quad 6$$

$$(a_i)_L = (\gamma_i)_L x_i \quad 7$$

where y_i, x_i = mol fractions of component i in the vapor and liquid phases respectively.

$(\gamma_i)_V, (\gamma_i)_L$ = activity coefficients of component i in the vapor and liquid phases respectively.

Substituting 6 and 7 into 5,
$$\frac{(\gamma_i)_V y_i}{(\gamma_i)_L x_i} = k_i$$

$$\text{or} \quad \left[\frac{(\delta_i)_L}{(\delta_i)_V} \right] k_i = \frac{y_i}{x_i} = K_i \quad 8$$

Equation 8 defines the widely used "K-value", known by such other titles as "vaporization ratio" and "equilibrium constant". In order to distinguish the K above from the previously defined vaporization equilibrium constant (k) the simple term "K-value" will be used for K throughout this work. Equation 8 indicates that K is not only a function of temperature and pressure, but also of the degree of "ideality" of the system. Composition, therefore, would be expected to influence the K-value under most conditions.

The variation of K-value with temperature, pressure, and composition, is so complex that empirical data and correlations are quite abundant. Hydrocarbon systems have received most of the attention because of their importance industrially. Vapor-liquid equilibria in the high temperature range have been widely explored, e.g. Sage and Lacey's recent publication (62).

Experimental investigations at below-atmospheric temperatures, however, are quite limited. Two component systems account for most of the work in this region. Ternary and multicomponent data are more rare. The following systems have been investigated:

<u>System</u>	<u>Source</u>
Methane-Ethylene	(25)(76)
Methane-Ethane	(10)(41)(60)
Methane-Propane	(1)(63)
Methane-Butane	(49)(68)
Ethylene-Ethane	(37)(44)
Ethylene-Propane	(61)(45)
Ethylene-Propylene	(45)
Methane-Ethylene-Ethane	(25)
Ethylene-Ethane-Acetylene	(45)
Natural Gases	(15)(20)(72)

Although the number of references above is considerable, many contain sparse data over a very limited region.

It appeared that, before the low temperature non-ideality effect on K-values could be evaluated effectively, more complete data were necessary. It was the purpose of this investigation to obtain such data and to seek a resolution of this effect. The ternary system methane-ethane-propane was selected because of its fundamental nature, yet multi-component behavior. Six temperatures were investigated, extending from 50°F to -200°F. Pressures at 100 and 200 psi intervals up to the critical region were chosen.

EXPERIMENTAL APPARATUS

I. Previous Methods Used for Vapor-Liquid Equilibrium Experiments

Bloomer and Parent (10) have presented a good discussion of the various experimental methods used to measure vapor-liquid equilibria. A brief description of the methods, their advantages and disadvantages, follows.

A. Dew Point - Bubble Point Method

A gas mixture of known composition is added to an equilibrium vessel held at constant temperature. Pressure is varied, and values at which condensation begins and ends are noted. By varying temperature, a phase envelope is obtained; and by using mixtures of various compositions, a family of envelopes can be found. By suitable plotting on temperature-composition or pressure-composition diagrams, equilibrium phase compositions may be determined.

The experimental apparatus needed is relatively simple, and the equilibrium phases need not be analyzed. Visual determination of the dew and bubble points, however, can be quite difficult and requires great care.

According to the phase rule,

$$F = C - P + 2$$

9

where C = number of independent components

P = number of phases

F = number of degrees of freedom

In the experimental method under discussion for binaries,

$$C = 2$$

$$P = 2 ,$$

therefore $F = 2 - 2 + 2 = 2$.

If pressure and temperature are fixed, as they are at the dew and bubble points, the two degrees of freedom are used, thus fixing the compositions of the phases. For this reason, the method is very useful for binary vapor-liquid equilibrium measurements. Although border curves for multi-component mixtures may be obtained, the phase compositions are difficult to determine without an excessive number of measurements.

B. Static Method

In this method, a mixture is contained in a closed equilibrium vessel at constant temperature and pressure, and the two phases are allowed to reach equilibrium. Agitation by stirring or rocking is often used to shorten the equilibrium time. Samples of the two phases are then withdrawn and analyzed. Care must be taken to insure against disturbing the equilibrium during sampling. Unless extremely small samples are taken relative to the amounts in each phase, some system of pressure compensation or sample isolation must be employed. Mercury is usually added directly to the equilibrium cell for this purpose but cannot be used below -38°F . A suitable substitute displacing fluid has not been found. Boomer and co-workers (11) have designed an ingenious

apparatus for isolating the two phases from each other prior to sampling.

C. Flow System

In this method, a gas mixture is passed slowly and continuously into a receiving vessel. The system is designed to condense a liquid phase at constant temperature and pressure, with continuous removal of the phases for analysis.

The advantage of the method is that samples can be taken without disturbing the equilibrium. On the other hand, a relatively large quantity of each gas mixture is required, and the relative amount of liquid to be condensed (as set by the overall composition, temperature, and pressure) must be very closely approached in order to attain equilibrium. Rapid condensation near the critical tends to flood the apparatus, and can cause serious errors in this region.

D. Vapor Recycle System

The vapor phase in this method is drawn from an equilibrium cell at constant temperature and pressure and bubbled through the liquid until equilibrium is reached. An external pump provides the vapor circulation. Since the phases must be analyzed, some method of pressure compensation (or phase isolation) must be employed during sampling. If suitable "on-stream" analytical methods are available, this complication can be avoided.

The method requires rather elaborate equipment, but is quite flexible and yields good accuracy. Excellent contact between the two phases is accomplished, resulting in rapid attainment of equilibrium. The possibility of retrograde condensation in the system outside the bath, however, must be considered during low-temperature investigations.

II. Experimental Apparatus for this Investigation

The vapor recycle system used by Harvey (30) was modified for this study. The high pressure sections of the apparatus were of stainless steel construction. Two tubing sizes were used, 3/16" and 1/8", rated at 10,000 and 15,000 psi respectively.

Copper tubing (3/8" and 1/4") was used in the cooling and vacuum systems.

The apparatus can be divided into six functional sections: equilibrium, pressure control, temperature control, charge, sampling, and vacuum.

A. Equilibrium Section (Figure 1)

The basic piece of equipment here was the equilibrium cell (C) submerged in a constant temperature bath. It was a modified Jerguson Transparent Gage, size 18-T-30, with inlet and outlet holes drilled in the top and bottom. Thermocouple wells of 1/8" stainless steel tubing were inserted about an inch from the top and bottom, and a liquid sample tap was drilled near the bottom. The cell was rated at 2000 psi

FIGURE 1
SIMPLIFIED FLOW DIAGRAM OF EQUILIBRIUM
SECTION

FIGURE 2
PRESSURE CONTROL SYSTEM

FIGURE 3
TEMPERATURE CONTROL SYSTEM

at 100°F, and had a capacity of about 100 cc. Teflon gaskets were used between the glass windows and the metal body.

Another Jerguson Transparent Gage (R), model 14-T-30, was located outside the bath. It was unmodified, with a pressure rating of 10,000 psi at 100°F, and a volume of 20cc. This permitted detection of any retrograde condensation in the recycle vapor as it left the equilibrium cell.

The vapor circulation was provided by a magnetic piston-type pump (P) rated at 7500 psi, purchased from the Coleman Instrument Co., Tulsa, Oklahoma. The pump operated on 110 V DC, had a volume displacement of 10 cc per stroke, and delivered 30 strokes per minute. The piston, containing two check valves, was moved by a solenoid and spring combination and was designed to operate without lubrication. Better performance resulted, however, when the cylinder wall was coated with a thin film of Apiezon stop-cock grease. A by-pass permitted control of flow rate. The absence of packing eliminated a common source of high pressure leaks.

The variable volume cell (V), constructed in the departmental shop, was vital to pressure regulation and the sampling process. With a volume of 350 cc, it was designed for 10,000 psi at room temperature. Circulating vapor entered through a perforated tube extending deep into the cell, while attached baffles provided mixing. Mercury was pumped in through the bottom for pressure control. An electric contact, in circuit with a light and bell, provided an alarm

system to warn the operator when the cell was full of mercury.

From the variable volume cell, the vapor stream passed through a submerged cooling coil consisting of 25 feet of 1/8" stainless steel tubing. This cooled the vapor to bath temperature prior to entering the equilibrium cell.

B. Pressure Control System

The variable volume cell just described was an integral part of the pressure control system. The rest of this section is shown in Figure 2. System pressure was indicated by a calibrated Heise gage, 2000 psi range, shown as G₂ in Figure 4.

A mercury pump (M), purchased from the Ruska Instrument Corporation, Houston, Texas, was used to force mercury into the variable volume cell. The pump was a piston-displacement type with a screw advance and rated at 25,000 psi. It could either be hand operated for slow delivery, or motor driven for more rapid rates. A complete piston advance delivered 100 cc of mercury, and more mercury could be added from the reservoir (H) as the piston was withdrawn.

During an experimental run, corrections for minor pressure changes as well as sample displacements were effected by mercury addition to (V). A 10,000 psi Heise pressure gage (G₁) was attached to the pump.

The mercury was also used to displace charge components from the charge cylinders, (1) and (2). They will receive further discussion in Section D.

C. Temperature Control System

The primary cooling system was similar to that used by Bloomer and others in their studies of methane-ethane mixtures (9). A diagram of the primary and auxiliary systems appears in Figure 3.

In the primary system compressed air from the laboratory lines passed through a low pressure regulator (RG), a silica gel drier (SG), and into a liquid nitrogen flask (NF). Liquid nitrogen was forced out of the flask through the submerged tube and into a vaporization coil (VC) in the bath. The vaporized nitrogen passed to a surge tank (TK) and then through a needle valve (N). Rotameter (RM) indicated nitrogen flow. By setting the needle valve and regulator to experimentally determined positions, the rate of liquid nitrogen vaporization was held constant. This refrigerating effect compensated for the heat introduced by the recycle stream and for heat "leaks". Since these heat loads were relatively constant during an equilibrium run, the rate of nitrogen vaporization was held constant. This was done automatically in the following manner. If the vaporization rate decreased, the pressure in the surge tank (TK) also decreased. This created a higher differential pressure between the regulator and surge tank, thus forcing more liquid nitrogen into the vaporization coil. In this manner a downward change in vaporization rate was counterbalanced. The system functioned in a reverse manner if the rate of

evaporation increased.

It should be emphasized that this was not an automatic temperature control; rather, it was an automatic refrigeration control. The desired temperature was attained by manually controlling the vaporized nitrogen flow or by using auxiliary cooling. Once the required temperature was reached, however, the rate of cooling was adjusted to equal the heat introduced. The rotameter (RM) indicated rate of vaporization and permitted reproduction of the nitrogen flow for use in future operations.

Denatured alcohol was used as the primary bath liquid for temperatures down to -50°F . Pentane and isopentane were used for investigations at lower temperatures. Circulation was provided by using an air powered stirrer to drive propellers inside a two-inch tube extending to the bottom of the bath. Self-aligning ball bearings at the top and bottom of the tube kept the shaft centered and prevented a downward thrust from binding the motor. The bath liquid was drawn up through the tube and emerged through a series of slots near the top.

The primary bath container was a four gallon Dewar flask, specially constructed by the H. S. Martin Company, St. Louis, Missouri. It had two unsilvered strips, 1" wide, down the side at diametrically opposite locations. The flask was contained in a block of styrofoam insulation enclosed in a metal box constructed of $1/8$ " steel plate. Slits were

cut in the box and insulation at positions corresponding to the strips on the Dewar. The box was mounted on a screw jack (powered by a manually operated wheel) with the slits aligned for viewing from the front. A fluorescent lamp, attached to the back of the box, extended the length of the slit. The windows of the equilibrium cell were centered with respect to the slits enabling visual observation of the interior. The lamp provided the lumination necessary to determine the presence of two phases by sight. Clear visibility was very important, especially at conditions near the critical when the two phases became difficult to distinguish.

The auxiliary cooling system (Figure 3) consisted of an alcohol-dry ice bath (AB) (-109°F) containing a 10' coil of $3/8$ " copper tubing (AC). Primary bath liquid was circulated through this coil by means of a small centrifugal pump (CP). The lines were also $3/8$ " copper tubing, insulated with "rock wool". Use of this system shortened the time required for cooling the primary bath and reduced the consumption of liquid nitrogen. In this manner, a temperature of -50°F could be reached in less than an hour. The auxiliary cooling could be used effectively only to about -80°F due to heat losses. Liquid nitrogen was used with the primary system to attain lower temperatures.

Control of the nitrogen evaporation rate provided the temperature regulation at all levels. Satisfactory performance of this system depended upon the constancy of

the heat load encountered. In the application here, a constant cooling requirement existed, and good control resulted. Temperatures were held constant to $\pm 0.1^{\circ}\text{F}$.

Calibrated copper-constantan thermocouples were placed in the two thermowells and at three locations in the primary bath. Temperatures were determined from potential measurements made with a Leeds & Northrup Portable Precision Potentiometer (Model No. 8662).

D. The Charge Mechanism

The phase rule stipulates three degrees of freedom for a ternary system with two phases in equilibrium. Therefore one other phase rule variable must be set (in addition to temperature and pressure) before the equilibrium phase compositions are fixed. The concentration of any of the components in either phase can be used. Thus, independent charging of the gases would give greater flexibility in selecting equilibrium conditions. In addition, this would eliminate the need for making up numerous gas mixtures at high pressure.

For these reasons the equipment was designed to enable addition of pure gases directly to the equilibrium system. Actually, three methods of charging were used, depending upon the conditions encountered.

(1) The simplest method involved direct addition from the gas cylinders. This section of the apparatus is shown in the lower right corner of Figure 4. Prior to

FIGURE 4
ASSEMBLY DIAGRAM OF EXPERIMENTAL APPARATUS

entering the equilibrium section, the gases passed through driers (D) and (A) containing Drierite and Ascarite to remove water and carbon dioxide respectively. In addition, activated carbon was used when any gas was suspected of containing heavy hydrocarbons. Components were usually charged in the order of increasing vapor pressures. Quite often, however, composition and liquid level adjustments required the addition of gases at pressures above their vapor pressures. This was accomplished by the second charging method.

(2) Containers 1 and 2 shown in Figures 2 and 4 were used to charge both ethane and propane at high pressures. The containers were filled with the liquefied gases, and mercury was injected through the bottom to reach the desired charge pressures. Further addition of mercury displaced the fluids into the equilibrium system.

The method of filling the containers with liquid varied with the component involved. In the case of propane, the cylinder was inverted and connected to the bottom of the container. By slowly venting propane through the valve at the top, liquid was forced in from the cylinder. When the container was full, the valve would frost over, followed by the appearance of the liquid. A small amount of propane was always vented to avoid possible high pressure build-up due to thermal expansion.

Because ethane was available in much smaller amounts than propane, the venting method described above was

undesirable." In addition, the only attempt at using the method for ethane was unsuccessful. The following procedure was finally adopted. A heavy paper sheath was placed around the container leaving an annular space of about one inch. The ethane cylinder was connected to the top valve, and crushed dry-ice was packed in the annulus described. Ethane was condensed in the container until it was full, such condition being determined by experience.

Both vessels were of Series 303 stainless steel and constructed in the departmental shop. Design pressures were 10,000 and 5,000 psi for 1 and 2 respectively. The corresponding volumes were 270 cc and 565 cc.

(3) The third method of charging involved the use of a pressure "generator" to facilitate the addition of methane at high pressures. As was often the case, the pressure required in the equilibrium section exceeded that of the methane supply by a considerable amount. Equipment was constructed in which methane could be condensed in pressure vessels submerged in liquid nitrogen. Upon removal of the cold bath, high pressures were generated as the vessels warmed to room temperature. A diagram of this section appears in Figure 5.

The containers PV-1, PV-2, and PV-3 were of Series 303 and 416 stainless steel and designed for pressures of 10,000, 50,000, and 50,000 psi respectively. Their combined volume was about 300 cc. A 10,000 psi rupture

**FIGURE 5
PRESSURE GENERATOR**

**FIGURE 6
GAS MIXING APPARATUS**

disk (RD) was attached and the equipment mounted behind a panel of 1/4" steel plate. The Dewar flask (DF) was on a movable platform to enable raising or lowering the bath for cooling or warming the pressure vessels.

Since the volume of the containers was considerably less than that of the equilibrium system, very high pressures were needed in order to have useful quantities of methane. Pressures up to 9,000 psi were developed with the apparatus.

E. Sampling System

This section appears on the Assembly Diagram (Figure 4) at the left hand edge. It consisted of two detachable sample containers (S_1 and S_2), a 200 psi pressure gage (G_3), vacuum attachment, and 1/8" stainless steel sample withdrawal lines leading from the equilibrium section.

The liquid phase line originated at a sample tap drilled in the cell about 1" from the bottom. A large portion of the line outside the bath was wrapped with resistance wire to enable heating the fluid during sampling. This was done to assure complete vaporization of the liquid. The vapor line led from a point near the variable volume cell, from which most of the vapor sample was taken. Nichrome wire (.064" diameter) was inserted in the liquid sample line between the sampling valve and equilibrium cell to minimize "dead" space. A small amount of each phase was bled through the lines prior to sampling. Both lines could be evacuated

external to the sampling valves.

Stainless steel pressure bombs, 150 cc and 500 cc sizes, rated at 1800 psi, (purchased from Hoke, Inc.) were used to take some of the samples. Others were withdrawn in specially constructed bombs (600 psi design pressure) made from 2" bronze tubing with brass plugs in the ends.

F. Vacuum System

Vacuum requirements were met by a Duo-Seal vacuum pump with a pressure rating of 0.05 microns. Connections are shown on the Assembly Diagram (Figure 4). By use of appropriate valves, the charge system, equilibrium system, and sampling system could be evacuated independently.

III. Experimental Procedure

The following procedure was usually employed for making equilibrium measurements.

A. Bath Temperature Adjustment

The proper bath liquid was selected, depending upon the final temperature to be attained (see Experimental Equipment--Temperature Control System). Initial cooling was begun by circulating the primary bath liquid through the coils of the auxiliary equipment submerged in an alcohol-dry ice bath. This method provided rapid cooling down to -80°F, below which the primary system was used. Upon attainment of the desired temperature, the control valve (N) was adjusted to give the flow rate necessary to hold the

temperature constant. Vaporization rate was indicated by the rotameter (RT).

Four hours was usually sufficient time to reach the lowest temperatures investigated.

B. Mixture Charging

During the cooling-down period, the equilibrium system was evacuated several times with subsequent purging by one of the gases to be charged. The components were charged in order of increasing vapor pressures, preferably directly from the original gas cylinders. (See Experimental Apparatus--Charge Mechanism) The amounts being charged were roughly estimated by observation of the system pressure and the liquid level in the equilibrium cell. The desired pressure was approximately set by the addition of the final component, fine adjustments being made in the variable volume cell by injecting or withdrawing mercury.

C. Attainment of Equilibrium

During the latter stages of charging and as the desired temperature was approached, vapor circulation was begun. This was continued for thirty minutes after temperature and pressure became constant. The rate of recycle was then reduced to be sure the recirculated gas reached the liquid temperature prior to bubbling through it. Circulation was continued at this low rate for another thirty minutes.

The preceding time intervals were selected following

tests to determine the approximate time required for attainment of equilibrium. Measurements were made with a methane-propane mixture by approaching the desired pressure from two directions. The procedure given here was followed during the test. The corresponding phase samples obtained were identical within the analytical accuracy.

D. Sampling Procedure

Prior to sampling, a small portion of each phase was bled to eliminate sample contamination due to "dead" volume. The sample containers were then evacuated and the liquid line heated.

The liquid phase was sampled first, slowly, to ensure complete vaporization in the line. Any pressure decline in the system was compensated by addition of mercury to the variable volume cell.

The vapor phase was then isolated from the liquid by closing valves marked N_3 and N_4 . This enabled sampling of the vapor without tedious pressure compensation. The sampling system was re-evacuated before withdrawing the vapor sample. Sample sizes varied with the equilibrium conditions and depended to a great extent upon the analytical method to be used. Infrared analysis required about one liter of gas at atmospheric conditions. On the other hand, the chromatographic method needed only about 50 cc.

E. Preparation for Subsequent Measurements

Following the completion of one equilibrium run (ternary), the proper components were added to alter the composition for the next measurement. In this manner, time lost between measurements was held at a minimum.

When a higher temperature was desired, the auxiliary cooling equipment was used in reverse, i.e. a warm liquid was placed in the auxiliary bath containing the cooling coils.

IV. Materials

Gases:

Methane

Phillips Petroleum Company; Research Grade..99.5%

Tennessee Gas Transmission Company; line
gas from selected dehydration station . . . 99.6%

Ethane

Phillips Petroleum Company; Research Grade..99.9 %

Propane

Phillips Petroleum Company; Pure Grade . . .99.0 %

Valves, Fittings, and Tubing:

Stainless steel items were purchased from the Ruska Instrument Corporation, Houston, Texas, or machined in the departmental shop.

ANALYTICAL METHODS

The accuracy of the K-values depends directly upon the accuracy of the equilibrium phase analyses. Consequently, considerable work was devoted to this part of the problem.

Two methods of analysis were used--infrared spectrophotometry and gas-liquid partition chromatography. Infrared analyses were performed when no component concentration was lower than 10%. Chromatography was used mostly for this region, but both methods were often employed as a check.

I. Infrared Analyses

A Beckman IR-2 Infrared Spectrophotometer was available for this purpose. It was modified to obtain better accuracy with gaseous samples by inserting an elongated 30 cm. gas cell. This provided greater absorption due to increased path length for the infrared rays.

Detailed theory will be omitted, but the basic principle of operation is the Beer-Lambert Law. It states that the absorption of monochromatic radiation passing through a homogeneous absorbing medium is proportional to the length of path and to the concentration of the medium.

The three components--methane, ethane, and propane--are strong absorbers of infrared light at various wavelengths. Hence, a wave length was chosen for each gas where its absorption was high and where the simultaneous absorption by the other two was low. In this work the following wave

lengths were chosen:

Methane: 7.78 microns

Ethane : 9.43 microns

Propane: 12.34 microns

As previously described, the amount of infrared absorption at the specified wavelengths is a measure of the concentrations of the components in the mixture. Because of interference among the constituents, however, calibration curves were needed relating absorption to concentration for each component. Interfering component concentrations were used as parameters.

Volumetric gas mixtures were synthesized for this purpose to an accuracy of about one part per thousand. A diagram of the apparatus used appears in Figure 6.

Three glass bulbs connected by sections of capillary tubing were surrounded by a thermostatic water bath. They were calibrated by Harvey (30) by weighing volumes of mercury corresponding to the volumes contained between appropriate markings on the tubing. The volumes thus determined are given below:

B_1 : 94.06 cc

B_2 : 188.3 cc

B_3 : 191.0 cc

By using these bulbs, samples of pure gases at known pressure, volume, and temperature could be displaced by mercury into large 4-liter glass mixing flasks (F). Accurate compressi-

bility factors obtained from McKetta (46) were used to calculate mols of gases added and, subsequently, mol percentages.

To facilitate the addition of large quantities of a component, the mixing flasks were also calibrated. The major component of a desired mixture could then be added directly to the flask at known conditions, leaving the lesser amounts of the remaining gases to be added by means of the bulbs. The flasks, identified by number, were also calibrated by Harvey (30) by weighing the flasks empty and full of water. The volumes measured were:

Flask #1	4308 cc.
Flask #2	4324 cc.
Flask #3	4290 cc.
Flask #4	4295 cc.
Flask #6	4281 cc.

Recalibration (by the author) of flask #4 following repair of broken stopcock yielded 4294 cc.

Mixing of the gases in the flasks was usually aided by induced convection currents. These were generated by placing an ice pack near the top of the flask and a heat source on the opposite side at the bottom. In addition, the gases were usually added in order of increasing molecular weight, a heavy gas entering the flask above a light one. Several hours were allowed for mixing in most cases.

To facilitate even better mixing, however, a known volume of mercury was added to each flask to provide mechanical mixing by shaking. The new volumes of the flasks, with

mercury, appear below:

Flask #1	4293 cc.
Flask #2	4311 cc.
Flask #3	4277 cc.
Flask #4	4282 cc.
Flask #6	4267 cc.

Approximately 40 mixtures were synthesized for the calibration. Example curves for ethane and propane appear as Figures 7 and 8. Optical density ($\log \frac{100}{\% \text{ transmission}}$) is plotted against "partial pressure" of the component-- defined here as mol fraction times total pressure. Methane did not interfere with either absorption; hence the parameters are shown as percent propane on the ethane plot and percent ethane on the propane calibration chart. Serious flattening of the pure methane curve (Figure 9) prevented accurate determination of this component by direct measurement. For actual use, the ethane and propane curves were plotted on a greatly expanded scale. A tabulation of smoothed values taken from the curves appears in Appendix A (Table A-I and A-II).

To analyze a mixture, optical density measurements were made on the gas at the ethane and propane wavelengths and corresponding total pressures. A rough estimation was made of the propane concentration from the propane calibration chart to be used in obtaining an ethane mol fraction. This, in turn, made possible a closer propane determination which was used to improve the ethane reading. The procedure was

continued until the values obtained ceased to change. Methane concentration was calculated by difference.

Accuracies of about 0.1 % (absolute) could be obtained by this method. At low concentrations, however, this accuracy was not satisfactory.

II. Chromatographic Analyses

Gas-liquid partition chromatography (GLPC) was investigated as an alternate analytical method due to inaccuracies in the infrared technique.

In this method a small sample of a gas mixture passes through a column packed with some granular material impregnated with a high-boiling liquid. The sample is "washed" through the column by an inert carrier gas, the components being separated by subsequent absorption and stripping operations in the supported liquid. Once separated, the relative amounts of the constituents in the original mixture can be determined.

At the time of this investigation into gas chromatography (Spring, 1955), the method was relatively unknown. Few papers had been published (13)(32)(33)(51)(52)(59), none developing high analytical accuracy. Therefore considerable development work was necessary. In addition to the publications, some basic ideas were obtained from the Houston Research Laboratory of Shell Chemical Corporation.

Because serious trailing often resulted with solid

adsorbents, gas-liquid partition chromatography was selected. Several liquids (dioctylphthalate, motor oil, and kerosene) were investigated for use as the fixed phase before satisfactory separation was obtained. Also, various gases were tried as the mobile phase--nitrogen, hydrogen, carbon dioxide, and helium. Kerosene and helium were selected for use in this separation involving methane, ethane, and propane.

A. Equipment

Figure 10 shows a diagram of the apparatus constructed.

The chromatographic column (C) consists of a twelve foot coil of 3/8" copper tubing submerged in an ice bath. The coil was packed with crushed firebrick (Johns Manville C-3), 60-80 mesh, impregnated with 40 grams of kerosene per 100 grams of solid. The packing was prepared by first dissolving the appropriate amount of kerosene in a large amount of pentane and slurring the solid with this liquid. The pentane was evaporated and the solid dried for about 12 hours at 85°C, accompanied by occasional stirring. The bulk density of the packing was about 0.5 grams/cc, with a 35 psi. pressure drop at a helium flow rate of 300 cc/min.

Helium was selected as a carrier gas because of the great difference between its thermal conductivity and that of the hydrocarbons. It was preferable to hydrogen for safety reasons.

A thermal conductivity cell (TCC) was used to

FIGURE 10
DIAGRAM OF CHROMATOGRAPHIC APPARATUS

FIGURE 11
TYPICAL ELUTION CURVES

detect the concentration of the hydrocarbons in the exit stream from the column. A Gow-Mac cell, Model 30-S (Gow-Mac Instrument Company, Madison, New Jersey) was available for use in this capacity. The output signal passed through a D.C. amplifier to an electronic recording potentiometer, yielding a plot of EMF vs. time. The amplifier (Leeds & Northrup Model **9835 B**) had a rated linearity of 1%. The basic electric circuit recommended by the manufacturer was used for the conductivity cell. The necessary direct current was supplied by a standard six volt lead storage battery.

Flow rate was controlled by valves N_1 and N_2 for the sample stream and reference stream respectively. Constant upstream pressure was maintained by the diaphragm regulator (RG). Flow rate was indicated by a glass rotameter (Fischer-Porter Tube #OB-150) with a range of 3-170 cc of standard air per minute.

The sample container (S) consisted of a 10" length of 1/4" copper tubing with wire solder inserted to adjust for proper size. The sample volume used was about 5 cc.

Column temperature was controlled by means of the ice bath (I). Selection of this temperature was due to separation requirements and to reduce kerosene losses.

B. Procedure

1. Stabilization

Preceding sample introduction a stabilizing

period of about two hours was allowed for the conductivity cell and flow rate. It was very important that the cell current, zero output base line, flow rate, and cell temperature remain constant during analyses. Variations in any of these could cause serious errors in analysis.

During this warm-up time the carrier gas was flowing through the sample by-pass, the column, conductivity cell, and rotameter to vent. At the same time a reference stream was tapped from the helium as it left the cylinder and passed through the reference side of the thermal conductivity cell. Its flow rate was about 125 cc/min. (atmospheric helium). When the apparatus was fully stabilized, the recorder showed a straight zero line since helium was flowing through both sides of the conductivity cell. The zero was adjusted to the proper chart reading if necessary.

2. Introduction of sample

In order to charge a gas for analysis, the sample system was evacuated and purged several times with the unknown mixture. A volume was then trapped between the two center valves (V_1 and V_2). After bleeding the sample pressure to one atmosphere, the by-pass valve was closed, and the carrier gas swept the sample mixture onto the column.

3. Elution and detection

The various components were then "washed" through the column at different rates, depending on their

solubilities in the liquid layer. They emerged from the column separately as dilute bands of hydrocarbons in the carrier stream. The concentrations in the stream were detected by the thermal conductivity cell and indicated by the EMF vs. time record from the recorder. The flow rates (both carrier and reference streams) were observed by means of the rotameter (RT). The valve manifold was to enable use of just one rotameter, since neither stream required constant checking.

4. Interpretation of chromatogram

Figure 11 shows a set of elution curves from a typical sample, this particular one being 50-40-10 in mol percentages of methane, ethane, and propane respectively. The degree of resolution between components depended upon the relative solubilities of the components, the length of the column, and slightly upon flow rate.

There is a direct relation between the areas under the peaks and the amount of the components in the sample. Because the concentration of the eluted gases in the carrier stream is so low (about 0.5%) the thermal conductivity vs. concentration curves are assumed straight for this region. The EMF from the conductivity cell is in direct proportion to the thermal conductivity of the mixture and the following equation can be written:

$$E = cy \qquad 10$$

where E = EMF from thermal conductivity cell (expressed in inches of needle deflection)

c = slope of EMF vs concentration curves at low concentrations

y = mol fraction of solute in the helium stream at any instant

Let Q_T = total gas flow rate through conductivity cell (cc/min)

Q_H = instantaneous point flow rate of hydrocarbon through conductivity cell (cc/min)

Then $Q_H = y Q_T$

$$y = \frac{Q_H}{Q_T} \quad 11$$

Substituting 11 into 10

$$E = \frac{c Q_H}{Q_T} \quad 12$$

Now, the area under one of the peaks is:

$$A = \int_{t_1}^{t_2} E dt \quad 13$$

where t_1, t_2 = break-through and trail-off times, respectively.

"Break-through time" is used here as the time of initial detection of the component. Similarly, "trail-off time" refers to the time of final detection of a component.

Substituting 12 into 13

$$A = \int_{t_1}^{t_2} \frac{c Q_H}{Q_T} dt = \frac{c}{Q_T} \int_{t_1}^{t_2} Q_H dt \quad 14$$

But $\int_{t_1}^{t_2} Q_H dt$ = mols (M) of the hydrocarbon in the sample charged.

$$\text{Therefore } A = \frac{c}{Q_T} M \quad 15$$

It is unnecessary to measure C , however, to determine the concentration of the component in the mixture. Instead, a

reference sample of the pure hydrocarbon, the same size as the unknown sample, is passed through the column. The area under the resulting peak can likewise be represented by

$$A_R = \frac{C_R}{(Q_T)_R} M_R \quad 16$$

Taking the ratio of equations 15 and 16:

$$\frac{A}{A_R} = \frac{C}{C_R} \frac{(Q_T)_R}{Q_T} \frac{M}{M_R}$$

Or

$$\frac{M}{M_R} = \frac{A}{A_R} \frac{Q_T}{(Q_T)_R} \frac{C_R}{C}$$

But, since concentrations are quite small, C and C_R are assumed equal and can be canceled.

Therefore (dropping T subscripts)

$$\frac{M}{M_R} = \frac{A}{A_R} \frac{Q}{Q_R} \quad 17$$

Now, if M_R were equal to the number of mols in the unknown mixture, this ratio $\frac{M}{M_R}$, would be the mol fraction of the component in the sample. Actually, however, two corrections are needed to obtain mol fractions--compressibility factor and atmospheric pressure fluctuation .

To convert M_R to the actual number of mols (M_S) in the sample, it was multiplied by the ratio of the compressibility factors $\frac{Z_S}{Z_R}$, where the subscripts R and S refer to the reference sample and unknown sample respectively.

In algebraic form,

$$M_R = M_S \frac{Z_S}{Z_R} \quad 18$$

Substituting 18 into 17:

$$\frac{M}{M_S} = \frac{A}{A_R} \frac{Q}{Q_R} \frac{Z_S}{Z_R} \quad 19$$

Actually, the two compressibilities were not expected to differ greatly, therefore an approximate method was used to estimate Z_S . A rough analysis of the mixture was calculated by taking the area ratio $\frac{A}{A_R}$ as mol fraction (m) for each component, with proper correction to have $\sum m = 1.0$. Then a molal average compressibility factor was calculated for the sample,

$$\text{i.e.} \quad Z_S = \sum_{i=1}^n m_i Z_i \quad 20$$

Compressibility factors were obtained from McKetta (46).

Because the samples were vented to the atmosphere prior to charging (in order to have an accurately known total pressure), changes in barometric pressure would affect the amounts charged. The mols of each component in the sample (M) was corrected to the same pressure as the reference mols (M_R) by multiplying M by $\frac{P_R}{P_S}$ to get M_C .

$$\text{Therefore,} \quad M = M_C \frac{P_S}{P_R} \quad 21$$

where P_R = barometric pressure during reference area measurement

P_S = barometric pressure during unknown sample measurement

M_C = mols of pure component in mixture, corrected for barometric pressure fluctuations

Substituting 21 into 19:

$$\frac{M_C}{M_S} = \frac{A}{A_R} \frac{Q_S}{Q_R} \frac{Z_S}{Z_R} \frac{P_R}{P_S} = m \quad 22$$

where m = mol fraction of a component in the sample mixture charged.

Equation 22 was used to calculate the composition of gas samples from measurements of unknown peak area, reference peak area, and the three correction factors (flow rate, compressibility factor, and barometric pressure). These correction factors were usually small, with a maximum of about 1% for the latter two and 10% for the first. The flow rate correction was determined by an indirect method because the rotameter was too insensitive to changes in flow. Since the break-through time for a component is inversely proportional to flow rate, the ratio $\left(\frac{t_R}{t_S}\right)$ was substituted for $\frac{Q_S}{Q_R}$, where t_R, t_S = break-through times for component in reference measurement and unknown sample, respectively.

The reference areas were checked periodically, but no significant variation was noted. The corresponding areas and break-through times at 30.000 "Hg barometric pressure were

<u>Component</u>	<u>Break-through Time</u> (min)	<u>Reference Peak</u> <u>Area (cm²)</u>
CH ₄	9.40	42.9
C ₂ H ₆	12.70	65.7
C ₃ H ₈	24.07	85.1

Peak areas were measured by planimeter to a relative accuracy of 1%. Other indications of area, (such as peak height, and peak height times width of elution curve at one half peak height) were investigated, but the accuracy was not satisfactory.

The method was evaluated by analyzing known mixtures

and having spot checks made by mass spectrometer. Four synthetic mixtures were prepared in the manner described under Infrared Analyses and analyzed by GLPC. In addition, five samples taken during equilibrium measurements were analyzed chromatographically and then sent to the Houston Refinery Research Laboratory of Shell Oil Company for mass spectrometer analysis. The results appear in Table I.

In many cases, both infrared and chromatographic analyses were made on the equilibrium samples. Agreement was usually quite good, but greater weight was given to the GLPC analyses. The infrared method was particularly valuable for approximate analyses during attempts to reach a desired composition. This type of analysis could be performed in a very few minutes, whereas a complete chromatographic analysis required about an hour.

EXPERIMENTAL RESULTS

Equilibrium measurements were made on more than 150 mixtures involving methane, ethane, and propane over a wide range of temperatures and pressures. Conditions investigated are given below:

<u>Temperature (°F)</u>	<u>Pressure (psia)</u>
50	100,200,400,600,800,1000,1100,1200
0	100,200,400,600,800,1000,1100,1200,1300
- 50	100,200,400,600,800,1000
-100	100,200,400,600
-150	100,200
-200	100

A complete tabulation of all binary and ternary data appears in Tables II-V. For comparison purposes, related data for methane-propane mixtures from Sage and Lacey (62) and Akers, Burns, and Fairchild (1), as well as methane-ethane data from Bloomer and others (9), appear in Appendix C (Tables C-I, C-II, C-III).

In addition, the pressure-temperature projection is included (Figure A-1) for methane, ethane, propane, and butane.

I. Presentation of Binary Data

The results of binary equilibrium measurements from this work have been plotted in the customary manner. Related data from other sources have been included where applicable.

Because of the limited interest and data concerning the ethane-propane binary, only the systems methane-ethane and methane-propane were represented graphically.

Figures 12 and 13 show pressure-composition graphs for the two systems with parameters of temperature.

K-value vs. pressure and K-value vs. temperature diagrams for the methane-ethane system appear in Figures 14 and 15. Similar plots for methane-propane mixtures are shown by Figures 16 and 17.

The K-P plots are particularly useful for indicating the degree of ideality of the system. Raoult's law states that the partial pressure of a solvent above a solution is equal to the concentration of the solvent in the liquid times its vapor pressure; that is,

$$p_s = x_s P^0 \quad 23$$

where p_s = partial pressure of solvent in vapor

x_s = mol fraction of solvent in liquid

P^0 = vapor pressure of solvent

Dividing each side by total pressure (P) and assuming

Dalton's law:

$$\frac{p_s}{P} = \frac{x_s P^0}{P} = y_s \quad 24$$

where y_s = mol fraction of solvent in vapor

Therefore,

$$\frac{y_s}{x_s} = \frac{P^0}{P} = K_s$$

and $\log K_s = \log P^0 - \log P$ 25

Consequently, if the laws of Raoult and Dalton hold, a plot of K vs. P on log-log coordinates should yield a straight line with a slope of -1 . At low pressures, the concentration of the heavier component in the binary mixtures is high and can be considered the solvent. This condition favors the validity of Dalton's law. The lower section of Figures 14 and 16, applying to ethane and propane, show this trend of ideality. In most cases, the curves approach the vapor pressure ($K=1$) at an angle of 45° .

Whereas Raoult's law applies to the solvent in a dilute solution, Henry's law considers the solute. It states that the amount of solute dissolved in a given quantity of solvent is proportional to the partial pressure of the solute above the solution. This is represented by

$$x_g = k_H p_g \quad 26$$

where x_g = mol fraction of solute in liquid

k_H = a constant of proportionality, called Henry's constant

p_g = partial pressure of solute in vapor above a solution

Again dividing both sides of the equation by P and assuming Dalton's law,

$$\frac{x_g}{P} = k_H \frac{p_g}{P} = k_H y_g \quad 27$$

where y_g = mol fraction of solute in the vapor

Therefore
$$\frac{y_g}{x_g} = \frac{k_H}{P} = K_g$$

or
$$\log K_g = \log k_H - \log P$$
 28

Thus, a plot of $\log K_g$ vs. $\log P$ would yield a straight line of slope -1 if Henry's and Dalton's laws hold. By the same reasoning as above, the lighter component is considered the solute. The upper sections of Figures 14 and 16 show the regions of ideality for the solute component.

Apparently Henry's law holds quite well over a large region for the systems shown, breaking down only near the critical. Deviations from Raoult's law, however, appear to be more serious. Variations from the 45° line begin at lower pressures for the heavier components in the binaries shown.

In both cases, the ideal laws discussed were used as a basis for constructing the low pressure region. The methane curves have been extended as 45° lines, and the -200° curves for ethane and propane were similarly drawn using the vapor pressures as anchor points.

It should be noted that the actual experimental data have been plotted on the K-P diagrams, whereas smoothed values, taken from these curves, appear on the K-T graphs (Figures 15 and 17). The dotted extensions of the curves for pressures below the critical are estimations and the accuracy should be interpreted accordingly. They terminate at vapor pressure curves similarly estimated.

II. Presentation of Ternary Equilibrium Data

Experimental results for the ternary system have been tabulated in Table V with the binaries included.

Because of the additional degree of freedom encountered, the system is no longer fixed by setting temperature and pressure. The necessity of including another phase rule variable makes graphical representation of a ternary system considerably more difficult than the binary case. Figure 18 shows a pressure-composition diagram for the ternary mixture at 0°F. The faces of the prism are recognized as being the binary P-X plots previously discussed. They bound the three dimensional figure representing the ternary system. Several constant pressure sections are shown, intersecting the equilibrium surfaces along the solid lines, with example tie lines being dotted. Such diagrams can be constructed for various temperatures, representing the entire vapor-liquid region. While this type of representation is important qualitatively, its quantitative value is limited. A more convenient method (and somewhat more accurate) is to project all the phase traces onto the base of the prism. This enables a complete isotherm to be represented by a single triangular diagram. Figures 19 - 24 show this type of diagram for the ternary system at the six temperatures investigated. These diagrams give the traces of the two phase regions studied to a fair degree of accuracy.

In order to represent the experimentally determined

FIGURE 18
PRESSURE-COMPOSITION DIAGRAM
FOR TERNARY SYSTEM AT 0° F

FIGURE 19
VAPOR-LIQUID
COMPOSITION DIAGRAM
50° F

FIGURE 20
VAPOR-LIQUID
COMPOSITION DIAGRAM
0° F

FIGURE 21
VAPOR—LIQUID
COMPOSITION DIAGRAM
— 50° F

FIGURE 22
VAPOR—LIQUID
COMPOSITION DIAGRAM
— 100° F

FIGURE 23
VAPOR-LIQUID
COMPOSITION DIAGRAM
- 150 ° F

FIGURE 24
VAPOR-LIQUID
COMPOSITION DIAGRAM
- 200 ° F

K-values, some composition variable must be included with temperature and pressure. It is customary to use the composition of a component in one of the equilibrium phases or some function of phase composition. In this work, the ethane concentration in the liquid was selected because its degree of variation was generally the greatest. The experimental data are plotted as $\log K$ vs. ethane concentration in the liquid with parameters of constant pressure for each temperature. The graphs appear as Figure 25-30.

Because of extremely low concentrations of methane in the liquid phase at 50°F, 100 and 200 psi, the analytical accuracy is doubtful. A method of predicting the data in this region was therefore selected. The binary K-values were obtained by assuming Henry's law and extending the curves as 45° lines into the low pressure region, as was previously discussed. Although not strictly applicable to ternaries, the method was used in a modified form. A hypothetical binary was assumed by taking values from the K-x plots at constant concentrations of ethane in the liquid. The K-P curves thus obtained were extended as before into the low pressure region to get K-values.

Analytical difficulties were also encountered at very low temperatures where the concentration of the heavier components in the vapor is quite low. Unfortunately, Raoult's law cannot be applied to smooth the K-values of ethane and propane at -200°F because their concentration in the liquid

is not high enough to consider them as solvents. Probably the best basis to use is the -200°F curve for propane K-value in the K-P diagram of the methane-propane binary (Figure 16). An experimental K-value for propane of 0.0035 appears quite plausible with relation to the higher isotherms. The measured propane concentration in the vapor phase was about 0.07 mol percent. As ethane is added to develop the ternary region, the concentration of propane in the liquid phase decreases (see Table V). It is not logical that the vapor composition would become richer in propane, rather it would be expected to become leaner, by comparison with previous data. The conservative position, then, is to assume the propane concentration in the vapor to remain constant--in the absence of reliable analyses. Such an assumption yields the curve appearing in Figure 30. This should represent the maximum K-value curve for propane at -200°F and 100 psia.

III. General Comments

No retrograde condensation was observed in the external visual cell during the experimental operations. Close watch was kept, especially at the higher temperatures.

Critical opalescence occurred in the equilibrium cell during measurements near the critical points of the various mixtures. A rust-brown color was observed with the transmitted fluorescent light. Reflected light gave only a gray-white color. The phase in which the opalescence occurred varied with the conditions encountered. The color effect was

FIGURE 25
K VALUE — COMPOSITION DIAGRAM
FOR TERNARY SYSTEM
50 °F

FIGURE 26
K VALUE—COMPOSITION DIAGRAM
FOR TERNARY SYSTEM
0°F

FIGURE 27
K VALUE - COMPOSITION DIAGRAM
FOR TERNARY SYSTEM

-50° F

FIGURE 28
K VALUE—COMPOSITION DIAGRAM
FOR TERNARY SYSTEM

-100° F

● METHANE
○ ETHANE
◊ PROPANE

FIGURE 29
K VALUE—COMPOSITION DIAGRAM
FOR TERNARY SYSTEM
—150°F

estimated as occurring in a region within 10 psi of the critical. It was more easily obtained by approaching the critical from the high pressure side.

This phenomenon of critical opalescence has been previously investigated, both from an experimental and theoretical standpoint (12)(21)(48)(50)(70)(73)(75)(79). It is apparently due to microscopic density fluctuations in the form of molecular clusters.

CALCULATION AND CORRELATION OF PHASE EQUILIBRIA DATA

Several methods for correlating the composition effect upon K-values have been proposed.

The use of apparent convergence pressure (at which the K-values for all components become unity) has received considerable attention (23)(26)(27)(77)(78). In this method, convergence pressure is used as the composition variable for relating K-value to temperature, pressure, and composition. Hadden (27) presented an excellent discussion of methods for predicting convergence pressure, including a quasi-convergence pressure for temperatures below the critical of the components.

Smith and Watson (69) have presented charts for evaluating the activity coefficients in the equilibrium phases (see equation 8) assuming no chemical dissimilarity. Vapor phase activity coefficients are given as a function of pseudoreduced temperature and pressure, with $\frac{T_{c,i}}{T_c}$ as the composition variable. An empirical "volatility index" (related to normal boiling point) was used to correlate the liquid phase coefficients.

Benedict, Webb, and Rubin (4)(5)(6) have developed an empirical equation of state for predicting the thermodynamic properties of light hydrocarbons. It involves the use of eight constants evaluated for pure components from volumetric data. A set of rules for combining the constants have been

proposed to enable application to mixtures.

Because the complexity of the equation hindered its use in predicting K-values, Benedict, Webb, Rubin, and Friend (7)(8) reduced it to a series of graphs known as the "Kellogg Charts" (36). This was accomplished by introducing the molal average boiling point for each phase as the composition-variable. Eight graphs were required to represent K-values for each compound. Twelve hydrocarbons were presented at conditions between 14.7 and 1000 psia and above -100°F .

Interpolation between the charts for a given component, however, often caused serious errors. De Priester (20) sought to remedy this difficulty by consolidating the charts to show the effect of all variables continuously. He was successful in reducing the number required to two graphs for each hydrocarbon while retaining practically full accuracy.

The accuracy indicated for the Benedict-Webb-Rubin (BWR) equation of state, as well as the De Priester modification of the Kellogg Charts, was very encouraging. The low-temperature region, however, lacked investigation due to absence of sufficient experimental data. With the results of the present study on the methane-ethane-propane system, such an evaluation could be carried out.

First, the equation of state was tested by calculating K-values at conditions corresponding to those experimental results given in Table V. Then the smoothed experimental data were presented in a form analogous to the De Priester

charts to enable better interpolation than provided by Figures 25 - 30. Correlating properties of these new charts were investigated.

Finally, a corresponding states correlation was applied to mixtures of light hydrocarbons over a wide range of conditions.

I. Calculations Using the Benedict-Webb-Rubin Equation of State

Investigations into the use of the equation to predict K-values at low temperatures are quite limited in number and scope. Stotler and Benedict (71) applied it to the nitrogen-methane system, and Schiller and Canjar (66) studied its accuracy for nitrogen-carbon monoxide mixtures. Methane was the only hydrocarbon involved, and only six equilibrium states were calculated for comparison with experimental data.

To better evaluate the low-temperature validity of this equation, K-values corresponding to the experimental points presented in Table V were calculated.

The equation is given as:

$$P = RT\rho + (B_0RT - A_0 - \frac{C_0}{T^2})\rho^2 + (bRT - a)\rho^3 + \alpha\rho^6 + \frac{c\rho^3}{T^2} (1 + \gamma\rho^2) e^{-\gamma\rho^2} \quad 29$$

where B_0 , A_0 , C_0 , b , a , c , α , and γ are the eight empirical constants. The following mixture rules (as proposed by the authors) were used to represent the effect of composition on the parameters:

$$\begin{aligned} B_0 &= \sum_i m_i B_{0,i} \\ A_0 &= \left[\sum_i m_i (A_{0,i})^{\frac{1}{2}} \right]^2 \\ C_0 &= \left[\sum_i m_i (C_{0,i})^{\frac{1}{2}} \right]^2 \end{aligned}$$

$$\begin{aligned}
 b &= \left[\sum_i m_i (b_i)^{1/3} \right]^3 \\
 a &= \left[\sum_i m_i (a_i)^{1/3} \right]^3 \\
 c &= \left[\sum_i m_i (c_i)^{1/3} \right]^3 \\
 \alpha &= \left[\sum_i m_i (\alpha_i)^{1/3} \right]^3 \\
 \gamma &= \left[\sum_i m_i (\delta_i)^{1/2} \right]^2
 \end{aligned}$$

The ratio of fugacity to composition for the i^{th} component in either phase (liquid here) can be obtained from the following relation:

$$RT \ln \frac{f_i}{x_i} = RT \ln p_{RT} + \int_0^p \left[\left(\frac{\partial PV}{\partial m_i} \right)_{m, V, T} - RT \right] d \ln p \quad 31$$

Manipulating the three preceding relations gives

$$\begin{aligned}
 RT \ln \frac{f_i}{x_i} &= RT \ln p_{RT} \\
 &+ \left[(B_o + B_{oi}) RT - 2(A_o A_{oi})^{1/2} - \frac{2(c_o c_{oi})^{1/2}}{T^2} \right] p \\
 &+ \frac{3}{2} \left[RT (b^2 b_i)^{1/3} - (a^2 a_i)^{1/3} \right] p^2 \\
 &+ \frac{3}{5} \left[a (\alpha^2 \alpha_i)^{1/3} + \alpha (a^2 \alpha_i)^{1/3} \right] p^5 \\
 &+ \frac{3p^2 (c^2 c_i)^{1/3}}{T^2} \left[\frac{1 - e^{-\gamma p^2}}{\gamma p^2} - \frac{e^{-\gamma p^2}}{2} \right] \\
 &- \frac{2p^2 c (\gamma_i)^{1/2}}{T^2} \left[\frac{1 - e^{-\gamma p^2}}{\gamma p^2} - e^{-\gamma p^2} - \frac{\gamma p^2 e^{-\gamma p^2}}{2} \right]
 \end{aligned} \quad 32$$

K-values can be calculated from:

$$K_i = \frac{y_i}{x_i} = \frac{(f_i)_L / x_i}{(f_i)_G / y_i} \quad 33$$

since $(f_i)_L = (f_i)_G$ at equilibrium

To calculate K-values in this manner for comparison with the tabulated experimental points would be an enormous

task without an automatic computer. Through the generosity of the Humble Oil and Refining Company, a Bendix Model G-15 A Electronic Computer was made available. The problem was programmed and coded for the machine, and calculations corresponding to 177 experimental points were carried out.

The basic program for calculation is shown below:

The "boxes" are explained in the following manner;

ENTER DATA - Experiments with the equilibrium apparatus yielded the following information: pressure, temperature, liquid phase composition, and vapor phase composition. In order to obtain a comparison between predicted and experimental K-values some common basis of composition was needed. Rather than assume either experimental phase composition to be identical with predicted values, an overall composition was selected as the basis for comparison. The mid-point of the experimental tie-lines was chosen. This provided the best assurance that the overall composition would lie within the two-phase region. It was equivalent to assuming equal molal quantities of the two phases.

As a first approximation, the experimental phase compositions were used in the BWR calculation. Therefore the following data were loaded into the machine for each calcu-

lation: pressure, temperature, experimental liquid and vapor phase compositions, and overall compositions as discussed above.

BWR CALCULATION - Calculations in this "box" can be broken down as follows:

(a) Evaluation of the eight parameters for mixtures according to Equations 30

(b) Solving Equation 29 for density using Newton's method of approximations

(c) Solving Equations 32 for $\frac{f_i}{\rho_i}$ and $\frac{f_i}{y_i}$ and substituting into 33 to calculate K_i .

Following this, one of two paths was taken, (I or II on the program flow diagram). On the first time through the calculation, path I was followed to the flash calculation. This yielded new phase compositions which, when returned to BWR calculation, provided new K-values. The K-values were compared with those previously calculated, and if they did not agree, another flash calculation was performed and the cycle repeated. When the K-values ceased to change by more than 1%, path II was followed to the type-out "box".

FLASH CALCULATION - A standard flash calculation was used, adapted to computer methods in a manner similar to Rachford's (58).

TYPE-OUT - This involved the selection and location of the desired information, followed by the typing-out of the answers. The following quantities were obtained for each calculation:

- (a) f_i/y_i from each "loop" through the BWR and flash calculation, beginning with that corresponding to the experimental vapor phase composition (first assumption).
- (b) Equilibrium phase compositions predicted in the final loop of the calculation.
- (c) Predicted phase densities from the same loop.
- (d) Final values for f_i/x_i and f_i/y_i
- (e) Final predicted K-values

Calculations were performed using the constants evaluated for the components by Benedict and co-workers (5). Table VI gives the calculated phase compositions and K-values analogous to the tabulated data of Table V. The remainder of the results appear in Table I of Appendix B.

In Table VII the predicted K-values are compared with smoothed experimental data taken from Figures 25 - 30. The deviations were calculated in the following manner:

$$\% \text{ Rel. Dev.} = \left(\frac{K_{\text{BWR}} - K_s}{K_s} \right) 100 \quad 34$$

where K_s = smoothed K-value

K_{BWR} = predicted K-value from BWR equation

In order to better illustrate the regions of error, a three dimensional plot was selected, relating temperature, pressure, and percent relative error. Averages of the algebraic deviations at each temperature and pressure were calculated for use in the graphs. The results are shown in Figures 31 - 33. The surfaces thus obtained are an approximate

measure of the deviations found between predicted and smoothed experimental K-values. Lines of constant temperature and constant pressure appear on the surfaces.

Methane K-values are predicted quite well over most of the region, but ethane and propane show serious deviations at high pressures and low temperatures. It is interesting to note that the temperature effect causes major errors starting near the boiling point of the component (ethane: -127.5°F , and propane: -43.7°F), increasing as the temperature decreases.

In an effort to correct for the deviations at low temperatures, Benedict and co-workers (5) proposed that C_0 be allowed to vary with temperature. Values have been tabulated for various temperatures down to -100°F . These corrected values were used in the preceding calculations, a linear extrapolation being employed for temperatures below those given in the literature.

Apparently a far more complex effect exists as indicated by the deviations in Figures 31 - 33. Stotler and Benedict (71) suggested a modification of one of the mixture rules for combining the constants. They presented an equation giving the effect of varying any parameter upon the difference between the calculated fugacities for components in the two phases. Since these fugacities should be equal at equilibrium, the authors proposed that the summation of the differences for all components be minimized. By using experimental data on the system nitrogen-methane, they adjusted the combination rule for A_0 according to the developed relation. The modified

rule was:

$$A_o = m_1^2 A_{o1} + 2.874 m_1 m_2 + m_2^2 A_{o2}$$

The method could be applied to other constants, and might resolve the inaccuracies of the equation. Such modification, however, would be strictly empirical, and the likelihood of obtaining a general correction did not seem good.

Errors at high pressures do not appear to be as serious as those encountered at low temperatures. They are far from negligible, however, as the critical pressure is approached.

II. Correlation of Experimental Data

The K value-composition graphs (Figures 25 - 30) are quite useful for smoothing the experimental results as already indicated. It is very difficult, however, to read K-values from the charts at temperatures different from those isotherms indicated. Cross-plots at constant pressure would help somewhat, but the increased number of graphs and the complicated interpolation involved would offset the advantages. For this reason, a graphical representation similar to the De Priester charts (20) has been developed.

A. Basis for the Correlation

Following the method of Benedict and co-workers (8), De Priester presented a liquid factor (A) and vapor factor (B) as functions of temperature, pressure, and molal average boiling points of the respective phases. K-value was obtained from the product of the two factors, i.e.

FIGURE 32
DEVIATION OF BWR PREDICTED K VALUES
FROM SMOOTHED EXPERIMENTAL DATA

ETHANE

$$K = A B \quad 35$$

The factors were defined as:

$$A = \frac{(f_i)_L}{P x_i} \quad 36$$

$$B = \frac{1}{\frac{(f_i)_G}{P y_i}} \quad 37$$

where $(f_i)_L$, $(f_i)_G$ = fugacities of the i^{th} component in liquid and vapor phases respectively.
(psia)

x_i , y_i = mol fractions of the i^{th} component in liquid and vapor phases, respectively

P = total pressure, (psia)

De Priester obtained both factors from the Kellogg Charts, which were based on calculations using the Benedict-Webb-Rubin equation of state.

Thus, before the experimental data could be represented by charts similar to De Priester's, some method for obtaining A and B factors was needed. Recalling that $\frac{(f_i)_L}{x_i}$ and $\frac{(f_i)_G}{y_i}$ were calculated for each experimental point from the equation of state, the following procedure was selected. The calculated ratio of vapor phase fugacity to composition was chosen as the basis because the accuracy of the equation was considered better at the lower densities. The B factors were then calculated according to Equation 37. Using the smoothed experimental K-values with these B's, corresponding A factors were calculated from Equation 35. It should be noted that the product of these A and B factors would yield the smoothed K-value exactly, the accuracy assumption being used only to

select the basis for the correlation.

The A and B factors thus obtained were plotted as functions of temperature, pressure, and molal average boiling points (MABP) of the phases. The MABP's were calculated from the tabulated experimental phase compositions (Table V) according to the equations:

$$(\text{MABP})_L = \sum_{i=1}^n x_i T_{Bi} \quad 38$$

$$(\text{MABP})_G = \sum_{i=1}^n y_i T_{Bi} \quad 39$$

where T_{Bi} = normal boiling point of the i^{th} component, $^{\circ}\text{K}$

n = number of components

B. Construction of the Charts

The procedure used for constructing the charts was very similar to that employed by De Priester (20). The same scale forms were used except for the methane "B Chart", on which the temperature and $(\text{MABP})_L$ scales were reversed. This was necessary because constant values of $(\text{MABP})_L$ could not be readily selected from the experimental data.

To construct the "A Charts", a 100 psia isobar with appropriate A values was used to anchor the isotherms at the top of the charts. Some of these could be used to establish the 200 psia isobar, which in turn helped to further locate the isotherms. This alternating procedure was continued until the best set of isotherms and isobars was obtained. Parallel pressure lines were obtained over most of the region.

The "B Charts" were constructed in a similar manner. The 100 psia line was drawn to cover the proper B factor range and then used to begin locating the constant temperature lines. A common crossing point of the $B = 1.0$ line was used for all pressures. As noted from the charts, straight lines exist for most of the range studied.

It should be emphasized that only those lines corresponding to the temperatures and pressures of Table VIII were located from the experimental data. The intermediate and low pressure lines were all interpolated from cross-plots of the experimentally determined lines.

C. Accuracy of the Charts

The completed charts for methane, ethane, and propane appear as Figures 34 - 39. The dotted lines on the "A Charts" are from De Priester's charts, shown for comparison. The temperature curves on the "B Charts" showed a branching effect at high pressures.

In order to check the accuracy of representation, values of each equilibrium state were read from the charts and compared with the corresponding smoothed value. The results are tabulated in Table VIII, percent deviation being previously defined.

In this case, where deviations greater than 20% are quite rare, an overall average deviation is of value. Simple arithmetic averages for the absolute relative deviations are given below with the number of points for each component.

<u>Component</u>	<u>No. of Points</u>	<u>Avg. of Abs. % Rel.Dev.</u>
CH_4	179	2.0%
C_2H_6	140	2.8%
C_3H_8	163	4.1%

The use of the charts is identical to that of De Priester's, as indicated by the dotted lines across the methane graphs. The procedure involves the following steps:

- (1) Assume compositions for the liquid and vapor phases and calculate MABP's for each.
- (2) Move horizontally across the A and B factor charts at the respective MABP's to the proper temperature.
- (3) Then travel vertically from these points to the line of desired pressure.
- (4) A horizontal movement across each chart to the ordinates gives the value of A and B for the component.
- (5) The product, AB, gives the first trial K-value for the component.
- (6) If this K-value differs greatly from that calculated from the assumed compositions, a flash calculation should be performed (using the new K-value) to obtain new phase compositions. With new MABP's calculated from these compositions, steps (2) through (5) are repeated. The above procedure is continued until the K-values are constant within the accuracy desired.

The above comparison indicates that the MABP charts represent the experimental results from this investigation

FIGURE 34

FIGURE 36

FIGURE 37

FIGURE 38

quite well. It is desirable, also, to compare data from other hydrocarbon systems with K-values calculated from the charts. Data in the appropriate region, however, are relatively scarce, and in many cases the accuracy of reported results is not sufficient. Comparisons were made, though, with the following systems:

<u>System</u>	<u>Source</u>
1. Methane-Ethylene	(25)
2. Ethane-Ethylene	(29)
3. Ethane-Propylene	(45)
4. Methane-Ethylene-Ethane	(25)
5. Various Mixtures of Methane, Ethane, Propane, Butanes, Pentanes, and Hexanes	(20)
6. Various Mixtures of Methane, Ethane, Propane, Butane, Pentane, and Iso-octane	(57)
7. A Condensate Fluid containing appreciable quantities of $C_{10}+$	(15)

The results of the comparison are shown in Table IX. Very good agreement is indicated for methane until the relatively heavy condensate fluids are reached. Deviations for ethane and propane become serious when constituents as heavy as octanes are encountered.

Whereas these comparisons are indicative, a fair evaluation of this MABP correlation must be delayed until additional data are available. For mixtures having components lighter than heptane, it appears that this correlation could be used as a supplement to the De Priester charts for the low

temperature range. It should be noted that the pressure range has been extended to include the critical region of the methane-ethane-propane system.

III. Corresponding States Correlation

The following correlation emerged from recent work with Dr. T. W. Leland at the Research Center of the Humble Oil and Refining Company. A method was developed for calculating the pseudocritical properties of mixtures to yield better accuracy than the conventional "molal average" procedure. The corresponding reduced values were used to obtain thermodynamic properties for mixtures from the generalized tables recently published by Lydersen, Greenkorn, and Hougen (43). These, in turn, were used to calculate ideal vaporization equilibrium constants analogous to the "k" of Equation 5. Then, by using experimental K-values, a correlation was developed relating a "non-ideality" factor to a function of the thermodynamic and reduced properties of the two phases.

A. The Principle of Corresponding States

As proposed by van der Waals, the principle of corresponding states implied that all substances obeyed the same equation of state in terms of the reduced variables. Mathematically,

$$f(P_R, V_R, T_R) = 0$$

40

where $P_R = \frac{P}{P_c}$, $T_R = \frac{T}{T_c}$, $V_R = \frac{V}{V_c}$

Subscript c refers to critical properties.

Recognizing the value of such a theory, Cope, Lewis and Weber (18) correlated the compressibility factors of several pure gases as a single function of reduced pressure and temperature; i.e.

$$Z = f(P_R, T_R) \quad 41$$

where $Z = \frac{PV}{RT}$ = compressibility factor

As additional compressibility charts were developed, serious inaccuracies of the method became apparent, especially in the critical region. For example, the critical ratio (Z_c) varied from 0.23 for water to 0.29 for methane.

Realizing this, Meissner and Seferian (47) proposed that Z_c be included as a correlating variable, i.e.

$$Z = f(P_R, T_R, Z_c) \quad 42$$

They presented a series of correction charts relating Z_c to the ratio of corrected to uncorrected Z for various values of T_R . A more recent effort in this direction is the publication by Lydersen, Greenkorn, and Hougen (43). They have compiled an excellent set of tables giving the generalized thermodynamic properties of pure fluids as functions of P_R , T_R , and Z_c .

Although the corresponding states theory was proposed for pure substances, it has proved very valuable for mixtures as well. Kay (35) discovered that the properties of a mixture of gases could be correlated by considering it as a hypothetical pure component. This required the characterization of the mixture by a set of pseudocritical constants

to obtain thermodynamic properties from generalized correlations. Kay found reasonable accuracy by calculating these pseudocritical properties as the molal average of the pure component values, i.e.

$$P_c' = \sum_i m_i P_{c_i}$$

$$T_c' = \sum_i m_i T_{c_i}$$

43

(primed values represent pseudo-properties)

Attempting to increase the accuracy, Joffe (34) developed several other empirical methods for calculating pseudocriticals. The preceding methods are satisfactory for gaseous mixtures at moderate pressures, but fail for liquids. Therefore they are not acceptable for the calculation of equilibrium data.

In recent years a theoretical approach to the problem has received increasing attention. Longuet-Higgins (42), Salsburg (64), Prigogine and co-workers (53)(54)(55) (56), and Scott⁽⁶⁷⁾ have developed the corresponding states treatment for mixtures of simple molecules. Such developments provide a basis for extending the principle to more complex systems. The treatment given in this work is a modification of the statistical derivation of pseudocriticals developed by Salsburg.

B. The Pseudocritical Properties

In the form of Equation 42, the law of corresponding states is, in reality, an equation of state. P_c , T_c

and Z_c represent three constants characteristic of the substance. Therefore, the problem of calculating pseudocriticals for a mixture is equivalent to combining the constants of an equation of state for pure components to represent a mixture. This can be done theoretically only for very simple substances under limited conditions. The method used here for combining the critical constants is valid for substances with the following characteristics:

(1) All molecules are spherical and distributed in a completely random manner.

(2) The intermolecular potential energy of the system can be expressed as the sum of the intermolecular potentials between pairs of molecules.

(3) The intermolecular potential is a function only of the distance (r) between molecular centers and two parameters characteristic of the substance described.

The derivation of the pseudocritical equations appears in Appendix E. The following equations are obtained:

$$T_c' = \frac{\sum_{i=1}^m \sum_{j=1}^m \kappa_i \kappa_j \alpha_{ij}}{\sum_{i=1}^m \sum_{j=1}^m \kappa_i \kappa_j \beta_{ij}} \quad 44$$

$$P_c' = \frac{\sum_{i=1}^m Z_{ci} T_{ci}'}{\sum_{i=1}^m \sum_{j=1}^m \kappa_i \kappa_j \beta_{ij}} \quad 45$$

$$Z_c' = \sum_{i=1}^m \kappa_i Z_{ci} \quad 46$$

(m = number of components)

where

$$\alpha_{ii} = \left(\frac{z_c T_c^2}{P_c} \right)_i = \alpha_i$$

$$\beta_{ii} = \left(\frac{z_c T_c}{P_c} \right)_i = \beta_i$$

$$\alpha_{ij} = (\alpha_{ii} \alpha_{jj})^{1/2}$$

$$\beta_{ij} = \left[\frac{1}{2} \beta_{ii}^{1/3} + \frac{1}{2} \beta_{jj}^{1/3} \right]^3$$

C. Calculation of Ideal Vaporization Equilibrium Constants

(1) Starting with the general expression for the free energy, G , of a mixture:

$$dG = \left(\frac{\partial G}{\partial n_1} \right)_{T, P, n_2, n_3, \dots} dn_1 + \left(\frac{\partial G}{\partial n_2} \right)_{T, P, n_1, n_3, \dots} dn_2 + \dots \quad 47$$

Chemical potential may be defined as:

$$\mu_i = \frac{\partial G}{\partial n_i} \quad , \quad \mu_m = \frac{\partial G}{\partial n}$$

where subscripts i and m refer to an individual component and the mixture respectively. Substituting into Equation 47,

$$\mu_m dn = \mu_1 dn_1 + \mu_2 dn_2 + \dots \quad 48$$

(2) Assume as a reference state $P \Rightarrow 0$ at the same temperature as in (1). Then

$$\mu_m^* dn = \mu_1^* dn_1 + \mu_2^* dn_2 + \dots \quad 49$$

where the * indicates the reference state.

(3) Subtracting 49 from 48,

$$(\mu_m - \mu_m^*) dn = (\mu_1 - \mu_1^*) dn_1 + (\mu_2 - \mu_2^*) dn_2 + \dots \quad 50$$

(4) By definition:

$$d\mu_m = RT d \ln f_m \quad , \quad d\mu_i = RT d \ln f_i$$

Integrating these two equations between the standard (*) and actual (a) states:

$$\int_{*}^a d\mu_m = \int_{f_m @ P=0}^{f_m @ P=P} RT d \ln f_m = RT \ln f_m - RT \ln P$$

$$\therefore (\mu_m - \mu_m^*) = RT \ln \frac{f_m}{P} \quad 51$$

$$\int_{*}^a d\mu_i = \int_{f_i @ P=0}^{f_i @ P=P} RT d \ln f_i = RT \ln f_i - RT \ln \chi_i P$$

$$\therefore (\mu_i - \mu_i^*) = RT \ln \frac{f_i}{\chi_i P} \quad 52$$

(5) Substituting 51 and 52 into 50:

$$(RT \ln \frac{f_m}{P}) dn = (RT \ln \frac{f_1}{\chi_1 P}) dn_1 + (RT \ln \frac{f_2}{\chi_2 P}) dn_2 + \dots \quad 53$$

(6) Integrating and cancelling RT:

$$n \ln \frac{f_m}{P} = n_1 \ln \frac{f_1}{\chi_1 P} + n_2 \ln \frac{f_2}{\chi_2 P} + \dots \quad 54$$

Therefore,

$$n \ln f_m = n_1 \ln \frac{f_1}{\chi_1} + n_2 \ln \frac{f_2}{\chi_2} + \dots \quad 55$$

(7) Rewriting Equation 55:

$$n \ln f_m = n_1 \ln f_1 + n_2 \ln f_2 + \dots$$

$$- n_1 \ln \chi_1 - n_2 \ln \chi_2 - \dots$$

Expressing in differential form:

$$\begin{aligned}
 n d \ln f_m + \ln f_m dn &= n_1 d \ln f_1 + n_2 d \ln f_2 + \dots \\
 &+ \ln f_1 dn_1 + \ln f_2 dn_2 + \dots \\
 &- n_1 d \ln \chi_1 - n_2 d \ln \chi_2 - \dots \\
 &- \ln \chi_1 dn_1 - \ln \chi_2 dn_2 - \dots
 \end{aligned} \quad 56$$

(8) But, by the Gibbs-Duhem relation:

$$n_1 d \ln f_1 + n_2 d \ln f_2 + \dots = 0 \quad 57$$

Also

$$\begin{aligned}
 -n_1 d \ln \chi_1 - n_2 d \ln \chi_2 - \dots &= -\frac{n_1}{\chi_1} d\chi_1 - \frac{n_2}{\chi_2} d\chi_2 - \dots \\
 &= -n d\chi_1 - n d\chi_2 - \dots \\
 &= -n (d\chi_1 + d\chi_2 + \dots)
 \end{aligned}$$

But, since

$$\begin{aligned}
 \chi_1 + \chi_2 + \dots &= 1 \\
 d\chi_1 + d\chi_2 + \dots &= 0
 \end{aligned}$$

Therefore,

$$-n_1 d \ln \chi_1 - n_2 d \ln \chi_2 - \dots = 0 \quad 58$$

(9) Applying Equations 57 and 58 to 56:

$$\begin{aligned}
 n d \ln f_m + \ln f_m dn &= \ln f_1 dn_1 + \ln f_2 dn_2 + \dots \\
 &- \ln \chi_1 dn_1 - \ln \chi_2 dn_2 - \dots
 \end{aligned}$$

Rearranging:

$$n d \ln f_m + \ln f_m dn = \ln \frac{f_1}{\chi_1} dn_1 + \ln \frac{f_2}{\chi_2} dn_2 + \dots \quad 59$$

(10) Taking 59 as the partial with respect to n_1 ,
holding $T, P, n_2, n_3, \dots$ constant:

$$n \left(\frac{\partial \ln f_m}{\partial n_1} \right)_{T, P, n_2, n_3, \dots} + \ln f_m \left(\frac{\partial n}{\partial n_1} \right)_{T, P, n_2, n_3, \dots} = \ln \frac{f_1}{x_1}$$

But with $n_2, n_3, \dots = \text{constant}$, $dn = dn_1$. Hence

$$\frac{\partial n}{\partial n_1} = 1$$

Therefore:

$$\ln \frac{f_1}{x_1} = n \left(\frac{\partial \ln f_m}{\partial n_1} \right)_{T, P, n_2, n_3} + \ln f_m \quad 60$$

The above equation may be applied to any phase, the x merely representing a mol fraction.

(11) Recalling that K-value may be expressed as

$$K_1 = \frac{(f_1)_L / x_1}{(f_1)_G / y_1}$$

$$\ln K_1 = \ln \frac{(f_1)_L}{x_1} - \ln \frac{(f_1)_G}{y_1} \quad 61$$

(12) Substituting 60 into 61:

$$\ln K_1 = \ln \frac{(f_m)_L}{(f_m)_G} + n_L \left[\frac{\partial \ln (f_m)_L}{\partial n_1} \right]_{T, P, n_2, n_3, \dots} - n_G \left[\frac{\partial \ln (f_m)_G}{\partial n_1} \right]_{T, P, n_2, n_3, \dots} \quad 62$$

The subscripts, m , will be omitted from future equations.

Before the equation can be used, however the partials

in the last two terms must be evaluated. This is accomplished by a corresponding states treatment using the proposed pseudocritical constants.

D. Application of the Corresponding States Principle

(1) According to this theory, f_L and f_G can be represented as a function of the reduced properties of the phases. Therefore,

$$\ln f_L = \phi(T_R', P_R')_L$$

$$\ln f_G = \psi(T_R', P_R')_G$$

(Primes indicate properties for mixtures)

Therefore,

$$d \ln f_L = \left(\frac{\partial \ln f_L}{\partial T_R'} \right)_{P_R'} d T_R' + \left(\frac{\partial \ln f_L}{\partial P_R'} \right)_{T_R'} d P_R'$$

$$d \ln f_G = \left(\frac{\partial \ln f_G}{\partial T_R'} \right)_{P_R'} d T_R' + \left(\frac{\partial \ln f_G}{\partial P_R'} \right)_{T_R'} d P_R'$$

63

But T_R' and P_R' are functions of T , P , n_1 , n_2 , $n_3, \dots$;

Therefore, evaluating Equations 63 as a partial with respect to n_1 :

$$\left(\frac{\partial \ln f_L}{\partial n_1} \right)_{T, P, n_2, n_3, \dots} = \left(\frac{\partial \ln f_L}{\partial T_R'} \right)_{P_R'} \left(\frac{\partial T_R'}{\partial n_1} \right)_{T, P, n_2, n_3, \dots} + \left(\frac{\partial \ln f_L}{\partial P_R'} \right)_{T_R'} \left(\frac{\partial P_R'}{\partial n_1} \right)_{T, P, n_2, n_3, \dots}$$

64

Similarly for

$$\left(\frac{\partial \ln f_G}{\partial n_1} \right)_{T, P, n_2, n_3, \dots}$$

Next, the partial terms of the right hand side of 64 will be evaluated.

(2) Evaluation of $\left(\frac{\partial \ln f_L}{\partial T_{R'}}\right)_{P_{R'}}$ and $\left(\frac{\partial \ln f_L}{\partial P_{R'}}\right)_{T_{R'}}$:

Starting with $T_{R'} = \frac{T}{T_c'}$,

then at constant composition, $d T_{R'} = \left(\frac{1}{T_c'}\right) dT$

Therefore,

$$\left(\frac{\partial \ln f_L}{\partial T_{R'}}\right)_{P_{R'}} = T_c' \left(\frac{\partial \ln f_L}{\partial T}\right)_{P, x_1, x_2, x_3, \dots} \quad 65$$

By the same argument,

$$\left(\frac{\partial \ln f_L}{\partial P_{R'}}\right)_{T_{R'}} = P_c' \left(\frac{\partial \ln f_L}{\partial P}\right)_{T, x_1, x_2, x_3, \dots} \quad 66$$

But,

$$\left(\frac{\partial \ln f_L}{\partial T}\right) = \left(\frac{H^* - H}{RT^2}\right)_L \quad 67$$

$$\frac{\partial \ln f_L}{\partial P} = \frac{v_L}{RT} \quad 68$$

where H^* , H = enthalpy of standard and normal states, respectively

v_L = molal volume of liquid phase

Substituting $T = T_C' T_R'$ into Equation 67:

$$\frac{\partial \ln f_L}{\partial T} = \frac{\Delta H}{R(T_C')^2 (T_R')^2} = \frac{\Delta H}{T_C'} \left[\frac{1}{R T_C' (T_R')^2} \right] \quad 69$$

Equation 68 can be rewritten as:

$$\frac{\partial \ln f_L}{\partial P} = \left(\frac{1}{P} \right) \left(\frac{P Z_L}{R T} \right) = \frac{Z_L}{P} \quad 70$$

where Z_L = compressibility factor of liquid

Therefore, substituting 69 and 70 into 65 and 66:

$$\left(\frac{\partial \ln f_L}{\partial T_R'} \right)_{P_R'} = \frac{\Delta H}{R T_C' (T_R')^2} \quad 71$$

$$\left(\frac{\partial \ln f_L}{\partial P_R'} \right)_{T_R'} = \frac{P_C' Z_L}{P} \quad 72$$

(3) Evaluation of $\left(\frac{\partial T_R'}{\partial m_1} \right)_{T, P, m_2, m_3, \dots}$ and $\left(\frac{\partial P_R'}{\partial m_1} \right)_{T, P, m_2, m_3, \dots}$ appearing in Equation 64:

Recalling that $T_R' = \frac{T}{T_C'}$, $P_R' = \frac{P}{P_C'}$

$$\left(\frac{\partial T_R'}{\partial m_1} \right)_{T, P, m_2, \dots} = \left(\frac{\partial T_R'}{\partial T_C'} \right) \left(\frac{\partial T_C'}{\partial m_1} \right) = - \frac{T}{(T_C')^2} \left(\frac{\partial T_C'}{\partial m_1} \right)_{T, P, m_2, \dots} \quad 73$$

$$\left(\frac{\partial P_R'}{\partial m_1} \right)_{T, P, m_2, \dots} = \left(\frac{\partial P_R'}{\partial P_C'} \right) \left(\frac{\partial P_C'}{\partial m_1} \right) = - \frac{P}{(P_C')^2} \left(\frac{\partial P_C'}{\partial m_1} \right)_{T, P, m_2, m_3, \dots} \quad 74$$

The partials in the right hand members of 73 and 74 must be evaluated by using the expressions for T_C' and P_C' given by Equations 44 and 45.

(a) Evaluation of $\left(\frac{\partial T_C'}{\partial m_1}\right)_{T, P, m_2, \dots}$

Equation 44 can be altered by:

$$T_C' = \frac{\sum \sum \alpha_i \alpha_j \alpha_{ij}}{\sum \sum \alpha_i \alpha_j \beta_{ij}} = \frac{\sum \sum m_i m_j \alpha_{ij} / n^2}{\sum \sum m_i m_j \beta_{ij} / n^2} = \frac{\sum \sum m_i m_j \alpha_{ij}}{\sum \sum m_i m_j \beta_{ij}}$$

Differentiating,

$$\left(\frac{\partial T_C'}{\partial m_1}\right)_{T, P, m_2, \dots} = \frac{(2 \sum m_j \alpha_{1j})(\sum \sum m_i m_j \beta_{ij}) - (2 \sum m_j \beta_{1j})(\sum \sum m_i m_j \alpha_{ij})}{(\sum \sum m_i m_j \beta_{ij})^2} \quad 75$$

(b) Evaluation of $\left(\frac{\partial P_C'}{\partial m_1}\right)_{T, P, m_2, \dots}$:

Working with Equation 45,

$$P_C' = \frac{(\sum \alpha_i Z_{ci})(\sum \sum \alpha_i \alpha_j \alpha_{ij})}{(\sum \sum \alpha_i \alpha_j \beta_{ij})^2} = \frac{(\sum \alpha_i Z_{ci})(\sum \sum m_i m_j \alpha_{ij})}{(\sum \sum m_i m_j \beta_{ij})^2}$$

$$P_C' = n \cdot \frac{(\sum m_i Z_{ci})(\sum \sum m_i m_j \alpha_{ij})}{(\sum \sum m_i m_j \beta_{ij})^2}$$

Differentiating and rearranging,

$$\left(\frac{\partial P_C'}{\partial m_1}\right)_{T, P, m_2, m_3, \dots} = P_C' \left[\frac{2 \sum m_j \alpha_{1j}}{\sum \sum m_i m_j \alpha_{ij}} + \frac{1}{n} + \frac{Z_{c1}}{\sum m_i Z_{ci}} - \frac{4 \sum m_j \beta_{1j}}{\sum \sum m_i m_j \beta_{ij}} \right] \quad 76$$

(c) Substituting for T_C' , P_C' , $\left(\frac{\partial T_C'}{\partial m_1}\right)$, and $\left(\frac{\partial P_C'}{\partial m_1}\right)$

in Equations 73 and 74, and manipulating the terms:

$$\left(\frac{\partial T_R'}{\partial m_1}\right) = 2T_R' \left[\frac{\sum x_j \beta_{1j}}{\sum \sum x_i x_j \beta_{ij}} - \frac{\sum x_j \alpha_{1j}}{\sum \sum x_i x_j \alpha_{ij}} \right] \left(\frac{1}{n}\right) \quad 77$$

$$\left(\frac{\partial P_R'}{\partial m_1}\right) = P_R' \left[\frac{4 \sum x_j \beta_{1j}}{\sum \sum x_i x_j \beta_{ij}} - \frac{2 \sum x_j \alpha_{1j}}{\sum \sum x_i x_j \alpha_{ij}} - \frac{Z_{c1}}{\sum x_i Z_{ci}} - 1 \right] \left(\frac{1}{n}\right) \quad 78$$

(4) Substituting Equations 71, 72, 77, 78 into Equation 64, cancelling factors and rearranging:

$$\begin{aligned} \left(\frac{\partial \ln f_1}{\partial m_1}\right)_{T, P, m_2, m_3, \dots} &= \left(\frac{1}{n_L}\right) \left(\frac{2}{RT_R'}\right) \left(\frac{\Delta H}{T_c'}\right) \left[\frac{\sum x_j \beta_{1j}}{\sum \sum x_i x_j \beta_{ij}} - \frac{\sum x_j \alpha_{1j}}{\sum \sum x_i x_j \alpha_{ij}} \right] \\ &+ \left(\frac{1}{n_L}\right) (Z_L) \left[\frac{4 \sum x_j \beta_{1j}}{\sum \sum x_i x_j \beta_{ij}} - \frac{2 \sum x_j \alpha_{1j}}{\sum \sum x_i x_j \alpha_{ij}} - \frac{Z_{c1}}{\sum x_i Z_{ci}} - 1 \right] \quad 79 \end{aligned}$$

By changing the "L" subscripts to "G" and the "x's" to "y's", the corresponding equation for the gaseous phase is obtained. For convenience, let

$$\Phi = \left[\frac{\sum x_j \beta_{1j}}{\sum \sum x_i x_j \beta_{ij}} - \frac{\sum x_j \alpha_{1j}}{\sum \sum x_i x_j \alpha_{ij}} \right] \left(\frac{2}{RT_R'}\right) \quad 80$$

$$\Theta = \left[\frac{4 \sum x_j \beta_{1j}}{\sum \sum x_i x_j \beta_{ij}} - \frac{2 \sum x_j \alpha_{1j}}{\sum \sum x_i x_j \alpha_{ij}} - \frac{Z_{c1}}{\sum x_i Z_{ci}} - 1 \right] \quad 81$$

Therefore Equation 79 is represented by

$$\left(\frac{\partial \ln f_L}{\partial m_1}\right)_{T, P, m_2, \dots} = \left(\frac{1}{n_L}\right) \left(\frac{\Delta H}{T_c'}\right)_L [\Phi]_L + \left(\frac{1}{n_L}\right) (Z_L) [\Theta]_L$$

Substituting Equation 82 (for both phases) into Equation 62 and cancelling n's,

$$\ln K_1 = \ln \frac{f_L}{f_G} + \left\{ \left(\frac{\Delta H}{T_c'} \right) [\Phi] + Z[\Theta] \right\}_L - \left\{ \left(\frac{\Delta H}{T_c'} \right) [\Phi] + Z[\Theta] \right\}_G \quad 83$$

This equation gives the K-value for component 1 in a system for which Equations 44 and 45 are the correct pseudocriticals. Such a system must obey the restrictions set up on page 87. Equation 83, therefore provides a new method for calculating ideal equilibrium vaporization constants. The terms f , $\frac{\Delta H}{T_c'}$, and z can be obtained from generalized tables of thermodynamic properties or from an appropriate equation of state.

It is convenient to abbreviate Equation 83 still further by introducing

$$\psi_L = \left[\left(\frac{\Delta H}{T_c'} \right) \Phi + Z\Theta \right]_L \quad 84$$

$$\psi_G = \left[\left(\frac{\Delta H}{T_c'} \right) \Phi + Z\Theta \right]_G \quad 85$$

Therefore, the equation becomes

$$\ln K_1 = \ln \frac{f_L}{f_G} + (\psi_L - \psi_G) \quad 86$$

The significance of the $(\psi_L - \psi_G)$ term is quite

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Actually, however, the equation is exact only for mixtures for which Equations 44, 45, and 46 represent the pseudocritical properties. Such a mixture must obey the restrictions set up on page 87. In a sense, Equation 86 defines a new ideal K-value, ideal to the extent that the mixture must conform to the model set up. Although more complex, the equation provides definite advantages over the conventional fugacity ratio definition (Equation 5).

(1) The problem of extrapolation into hypothetical states for the pure components is avoided.

(2) A framework is provided around which more accurate equations may be developed by assuming molecular models closer to reality and more accurate equations of state.

(3) A basis is provided for a new correlation of experimental K-values.

E. Correlation of K-Values for Hydrocarbon Systems

Because of serious differences between the restrictions imposed on page 87 and the actual behaviour of hydrocarbon systems, Equation 86 is only an approximation. An experimental correction term, $\log \Delta$, has been added, giving

$$\ln K = \ln \frac{f_L}{f_G} + (\psi_L - \psi_G) + \ln \Delta \quad 91$$

By using experimental K-values and phase compositions, $\ln \Delta$ was evaluated from Equation 91 for several systems. A correlation was obtained by plotting $\ln \Delta$ vs. $\frac{(P_R')_L}{(P_R)_L} (\psi_L - \psi_G)$

The correction factor was applied in the latter term to improve the correlation at high values of $(\psi_L - \psi_G)$. It is a negligible correction in the low ranges.

Results with light hydrocarbon systems indicate that $\ln \Delta$ is very nearly a parabolic function of $\frac{(P_R')_L}{(P_R)_L} (\psi_L - \psi_G)$.

For such systems (containing components no heavier than decane), a group of parabolas is obtained, one for each component. The relative shapes are shown schematically below:

These curves verify the increase in the correction term ($\ln \Delta$) expected from greater dissimilarity of components (increasing value of $|\psi_L - \psi_G|$).

Analytical expressions were fitted to the parabolas, and are given as:

(1) Methane

$$\ln \Delta_{C_1} = 0.0150 \left[\frac{(P_R')_L}{(P_R)_{C_1}} (\psi_L - \psi_G)_{C_1} - 1 \right]^2 - 0.01 \quad 92$$

(2) Ethane and Ethylene

$$\ln \Delta_{C_2} = 0.0311 \left[\frac{(P_R')_L}{(P_R)_{C_2}} (\psi_L - \psi_G)_{C_2} - 0.5 \right]^2 + 0.04 \quad 93$$

(3) Propane and Propylene

$$\ln \Delta_{C_3} = 0.050 \left[\frac{(P_R')_L}{(P_R)_{C_3}} (\psi_L - \psi_G)_{C_3} \right]^2 + 0.05 \quad 94$$

(4) Butane and Isobutane

$$\ln \Delta_{C_4} = 0.0475 \left[\frac{(P_R')_L}{(P_R)_{C_4}} (\psi_L - \psi_G)_{C_4} - 0.25 \right]^2 + 0.08 \quad 95$$

(5) Pentane and Isopentane

$$\ln \Delta_{C_5} = 0.0778 \left[\frac{(P_R')_L}{(P_R)_{C_5}} (\psi_L - \psi_G)_{C_5} - 0.25 \right]^2 + 0.06 \quad 96$$

As an example the methane curve is shown in Figure 40 with the experimental points.

Comparison of K-values calculated from Equations 91, 92-96 with experimental results are shown in Table X. Fair agreement is indicated, with the greatest deviations occurring at very low temperatures and in systems with widely dissimilar components. Failure under such conditions, however, was not unexpected, considering the restrictions imposed on the system by the assumptions on page 87.

For components heavier than pentanes, experimental data were too uncertain to obtain a correlation. In such

cases, it is recommended that the K-value be calculated neglecting the $\ln \Delta$ term.

For many systems and conditions, the accuracy of this correlation is only fair. It does provide a new theoretical approach to the problem of correlating K-values in complex systems. Much work is still needed, however, before the method will yield K-values of sufficient accuracy.. The investigation is being continued at the present time under the direction of Dr. Leland.

Because of the complex algebra involved, extensive use of this type of correlation would be almost impossible without an automatic computer. The Bendix computer used in the equation of state calculations previously discussed was also used in developing this correlation.

TABLES

TABLE I

ACCURACY EVALUATION OF CHROMATOGRAPHIC METHOD

Component	BY SYNTHETIC MIXTURES			Component	BY MASS SPECTROMETER		
	GLPC	mol fraction True Comp.	% Rel. Dev.		mol fraction GLPC	Mass Spec.	% Rel. Dev.
Methane	0.801	0.7994	+0.3	Methane	0.884	0.882	+0.2
Ethane	0.147	0.1498	-1.9	Ethane	0.0949	0.097	-2.2
Propane	0.0519	0.0508	+2.2	Propane	0.0212	0.021	+1.0
Methane	0.0486	0.0483	+0.6	Methane	0.441	0.435	+1.4
Ethane	0.193	0.1955	-1.3	Ethane	0.248	0.255	-2.7
Propane	0.758	0.7562	+0.2	Propane	0.311	0.309	+0.7
Methane	0.745	0.7441	+0.1	Methane	0.424	0.431	-1.6
Ethane	0.231	0.2314	-0.2	Ethane	0.150	0.153	-2.0
Propane	0.0248	0.0245	+1.2	Propane	0.426	0.417	+2.2
Methane	0.490	0.4905	-0.1	Methane	0.801	0.794	+0.9
Ethane	0.0112	0.0111	+0.9	Ethane	0.143	0.147	-2.7
Propane	0.498	0.4983	-0.6	Propane	0.0559	0.058	-3.6
				Methane	0.441	0.436	+1.1
				Ethane	0.366	0.371	-1.3
				Propane	0.193	0.192	+0.5

TABLE II

EXPERIMENTAL RESULTS: METHANE-ETHANE BINARY

Temp of	Press psia	Liquid Composition mol fraction		Vapor Composition mol fraction		K - Values	
		CH ₄	C ₂ H ₆	CH ₄	C ₂ H ₆	CH ₄	C ₂ H ₆
50	600 ^b	0.083	0.917	0.210	0.790	2.53	0.861
50	800 ^b	0.207	0.793	0.325	0.675	1.58	0.852
0	400 ^b	0.123	0.877	0.410	0.590	3.33	0.673
0	600 ^b	0.256	0.744	0.561	0.439	2.18	0.591
0	800 ^b	0.390	0.610	0.619	0.381	1.59	0.621
0	980	0.498	0.502	0.590	0.410	1.18	0.816
0	1000	0.522	0.478	0.544	0.456	1.04	0.953
-50	100 ^b	0.006	0.994	0.066	0.934	9.61	0.940
-50	200	0.0968	0.9032	0.505	0.495	5.22	0.548
-50	400	0.282	0.718	0.724	0.276	2.57	0.384
-50	600	0.438	0.562	0.800	0.200	1.83	0.356
-50	800	0.622	0.378	0.832	0.168	1.34	0.445
-50	920	0.727	0.273	0.820	0.180	1.13	0.659
-100	100	0.101	0.899	0.680	0.320	6.73	0.356
-100	200	0.250	0.750	0.814	0.186	3.26	0.248
-100	400	0.528	0.472	0.9165	0.0835	1.72	0.177
-100	600	0.784	0.216	0.9498	0.0502	1.21	0.232
-100	740	0.9281	0.0719	0.9574	0.0426	1.032	0.593
-150	100	0.251	0.749	0.9312	0.0688	3.71	0.0918
-150	200	0.549	0.451	0.9768	0.0232	1.78	0.0515
-200	100	0.833	0.167	0.9965	0.0035	1.20	0.0210

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TABLE III
EXPERIMENTAL RESULTS: METHANE-PROPANE BINARY

Temp of	Press psia	Liquid Composition		Vapor Composition		K - Values	
		CH ₄	C ₃ H ₈	CH ₄	C ₃ H ₈	CH ₄	C ₃ H ₈
50	100	0.0028 ^h	0.998	0.057	0.943	20.5 ^h	0.945
50	200	0.044 ^h	0.960	0.471	0.529	10.7 ^h	0.551
50	200	0.044 ^h	0.962	0.471	0.529	10.7 ^h	0.550
50	400	0.128	0.872	0.685	0.315	5.35	0.361
50	600	0.216	0.784	0.762	0.238	3.53	0.304
50	800	0.300	0.700	0.788	0.212	2.63	0.303
50	1000	0.413	0.587	0.805	0.195	1.95	0.332
50	1100	0.451	0.549	0.803	0.197	1.78	0.359
50	1200	0.498	0.502	0.784	0.216	1.57	0.430
50	1300	0.545	0.455	0.766	0.234	1.40	0.514
50	1367	0.603	0.397	0.720	0.280	1.19	0.705
0	100	0.0358	0.9642	0.573	0.427	15.9	0.445
0	200	0.0904	0.9096	0.768	0.232*	8.47	0.256
0	400	0.199	0.7910	0.862	0.138	4.33	0.172
0	600	0.311	0.689	0.891	0.109	2.86	0.158
0	800	0.415	0.585	0.899	0.101	2.16	0.173
0	1000	0.522	0.478	0.895	0.105	1.71	0.220
0	1100	0.582	0.418	0.888	0.112	1.53	0.268
0	1200	0.637	0.363	0.873	0.127	1.37	0.350
0	1300	0.708	0.292	0.845	0.155	1.19	0.531
-50	100	0.0769	0.9231	0.840	0.160	10.9	0.173
-50	200	0.146	0.854	0.9216	0.0784	6.31	0.0918
-50	400	0.296	0.704	0.9493	0.0507	3.20	0.0735
-50	600	0.438	0.562	0.9585	0.0415	2.19	0.0739
-50	800	0.581	0.419	0.9590	0.0410	1.65	0.0978
-50	1000	0.736	0.264	0.9458	0.0542	1.29	0.205
-50	1100	0.851	0.149	0.899	0.101	1.06	0.678

TABLE III (continued)

Temp OF	Press psia	Liquid Composition		Vapor Composition		K - Values	
		CH ₄	C ₃ H ₈	CH ₄	C ₃ H ₈	CH ₄	C ₃ H ₈
-100	100	0.125	0.875	0.9591	0.0409	7.67	0.0468
-100	115	0.144	0.856	0.970	0.030	6.74	0.0350
-100	200	0.222	0.778	0.9792	0.0208	4.41	0.0268
-100	215	0.250	0.750	0.981	0.019	3.93	0.0254
-100	315	0.372	0.628	0.9855	0.0145	2.65	0.0231
-100	415	0.501	0.499	0.9855	0.0145	1.97	0.0290
-100	600	0.744	0.256	0.9852	0.0148	1.32	0.0556
-100	615	0.772	0.228	0.9842	0.0158	1.275	0.0693
-100	750	0.9396	0.0604	0.9851	0.0149	1.05	0.246
-100	765	0.9533	0.0467	0.9854	0.0146	1.03	0.312
-150	100	0.238	0.762	0.9932	0.0068	4.17	0.0089
-150	200	0.502	0.498	0.9955	0.0045	1.98	0.0090
-150	230	0.584	0.416	0.9958	0.0042	1.71	0.0101
-150	348	0.9589	0.0411	0.9986	0.0014	1.04	0.0341
-200	100	0.802	0.198	0.9993	0.0007	1.24	0.0035

* Interpolated
h Calculated by Henry's Law

TABLE IV

EXPERIMENTAL RESULTS: ETHANE-PROPANE BINARY

Temp of	Press psia	Liquid Composition mol fraction		Vapor Composition mol fraction		K - Values	
		C ₂ H ₆	C ₃ H ₈	C ₂ H ₆	C ₃ H ₈	C ₂ H ₆	C ₃ H ₈
50	100	0.0236	0.9759	0.0720	0.9267	3.05	0.951
50	200	0.357	0.643	0.612	0.388	1.72	0.603
50	300	0.651	0.350	0.848	0.152	1.30	0.434
50	400	0.9108	0.0892	0.9606	0.0394	1.05	0.442
0	100	0.373	0.627	0.692	0.308	1.85	0.491
0	200	0.9013	0.0987	0.9717	0.0283	1.08	0.287

TABLE V

EXPERIMENTAL RESULTS: BINARY AND TERNARY DATA

Code No.	Temp. °F	Press. psia	Liquid Composition			Vapor Composition			K - Values		
			CH ₄	C ₂ H ₆	C ₃ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈
1	50	100	0.0028 ^h		0.998	0.057		0.943	20.5 ^h		0.945
2	50	100	0.0022 ^h	0.0080	0.9897	0.0452	0.0280	0.9268	20.4 ^h	3.50	0.936
4	50	100		0.0236	0.9764		0.0720	0.9280		3.05	0.951
5	50	200	0.044 ^h		0.960	0.471		0.529	10.7 ^h		0.551
6	50	200	0.044 ^h		0.962	0.471		0.529	10.7 ^h		0.550
7	50	200	0.0396 ^h	0.0655	0.8966	0.412	0.112	0.476	10.4 ^h	1.86	0.531
8	50	200	0.0270 ^h	0.160	0.811	0.275	0.284	0.441	10.2 ^h	1.77	0.543
9	50	200	0.0128 ^h	0.264	0.7193	0.127	0.476	0.397	9.95	1.80	0.552
10	50	200		0.357	0.643		0.612	0.388		1.72	0.603
11	50	400	0.128		0.872	0.685		0.315	5.35		0.361
12	50	400	0.110	0.175	0.715	0.557	0.193	0.250	5.06	1.10	0.350
13	50	400	0.0697	0.500	0.4303	0.306	0.535	0.159	4.39	1.07	0.369
14	50	400	0.0620	0.553	0.385	0.282	0.570	0.148	4.54	1.03	0.348
15	50	400	0.0302	0.7578	0.212	0.115	0.7989	0.0861	3.81	1.05	0.406
16	50	400		0.9066	0.0934		0.9616	0.0384		1.06	0.411
17	50	400		0.9108	0.0892		0.9606	0.0394		1.05	0.442
18	50	600	0.216		0.784	0.762		0.238	3.53		0.304
19	50	600	0.214	0.151	0.635	0.663	0.133	0.204	3.10	0.880	0.321
20	50	600	0.204	0.178	0.618	0.654	0.150	0.196	3.20	0.843	0.317
21	50	600	0.178	0.376	0.446	0.521	0.332	0.147	2.93	0.883	0.330
22	50	600	0.174	0.457	0.369	0.487	0.382	0.131	2.80	0.836	0.355
23	50	600	0.137	0.647	0.216	0.371	0.5501	0.0789	2.71	0.849	0.365
24	50	600	0.113	0.768	0.119	0.286	0.6668	0.0472	2.53	0.868	0.397

TABLE V (continued)

Code No.	Temp. °F	Press. psia	Liquid Composition			Vapor Composition			K - Values		
			CH ₄	C ₂ H ₆	C ₃ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈
25	50	600 ^b	0.083	0.917		0.210	0.790		2.53	0.861	
26	50	800	0.300		0.700	0.788		0.212	2.63		0.303
27	50	800	0.286	0.121	0.593	0.7224	0.0906	0.187	2.53	0.749	0.315
28	50	800	0.268	0.359	0.373	0.588	0.282	0.130	2.19	0.786	0.348
29	50	800	0.255	0.454	0.291	0.534	0.357	0.109	2.10	0.787	0.374
30	50	800	0.237	0.566	0.197	0.4632	0.455	0.0818	1.95	0.803	0.415
31	50	800 ^b	0.207	0.793		0.325	0.675		1.58	0.852	
32	50	1000	0.413		0.587	0.805		0.195	1.95		0.332
33	50	1000	0.389	0.169	0.442	0.707	0.126	0.167	1.82	0.745	0.378
34	50	1000	0.385	0.225	0.390	0.680	0.164	0.156	1.76	0.729	0.400
35	50	1000	0.373	0.357	0.270	0.600	0.268	0.132	1.61	0.751	0.442
36	50	1000	0.349	0.505	0.146	0.4826	0.431	0.0864	1.38	0.853	0.591
37	50	1000	0.3755	0.5241	0.1004	0.4345	0.490	0.0755	1.16	0.933	0.751
38	50	1100	0.451		0.549	0.803		0.197	1.78		0.359
39	50	1100	0.4365	0.0409	0.5226	0.7746	0.0306	0.1948	1.77	0.748	0.373
40	50	1100	0.430	0.110	0.460	0.7341	0.0849	0.181	1.71	0.771	0.394
41	50	1100	0.438	0.192	0.370	0.692	0.143	0.165	1.58	0.744	0.446
42	50	1100	0.438	0.223	0.339	0.665	0.173	0.162	1.52	0.776	0.478
43	50	1100	0.435	0.259	0.306	0.630	0.209	0.151	1.45	0.807	0.526
44	50	1100	0.440	0.376	0.184	0.504	0.351	0.145	1.15	0.934	0.788
45	50	1200	0.498		0.502	0.784		0.216	1.57		0.430
46	50	1200	0.4997	0.0375	0.4628	0.7558	0.0302	0.214	1.51	0.806	0.462
47	50	1200	0.504	0.176	0.320	0.673	0.143	0.184	1.34	0.813	0.575
48	50	1200	0.508	0.243	0.249	0.584	0.219	0.197	1.15	0.901	0.791

TABLE V (continued)

Code No.	Temp. °F	Press. psia	Liquid Composition			Vapor Composition			K - Values		
			CH ₄	C ₂ H ₆	C ₃ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈
49	0	100	0.0358		0.9642	0.573		0.427	15.9		0.445
50	0	100	0.0335	0.0174	0.9491	0.5589	0.0336	0.4075	16.7	1.93	0.430
51	0	100	0.0279	0.1284	0.8437	0.400	0.246	0.354	14.3	1.92	0.420
52	0	100	0.0210	0.166	0.813	0.325	0.349	0.326	15.5	2.10	0.401
53	0	100	0.0107	0.272	0.7173	0.159	0.534	0.307	14.9	1.96	0.428
54	0	100		0.373	0.627		0.692	0.308		1.85	0.491
55	0	200	0.0904		0.9096	0.768		0.232*	8.47		0.256
56	0	200	0.0917	0.0127	0.8956	0.7717	0.0133	0.215	8.43	1.05	0.240
57	0	200	0.0702	0.250	0.6798	0.560	0.270	0.170	7.98	1.08	0.250
58	0	200	0.0457	0.4843	0.470	0.359	0.519	0.122	7.85	1.07	0.260
59	0	200	0.0127	0.8133	0.174	0.0778	0.8746	0.0476	6.12	1.08	0.274
60	0	200		0.9013	0.0987		0.9717	0.0283		1.08	0.287
61	0	400	0.199		0.801	0.862		0.138	4.33		0.172
62	0	400	0.159	0.347	0.494	0.6985	0.217	0.0845	4.39	0.626	0.171
63	0	400	0.1557	0.5293	0.315	0.6003	0.343	0.0567	3.86	0.648	0.180
64	0	400 ^b	0.1364	0.7243	0.1393	0.4869	0.4852	0.0279	3.57	0.670	0.200
65	0	400 ^b	0.123	0.877		0.410	0.590		3.33	0.673	
66	0	600	0.311		0.689	0.891		0.109	2.86		0.158
67	0	600	0.293	0.266	0.441	0.781	0.1377	0.0813	2.67	0.518	0.185
68	0	600	0.288	0.343	0.369	0.7514	0.184	0.0646	2.61	0.537	0.175
69	0	600	0.272	0.481	0.247	0.6896	0.260	0.0504	2.54	0.540	0.204
70	0	600 ^b	0.271	0.6204	0.1086	0.6138	0.361	0.0252	2.28	0.582	0.232
71	0	600 ^b	0.256	0.744		0.561	0.439		2.18	0.591	

TABLE V (continued)

Code No.	Temp. °F	Press. psia	Liquid Composition			Vapor Composition			K - Values		
			CH ₄	C ₂ H ₆	C ₃ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈
72	0	800	0.415		0.585	0.899		0.101	2.16		0.173
73	0	800	0.391	0.188	0.421	0.8239	0.0939	0.0822	2.11	0.499	0.195
74	0	800	0.378	0.354	0.268	0.7727	0.1702	0.0517	2.05	0.481	0.213
75	0	800	0.380	0.418	0.202	0.7318	0.224	0.0442	1.93	0.536	0.219
76	0	800 ^b	0.380	0.5142	0.1058	0.6795	0.296	0.0245	1.80	0.576	0.232
77	0	800	0.390	0.610		0.619	0.381		1.59	0.621	
78	0	1000	0.522		0.478	0.895		0.105	1.71		0.220
79	0	1000	0.515	0.0780	0.407	0.8623	0.0443	0.0934	1.68	0.568	0.230
80	0	1000	0.512	0.187	0.301	0.8174	0.1027	0.0799	1.60	0.549	0.266
81	0	1000	0.514	0.239	0.247	0.791	0.140	0.0690	1.54	0.586	0.280
82	0	1000	0.5161	0.3378	0.1461	0.7234	0.226	0.0506	1.40	0.669	0.346
83	0	1000	0.5258	0.4467	0.0275	0.6357	0.349	0.0153	1.21	0.781	0.554
84	0	1000*	0.522	0.478		0.569	0.431		1.09	0.901	

TABLE V (Continued)

Code No.	Temp OF	Press Psia	Liquid Composition			Vapor Composition			K Values		
			C ₁	C ₂	C ₃	C ₁	C ₂	C ₃	C ₁	C ₂	C ₃
85	0	1100	0.582		0.418	0.888		0.112	1.53		0.268
86	0	1100	0.5759	0.0581	0.366	0.8619	0.0341	0.104	1.50	0.587	0.284
87	0	1100	0.585	0.107	0.308	0.8377	0.0635	0.0988	1.43	0.593	0.321
88	0	1100	0.584	0.157	0.259	0.8237	0.0928	0.0835	1.41	0.591	0.322
89	0	1100	0.587	0.192	0.221	0.7947	0.1231	0.0822	1.35	0.641	0.372
90	0	1100	0.582	0.228	0.190	0.7707	0.154	0.0753	1.32	0.675	0.396
91	0	1100	0.5917	0.2483	0.1600	0.7545	0.1758	0.0697	1.275	0.708	0.436
92	0	1100	0.6043	0.259	0.1367	0.7484	0.1855	0.0661	1.24	0.716	0.484
93	0	1100	0.604	0.273	0.123	0.7142	0.2177	0.0681	1.18	0.797	0.554
94	0	1200	0.637		0.363	0.873		0.127	1.37		0.350
95	0	1200	0.6456	0.0874	0.267	0.8218	0.0625	0.1157	1.27	0.716	0.433
96	0	1200	0.653	0.106	0.241	0.8158	0.0751	0.1091	1.25	0.708	0.453
97	0	1200	0.650	0.118	0.232	0.795	0.089	0.116	1.22	0.754	0.500
98	0	1200	0.693	0.161	0.146	0.721	0.144	0.135	1.04	0.894	0.925
99	0	1300	0.708		0.292	0.845		0.155	1.19		0.531
100	0	1300	0.7103	0.0297	0.260	0.8294	0.0246	0.146	1.17	0.828	0.561
101	0	1300	0.7315	0.0345	0.234	0.8086	0.0322	0.1592	1.11	0.933	0.681
102	0	1300	0.7364	0.0396	0.224	0.7978	0.0384	0.1638	1.08	0.970	0.731
103	-50	100	0.0769		0.9231	0.840		0.160	10.9		0.173
104	-50	100	0.0614	0.1718	0.7668	0.7195	0.1628	0.1177	11.7	0.947	0.153
105	-50	100	0.0486	0.302	0.6494	0.605	0.292	0.103	12.4	0.967	0.159
106	-50	100	0.0479	0.399	0.5531	0.5287	0.380	0.0913	11.0	0.952	0.165
107	-50	100	0.0467	0.448	0.5053	0.4952	0.425	0.0798	10.6	0.949	0.158
108	-50	100	0.0261	0.7259	0.248	0.280	0.682	0.0380	10.7	0.939	0.153
109	-50	100 ^b	0.006	0.994		0.066	0.934		11.0	0.940	
110	-50	200	0.146		0.854	0.9216		0.0784	6.31		0.0918
111	-50	200	0.125	0.268	0.607	0.804	0.140	0.0560	6.43	0.522	0.0922
112	-50	200	0.125	0.368	0.507	0.7478	0.206	0.0462	5.98	0.560	0.0911
113	-50	200	0.119	0.627	0.254	0.6383	0.333	0.0287	5.35	0.531	0.115
114	-50	200	0.0968	0.9032		0.505	0.495		5.22	0.548	

TABLE V (Continued)

Code No.	Temp °F	Press Psia	Liquid Composition			Vapor Composition			K Values		
			C ₁	C ₂	C ₃	C ₁	C ₂	C ₃	C ₁	C ₂	C ₃
115	-50	400	0.296		0.704	0.9493		0.0507	3.20		0.0735
116	-50	400	0.292	0.126	0.582	0.920	0.0383	0.0417	3.15	0.304	0.0717
117	-50	400	0.271	0.289	0.440	0.8791	0.0907	0.0302	3.24	0.314	0.0687
118	-50	400	0.274	0.448	0.278	0.8245	0.154	0.0215	3.02	0.344	0.0773
119	-50	400	0.270	0.512	0.218	0.8084	0.1742	0.0174	2.99	0.340	0.0798
120	-50	400	0.277	0.523	0.200	0.7986	0.1880	0.0134	2.88	0.359	0.0805
121	-50	400	0.278	0.571	0.151	0.7901	0.194	0.0159	2.74	0.340	0.105
122	-50	400	0.282	0.718		0.724	0.276		2.57	0.384	
123	-50	600	0.438		0.562	0.9585		0.0415	2.19		0.0739
124	-50	600	0.440	0.145	0.415	0.9179	0.0485	0.0336	2.06	0.334	0.0809
125	-50	600	0.424	0.150	0.426	0.919	0.0446	0.0364	2.17	0.298	0.0855
126	-50	600	0.443	0.243	0.314	0.8952	0.0790	0.0258	2.02	0.325	0.0822
127	-50	600	0.441	0.366	0.193	0.8637	0.119	0.0173	1.96	0.327	0.0896
128	-50	600	0.438	0.562		0.800	0.200		1.83	0.356	
129	-50	800	0.581		0.419	0.959		0.0410	1.65		0.0978
130	-50	800	0.598	0.109	0.293	0.9275	0.362	0.0363	1.55	0.332	0.124
131	-50	800	0.611	0.249	0.140	0.8901	0.0886	0.0213	1.46	0.356	0.152
132	-50	800	0.622	0.378		0.832	0.168		1.34	0.445	
133	-50	1000	0.736		0.264	0.9458		0.0542	1.29		0.205
134	-50	1000	0.7609	0.0651	0.174	0.9216	0.0331	0.0453	1.21	0.509	0.260
135	-50	1000	0.7662	0.0892	0.1446	0.9026	0.0504	0.0470	1.18	0.565	0.325
136	-50	1000	0.7749	0.1261	0.0990	0.8838	0.0758	0.0404	1.14	0.609	0.408
137	-50	1000	0.7837	0.1491	0.0672	0.8631	0.1001	0.0368	1.10	0.671	0.547
138	-50	1000	0.8332	0.1318	0.0350	0.8363	0.1288	0.0349	1.00	0.977	0.997
139	-100	100	0.125		0.875	0.9591		0.0409	7.67		0.0468
140	-100	100	0.118	0.144	0.738	0.9186	0.0472	0.0342	7.78	0.328	0.0463
141	-100	100	0.110	0.320	0.570	0.8651	0.110	0.0249	7.77	0.344	0.0437
142	-100	100	0.110	0.580	0.310	0.7916	0.194	0.0144	7.20	0.334	0.0464
143	-100	100	0.101	0.899		0.680	0.320		6.73	0.356	

TABLE V (Continued)

Code No.	Temp °F	Press Psia	Liquid Composition			Vapor Composition			K Values		
			C ₁	C ₂	C ₃	C ₁	C ₂	C ₃	C ₁	C ₂	C ₃
144	-100	200	0.222		0.778	0.9792		0.0208	4.41		0.0268
145	-100	200	0.235	0.121	0.644	0.9615	0.0228	0.0157	4.09	0.188	0.0254
146	-100	200	0.232	0.435	0.333	0.9070	0.0840	0.00897	3.91	0.193	0.0269
147	-100	200	0.236	0.483	0.281	0.8926	0.0983	0.00909	3.78	0.204	0.0324
148	-100	200	0.250	0.750		0.814	0.186		3.26	0.248	
149	-100	400	0.477		0.523	0.9855		0.0145*	2.06		0.0277
150	-100	400	0.492	0.175	0.333	0.963	0.0266	0.0104	1.96	0.152	0.0312
151	-100	400	0.496	0.242	0.262	0.9562	0.0364	0.00741	1.93	0.150	0.0283
152	-100	400	0.504	0.308	0.188	0.9446	0.0486	0.00685	1.88	0.158	0.0364
153	-100	400	0.5191	0.386	0.0949	0.9321	0.0630	0.00486	1.80	0.163	0.0512
154	-100	400	0.528	0.472		0.9165	0.0835		1.72	0.177	
155	-100	600	0.744		0.256	0.9852		0.0148	1.32		0.0556
156	-100	600	0.745	0.0520	0.203	0.9775	0.0119	0.0106	1.31	0.229	0.0522
157	-100	600	0.7647	0.1612	0.0741	0.9583	0.0366	0.00512	1.25	0.227	0.0691
158	-100	600	0.784	0.216		0.9498	0.0502		1.21	0.232	
159	-150	100	0.238		0.762	0.9932		0.0068	4.17		0.0089
160	-150	100	0.242	0.258	0.500	0.9686	0.0282	0.0032	4.00	0.109	0.0064
161	-150	100	0.240	0.275	0.485	0.9653	0.0308	0.0039	4.02	0.112	0.0080
162	-150	100	0.249	0.446	0.305	0.9538	0.0433	0.0030	3.68	0.0970	0.0098
163	-150	100	0.252	0.6762	0.0718	0.9299	0.0682	0.0019	3.67	0.102	0.0265
164	-150	100	0.251	0.749		0.9312	0.0688		3.71	0.0918	
165	-150	200	0.502		0.498	0.9955		0.0045	1.98		0.0090
167	-150	200	0.514	0.208	0.278	0.9806	0.0167	0.0027	1.91	0.0805	0.0097
168	-150	200	0.528	0.319	0.153	0.9742	0.0234	0.0024	1.84	0.0734	0.0157
169	-150	200	0.5532	0.400	0.0468	0.969	0.0294	0.0016	1.75	0.0735	0.0342
170	-150	200	0.561	0.439		0.970	0.030		1.73	0.0683	
171	-200	100	0.802		0.198	0.9993		0.0007	1.24		0.0035
172	-200	100	0.8075	0.0735	0.119	0.9962	0.0021	0.0007**	1.23	0.0286	0.0059
173	-200	100	0.8187	0.124	0.0573	0.9961	0.0029	0.0007**	1.22	0.0234	0.012
175	-200	100	0.833	0.167		0.9965	0.0035		1.20	0.0210	

* Interpolated
** Estimated

^h Calculated by Henry's Law
^b Bloomer (9)

TABLE VI

Predicted Equilibrium Data from BWR Equation

Code No.	Conditions Temp. OF.	Press. Psia	Liquid Phase			Vapor Phase		
			CH ₄	C ₂ H ₆	C ₃ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈
1	50	100	0.0035		0.9965	0.0644		0.9356
2	50	100	0.0024	0.0083	0.9893	0.0439	0.0272	0.9289
4	50	100		0.0262	0.9738		0.0855	0.9145
5	50	200	0.0504		0.9496	0.485		0.515
7	50	200	0.0420	0.0629	0.8951	0.400	0.114	0.486
8	50	200	0.0291	0.158	0.8129	0.270	0.283	0.447
9	50	200	0.0141	0.264	0.7219	0.128	0.472	0.400
10	50	200		0.362	0.638		0.643	0.357
11	50	400	0.141		0.859	0.700		0.300
12	50	400	0.117	0.179	0.704	0.557	0.190	0.253
13	50	400	0.0690	0.502	0.429	0.303	0.532	0.165
14	50	400	0.0624	0.5436	0.394	0.270	0.577	0.153
15	50	400	0.0281	0.7559	0.216	0.113	0.7982	0.0888
17	50	400		0.9127	0.0873		0.9625	0.0375
18	50	600	0.228		0.772	0.768		0.232
19	50	600	0.209	0.155	0.636	0.672	0.129	0.199
20	50	600	0.205	0.179	0.616	0.656	0.149	0.195
21	50	600	0.175	0.384	0.441	0.527	0.324	0.149
22	50	600	0.164	0.456	0.380	0.482	0.386	0.132
23	50	600	0.133	0.647	0.220	0.362	0.555	0.0830
24	50	600	0.112	0.769	0.119	0.286	0.6662	0.0478
25	50	600	0.0838	0.9162		0.199	0.801	
26	50	800	0.312		0.688	0.794		0.206
27	50	800	0.296	0.121	0.583	0.7263	0.0898	0.1839
28	50	800	0.266	0.363	0.371	0.589	0.278	0.133
29	50	800	0.252	0.457	0.291	0.534	0.355	0.111
30	50	800	0.235	0.569	0.196	0.4653	0.4524	0.0823
31	50	800	0.201	0.799		0.318	0.682	

TABLE VI (Continued)

Code No.	Conditions Temp. °F.	Press. Psia	Liquid Phase			Vapor Phase		
			CH ₄	C ₂ H ₆	C ₃ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈
32	50	1000	0.406		0.594	0.804		0.196
33	50	1000	0.384	0.171	0.445	0.707	0.125	0.168
34	50	1000	0.379	0.224	0.397	0.678	0.166	0.156
35	50	1000	0.368	0.353	0.279	0.596	0.275	0.129
36	50	1000	0.348	0.507	0.145	0.4827	0.4298	0.0875
37	50	1000	0.3727	0.5282	0.0991	0.4359	0.4868	0.0773
38	50	1100	0.448		0.552	0.801		0.199
39	50	1100	0.4379	0.0416	0.5205	0.7754	0.0298	0.1948
40	50	1100	0.430	0.112	0.458	0.7351	0.0823	0.1826
41	50	1100	0.432	0.192	0.376	0.689	0.145	0.166
42	50	1100	0.432	0.224	0.344	0.665	0.173	0.162
43	50	1100	0.422	0.263	0.315	0.635	0.207	0.158
44	50	1100	0.427	0.383	0.190	0.515	0.345	0.140
45	50	1200	0.492		0.508	0.788		0.212
46	50	1200	0.4882	0.0389	0.4729	0.7639	0.0289	0.2072
47	50	1200	0.494	0.177	0.329	0.671	0.144	0.185
48	50	1200	0.495	0.245	0.260	0.593	0.218	0.189
	50	1300	0.540		0.460	0.769		0.231
	50	1367	0.579		0.421	0.744		0.256
49	0	100	0.0375		0.9625	0.597		0.403
50	0	100	0.0358	0.0174	0.9468	0.570	0.0340	0.396
51	0	100	0.0253	0.1259	0.8488	0.396	0.246	0.358
52	0	100	0.0205	0.1733	0.8062	0.320	0.339	0.341
53	0	100	0.0105	0.2741	0.7154	0.160	0.534	0.306
55	0	200	0.0960		0.9040	0.781		0.219
57	0	200	0.0712	0.2500	0.6788	0.560	0.270	0.170
58	0	200	0.0472	0.4823	0.4705	0.357	0.521	0.122
59	0	200	0.0111	0.8121	0.1768	0.0774	0.8740	0.0486
60	0	200		0.9061	0.0939		0.9737	0.0263

TABLE VI (Continued)

Code No.	Conditions		Liquid Phase			Vapor Phase		
	Temp. °F.	Press. Psia.	CH ₄	C ₂ H ₆	C ₃ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈
61	0	400	0.208		0.792	0.870		0.130
62	0	400	0.174	0.339	0.487	0.6913	0.2233	0.0854
63	0	400	0.156	0.526	0.318	0.5912	0.3498	0.0590
64	0	400	0.135	0.724	0.141	0.4827	0.4891	0.0282
65	0	400	0.117	0.883		0.395	0.605	
66	0	600	0.315		0.685	0.896		0.104
67	0	600	0.292	0.262	0.446	0.7839	0.142	0.0741
68	0	600	0.286	0.342	0.372	0.7488	0.187	0.0642
69	0	600	0.272	0.476	0.252	0.6875	0.266	0.0465
70	0	600	0.257	0.629	0.114	0.6159	0.361	0.0231
71	0	600	0.246	0.745		0.554	0.446	
72	0	800	0.419		0.581	0.9049		0.0951
73	0	800	0.404	0.184	0.412	0.8310	0.0938	0.0752
74	0	800	0.393	0.340	0.267	0.764	0.181	0.0550
75	0	800	0.388	0.413	0.199	0.731	0.225	0.0440
76	0	800	0.381	0.515	0.104	0.6801	0.294	0.0259
77	0	800	0.380	0.620		0.618	0.382	
78	0	1000	0.519		0.481	0.9016		0.0984
79	0	1000	0.5141	0.0799	0.406	0.8693	0.0417	0.0890
80	0	1000	0.510	0.187	0.303	0.8212	0.103	0.0758
81	0	1000	0.508	0.242	0.250	0.7942	0.138	0.0678
82	0	1000	0.507	0.347	0.146	0.7361	0.215	0.0489
83	0	1000	0.5154	0.4563	0.0283	0.6442	0.3411	0.0147
84	0	1000	0.523	0.477		0.544	0.456	
85	0	1100	0.570		0.430	0.896		0.104
86	0	1100	0.5667	0.0595	0.3738	0.8704	0.0328	0.0968
87	0	1100	0.568	0.109	0.323	0.8459	0.0626	0.0915
88	0	1100	0.577	0.158	0.265	0.8222	0.0942	0.0836
89	0	1100	0.569	0.198	0.233	0.7985	0.1221	0.0794

TABLE VI (Continued)

Code No.	Conditions Temp. OF.	Press. Psia.	Liquid Phase			Vapor Phase		
			CH ₄	C ₂ H ₆	C ₃ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈
90	0	1100	0.572	0.233	0.195	0.7750	0.1511	0.0739
91	0	1100	0.574	0.258	0.168	0.7583	0.1727	0.0690
92	0	1100	0.576	0.272	0.152	0.7477	0.1866	0.0657
93	0	1100	0.577	0.290	0.133	0.7302	0.2068	0.0630
94	0	1200	0.620		0.380	0.886		0.114
95	0	1200	0.6235	0.0923	0.2842	0.8357	0.0589	0.1054
96	0	1200	0.626	0.112	0.262	0.8240	0.0730	0.1030
97	0	1200	0.626	0.125	0.249	0.8138	0.0834	0.1028
98	0	1200	0.638	0.176	0.186	0.7871	0.1249	0.0880
99	0	1300	0.675		0.325	0.867		0.133
100	0	1300	0.6803	0.0288	0.2909	0.848	0.0200	0.132
101	0	1300	0.6812	0.0399	0.2789	0.8397	0.0282	0.1321
102	0	1300	0.6829	0.0462	0.2709	0.8342	0.0332	0.1326
103	-50	100	0.0747		0.9253	0.861		0.139
104	-50	100	0.0629	0.1736	0.7635	0.723	0.161	0.116
105	-50	100	0.0538	0.3073	0.6389	0.6155	0.2861	0.0984
106	-50	100	0.0475	0.4028	0.5497	0.5389	0.3757	0.0854
107	-50	100	0.0443	0.4516	0.5041	0.5000	0.4213	0.0787
108	-50	100	0.0255	0.726	0.2469	0.2800	0.6804	0.0396
109	-50	100	0.0067	0.9933		0.0701	0.9299	
110	-50	200	0.156		0.844	0.9240		0.0760
111	-50	200	0.138	0.266	0.596	0.8045	0.1399	0.0556
112	-50	200	0.131	0.373	0.496	0.7556	0.1974	0.0470
113	-50	200	0.115	0.626	0.259	0.6394	0.3350	0.0256
114	-50	200	0.0957	0.9043		0.510	0.490	
115	-50	400	0.310		0.690	0.9532		0.0468
116	-50	400	0.302	0.122	0.576	0.9186	0.0414	0.0400
117	-50	400	0.294	0.278	0.428	0.8732	0.0959	0.0309
118	-50	400	0.284	0.442	0.274	0.8244	0.1548	0.0208

TABLE VI (Continued)

Code No.	Conditions Temp. OF.	Press. Psia.	Liquid Phase			Vapor Phase		
			CH ₄	C ₂ H ₆	C ₃ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈
119	-50	400	0.282	0.503	0.215	0.8059	0.1774	0.0167
120	-50	400	0.282	0.522	0.196	0.7997	0.1849	0.0154
121	-50	400	0.280	0.565	0.155	0.7864	0.2012	0.0124
122	-50	400	0.273	0.727		0.733	0.267	
123	-50	600	0.452		0.548	0.9603		0.0397
124	-50	600	0.450	0.145	0.405	0.9238	0.0448	0.0314
125	-50	600	0.450	0.144	0.406	0.9242	0.0443	0.0315
126	-50	600	0.447	0.243	0.310	0.8982	0.0764	0.0254
127	-50	600	0.444	0.364	0.192	0.8646	0.1184	0.0170
128	-50	600	0.442	0.558		0.804	0.196	
129	-50	800	0.588		0.412	0.9598		0.0402
130	-50	800	0.594	0.109	0.297	0.9309	0.0365	0.0326
131	-50	800	0.605	0.250	0.145	0.8876	0.0925	0.0199
132	-50	800	0.614	0.386		0.832	0.168	
	-50	920	0.714	0.286		0.824	0.176	
133	-50	1000	0.730		0.270	0.9502		0.0498
134	-50	1000	0.7362	0.0703	0.1935	0.9247	0.0322	0.0431
135	-50	1000	0.7402	0.0972	0.1626	0.9131	0.0469	0.0400
136	-50	1000	0.748	0.137	0.115	0.8928	0.0728	0.0344
137	-50	1000	0.7580	0.1615	0.0805	0.8742	0.0959	0.0299
138	-50	1000	0.8337	0.1310	0.0353	0.8364	0.1292	0.0344
	-50	1100	0.801		0.199	0.9358		0.0642
139	-100	100	0.137		0.863	0.9678		0.0322
140	-100	100	0.130	0.140	0.730	0.9235	0.0491	0.0274
141	-100	100	0.121	0.315	0.564	0.8677	0.1109	0.0214
142	-100	100	0.110	0.575	0.315	0.7846	0.2032	0.0122
143	-100	100	0.0979	0.9021		0.678	0.322	
144	-100	200	0.265		0.735	0.9820		0.0180
145	-100	200	0.260	0.116	0.624	0.9603	0.0243	0.0154
146	-100	200	0.248	0.424	0.328	0.9020	0.0896	0.0084

TABLE VI (Continued)

Code No.	Conditions Temp. OF.	Press. Psia.	Liquid Phase			Vapor Phase		
			CH ₄	C ₂ H ₆	C ₃ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈
147	-100	200	0.247	0.474	0.279	0.8921	0.1007	0.0072
148	-100	200	0.242	0.758		0.835	0.165	
149	-100	400	0.507		0.493	0.9884		0.0116
150	-100	400	0.505	0.170	0.325	0.9647	0.0272	0.0081
151	-100	400	0.507	0.236	0.257	0.9555	0.0380	0.0065
152	-100	400	0.511	0.302	0.187	0.9454	0.0496	0.0050
153	-100	400	0.5179	0.3849	0.0972	0.9323	0.0649	0.0028
154	-100	400	0.524	0.476		0.9168	0.0832	
155	-100	600	0.743		0.257	0.9894		0.0106
156	-100	600	0.7494	0.0524	0.1982	0.9811	0.0100	0.0089
157	-100	600	0.7682	0.1592	0.0726	0.9618	0.0341	0.0041
158	-100	600	0.780	0.220		0.9476	0.0524	
	-100	740	0.9201	0.0799		0.9609	0.0391	
	-100	765	0.9378		0.0622	0.9873		0.0127
159	-150	100	0.285		0.715	0.9966		0.0034
160	-150	100	0.271	0.253	0.476	0.9773	0.0205	0.0022
161	-150	100	0.270	0.270	0.460	0.9760	0.0218	0.0022
162	-150	100	0.264	0.440	0.296	0.9629	0.0357	0.0014
163	-150	100	0.2598	0.6692	0.0710	0.9451	0.0545	0.00034
164	-150	100	0.259	0.741		0.9396	0.0604	
165	-150	200	0.529		0.471	0.9982		0.0018
166	-150	200	0.526	0.131	0.343	0.9914	0.0073	0.0013
167	-150	200	0.531	0.203	0.266	0.9876	0.0114	0.0010
168	-150	200	0.538	0.313	0.149	0.9816	0.0178	0.00060
169	-150	200	0.5495	0.4027	0.0478	0.9764	0.0234	0.00020
170	-150	200	0.553	0.447		0.9738	0.0262	

TABLE VI (Continued)

Code No.	Conditions Temp. °F.	Press. Psia.	Liquid Phase			Vapor Phase		
			CH ₄	C ₂ H ₆	C ₃ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈
	-150	230	0.603		0.397	0.9985		0.0015
	-150	348	0.9549		0.0451	0.9995		0.0005
171	-200	100	0.847		0.153	0.99997		0.00003
172	-200	100	0.8660	0.0515	0.0823	0.99948	0.0005	0.00002
173	-200	100	0.8796	0.0824	0.0380	0.99913	0.00086	0.00001
175	-200	100	0.888	0.112		0.9987	0.0013	

TABLE VII
COMPARISON OF BWR PREDICTED K - VALUES WITH

SMOOTHED-EXPERIMENTAL DATA

Code No.	Temp. °F	Press. psia	Methane			Ethane			Propane		
			K _S	K _{BWR}	% Rel. Dev.	K _S	K _{BWR}	% Rel. Dev.	K _S	K _{BWR}	% Rel. Dev.
1	50	100	20.5	18.4	-10.2	3.27	3.27	0.0	0.945	0.939	-0.6
2	50	100	20.4	18.4	-9.8	3.26	3.26	0.0	0.947	0.939	-0.8
3	50	100							0.951	0.939	-1.3
5	50	200	10.3	9.59	-6.9				0.540	0.541	+0.2
7	50	200	10.2	9.48	-7.1	1.80	1.80	0.0	0.542	0.544	+0.4
8	50	200	10.1	9.30	-7.9	1.78	1.80	+1.1	0.545	0.549	+0.7
9	50	200	9.95	9.07	-8.8	1.77	1.79	+1.1	0.551	0.555	+0.7
10	50	200				1.75	1.77	+1.1	0.587	0.560	-4.6
11	50	400	5.55	4.93	-11.2				0.350	0.347	-0.9
12	50	400	5.12	4.76	-7.0	1.07	1.06	-0.9	0.357	0.359	-0.6
13	50	400	4.42	4.38	-0.9	1.07	1.06	-0.9	0.374	0.385	-2.9
14	50	400	4.33	4.33	0.0	1.07	1.06	-0.9	0.378	0.389	-2.9
15	50	400	3.94	4.02	+2.0	1.07	1.06	-0.9	0.398	0.410	-3.2
17	50	400				1.06	1.05	-0.9	0.424	0.430	-1.4
18	50	600	3.46	3.34	-3.5				0.304	0.300	-1.3
19	50	600	3.26	3.22	-1.2	0.860	0.831	-3.4	0.316	0.313	-0.9
20	50	600	3.23	3.20	-0.9	0.860	0.833	-3.1	0.320	0.316	-1.3
21	50	600	2.95	3.01	+2.0	0.860	0.843	-2.0	0.343	0.339	-1.2
22	50	600	2.88	2.94	+2.1	0.860	0.847	-1.5	0.352	0.348	-1.1
23	50	600	2.69	2.72	+1.1	0.860	0.857	-0.3	0.374	0.378	+1.1
24	50	600	2.57	2.56	-0.4	0.860	0.865	+0.6	0.390	0.403	+3.0
25	50	600	2.43	2.35	-3.3	0.860	0.876	+1.9			

TABLE VII (Continued)

Code No.	Temp. °F	Press. psia	Methane			Ethane			Propane		
			K _S	K _{BWR}	% Rel. Dev.	K _S	K _{BWR}	% Rel. Dev.	K _S	K _{BWR}	% Rel. Dev.
26	50	800	2.63	2.52	-4.2				0.303	0.299	-1.3
27	50	800	2.51	2.44	-2.8	0.748	0.741	-0.9	0.312	0.315	+1.0
28	50	800	2.18	2.22	+1.8	0.780	0.765	-1.9	0.350	0.358	+2.3
29	50	800	2.07	2.12	+2.4	0.790	0.777	-1.6	0.373	0.381	+2.1
30	50	800	1.91	1.98	+3.7	0.803	0.795	-1.0	0.415	0.418	+0.7
31	50	800	1.58	1.59	+0.6	0.852	0.855	+0.4			
32	50	1000	1.95	1.99	+2.1				0.332	0.330	-0.6
33	50	1000	1.82	1.85	+1.6	0.732	0.731	-0.1	0.379	0.376	-0.8
34	50	1000	1.76	1.80	+2.3	0.732	0.741	+1.2	0.397	0.394	-0.8
35	50	1000	1.61	1.64	+1.9	0.745	0.777	+4.3	0.442	0.459	+3.8
36	50	1000	1.38	1.39	+0.7	0.855	0.848	-0.8	0.596	0.602	+1.0
37	50	1000	1.16	1.17	+0.9	0.940	0.920	-2.1	0.776	0.776	0.0
38	50	1100	1.77	1.79	+1.1				0.365	0.360	-1.4
39	50	1100	1.77	1.77	0.0	0.748	0.716	-4.3	0.370	0.374	+1.1
40	50	1100	1.71	1.71	0.0	0.749	0.732	-2.3	0.394	0.400	+1.5
41	50	1100	1.58	1.60	+1.3	0.750	0.755	+0.7	0.445	0.441	-0.9
42	50	1100	1.52	1.55	+2.0	0.773	0.770	-0.4	0.478	0.468	-2.1
43	50	1100	1.42	1.51	+6.3	0.815	0.787	-3.4	0.527	0.497	-5.7
44	50	1100	1.12	1.21	+7.8	0.938	0.898	-4.3	0.830	0.730	-12.0
45	50	1200	1.56	1.61	+3.2				0.432	0.414	-4.2
46	50	1200	1.53	1.57	+2.6	0.800	0.742	-7.2	0.458	0.435	-5.0
47	50	1200	1.34	1.37	+2.2	0.813	0.808	-0.6	0.597	0.556	-6.9
48	50	1200	1.15	1.20	+4.3	0.901	0.888	-1.4	0.810	0.719	-11.2
--	50	1300	1.40	1.43	+2.1				0.514	0.497	-3.3
--	50	1367	1.19	1.29	+8.4				0.705	0.603	-14.5

TABLE VII (Continued)

Code No.	Temp. °F	Press. psia	Methane			Ethane			Propane		
			K _S	K _{BWR}	% Rel. Dev.	K _S	K _{BWR}	% Rel. Dev.	K _S	K _{BWR}	% Rel. Dev.
49	0	100	15.9	15.9	0.0				0.412	0.417	+1.2
50	0	100	15.8	15.9	-0.6	1.95	1.96	+0.5	0.412	0.418	+1.5
51	0	100	15.6	15.7	+0.6	1.95	1.96	+0.5	0.418	0.422	+1.0
52	0	100	15.4	15.6	+1.3	1.95	1.95	0.0	0.421	0.424	+0.7
53	0	100	14.8	15.3	+3.4	1.95	1.95	0.0	0.437	0.427	-2.3
55	0	200	8.47	8.12	-4.1				0.247	0.241	-2.4
57	0	200	8.04	7.87	-2.1	1.07	1.08	+0.9	0.256	0.250	-2.3
58	0	200	7.51	7.56	+0.7	1.07	1.08	+0.9	0.264	0.259	-1.9
59	0	200	6.33	7.01	+10.7	1.07	1.08	+0.9	0.278	0.275	-1.1
60	0	200				1.08	1.07	-0.9	0.283	0.280	-1.1
61	0	400	4.33	4.17	-3.7				0.168	0.163	-2.9
62	0	400	4.17	3.95	-5.3	0.626	0.659	+5.3	0.173	0.176	+1.7
63	0	400	3.94	3.78	-4.1	0.648	0.666	+2.8	0.181	0.187	+3.3
64	0	400	3.63	3.58	-1.3	0.662	0.676	+2.1	0.198	0.200	+1.0
65	0	400	3.29	3.40	+3.3	0.680	0.686	+0.8			
66	0	600	2.86	2.84	-0.7				0.158	0.150	-5.1
67	0	600	2.70	2.69	-0.4	0.518	0.541	+4.4	0.171	0.166	-2.9
68	0	600	2.64	2.63	-0.4	0.527	0.547	+3.8	0.184	0.172	-6.5
69	0	600	2.50	2.53	+1.2	0.549	0.558	+1.6	0.202	0.185	-3.5
70	0	600	2.32	2.39	+3.0	0.575	0.574	-0.2	0.240	0.203	-15.4
71	0	600	2.15	2.26	+5.1	0.596	0.592	-0.7			
72	0	800	2.16	2.16	0.0				0.173	0.163	-5.8
73	0	800	2.13	2.05	-3.8	0.498	0.510	+2.4	0.191	0.183	-4.2
74	0	800	2.03	1.94	-4.4	0.520	0.533	+2.5	0.210	0.206	-1.9
75	0	800	1.97	1.88	-4.6	0.540	0.546	+1.1	0.220	0.221	+0.5

TABLE VII (Continued)

Code No.	Temp. °F	Press. psia	Methane		Ethane		Propane	
			K_{BWR}	% Rel. Dev.	K_{BWR}	% Rel. Dev.	K_{BWR}	% Rel. Dev.
76	0	800	1.81	-1.1	0.576	-1.0	0.249	+6.9
77	0	800	1.58	+4.4	0.621	-1.5		
78	0	1000	1.71	+1.8			0.203	-7.7
79	0	1000	1.68	+0.6	0.548	-4.7	0.219	-6.8
80	0	1000	1.60	+0.6	0.562	-2.3	0.250	-6.0
81	0	1000	1.54	+1.3	0.583	-2.6	0.271	-5.9
82	0	1000	1.40	+3.6	0.643	-3.7	0.334	-5.9
83	0	1000	1.15	+8.7	0.840	-11.1	0.519	-42.3
84	0	1000	1.09	-4.6	0.901	+6.4		
85	0	1100	1.53	+3.3			0.268	-10.4
86	0	1100	1.50	+2.7	0.585	-5.8	0.259	-8.8
87	0	1100	1.46	+2.1	0.585	-2.4	0.282	-8.2
88	0	1100	1.41	+2.1	0.602	-1.2	0.312	-6.0
89	0	1100	1.35	+4.3	0.630	-2.2	0.338	-7.1
90	0	1100	1.28	+6.2	0.666	-3.3	0.375	-8.5
91	0	1100	1.23	+7.3	0.712	-6.2	0.408	-11.3
92	0	1100	1.19	+9.2	0.770	-11.3	0.430	-18.1
93	0	1100	1.10	+15.4	0.920	-22.8	0.468	-48.0
94	0	1200	1.37	+4.4			0.298	-14.9
95	0	1200	1.27	+5.5	0.710	-10.6	0.368	-15.0
96	0	1200	1.23	+7.3	0.720	-9.6	0.390	-17.2
97	0	1200	1.20	+8.3	0.740	-10.1	0.409	-19.3
98	0	1200	1.00	+23.0	1.00	-28.8	0.478	-52.2
99	0	1300	1.19	+8.4			0.405	-23.6
100	0	1300	1.17	+6.8	0.828	-16.4	0.450	-19.7

TABLE VII (Continued)

Code No.	Temp. °F	Press. psia	Methane			Ethane			Propane		
			K_{BWR}	% Rel. Dev.	K_S	K_{BWR}	% Rel. Dev.	K_S	K_{BWR}	% Rel. Dev.	
124	-50	600	2.11	2.05	-2.8	0.310	0.308	0.0795	0.0776	-2.4	
125	-50	600	2.11	2.05	-2.8	0.310	0.308	0.0800	0.0775	-3.1	
126	-50	600	2.04	2.01	-1.4	0.317	0.315	0.0840	0.0819	-2.5	
127	-50	600	1.96	1.94	-1.0	0.330	0.325	0.0896	0.0888	-0.9	
128	-50	600	1.83	1.82	-0.5	0.356	0.351			-1.4	
129	-50	800	1.65	1.62	-1.8			0.0978	0.0980	+0.2	
130	-50	800	1.55	1.57	+1.3	0.322	0.336	0.120	0.110	-8.3	
131	-50	800	1.44	1.47	+2.0	0.356	0.369	0.157	0.136	-13.4	
132	-50	800	1.34	1.36	+1.5	0.445	0.433				
---	-50	920	1.13	1.16	+2.7	0.659	0.609	-7.6			
133	-50	1000	1.29	1.30	+0.8			0.205	0.183	-10.7	
134	-50	1000	1.25	1.26	+0.8	0.510	0.458	0.275	0.222	-19.3	
135	-50	1000	1.22	1.23	+0.8	0.544	0.482	0.320	0.246	-23.1	
136	-50	1000	1.13	1.19	+5.3	0.635	0.531	0.425	0.299	-29.6	
137	-50	1000	1.10	1.16	+5.5	0.800	0.590	0.650	0.367	-43.6	
138	-50	1000	1.00	1.00	0.0	0.977	0.985	0.995	0.972	-2.3	
---	-50	1100	1.06	1.17	+10.4			0.678	0.321	-52.8	
139	-100	100	7.90	7.06	-10.6			0.0452	0.0372	-17.7	
140	-100	100	7.78	7.10	-8.8	0.327	0.350	0.0452	0.0375	-17.0	
141	-100	100	7.60	7.13	-6.2	0.335	0.352	0.0453	0.0379	-16.3	
142	-100	100	7.26	7.10	-2.2	0.345	0.354	0.0456	0.0387	-15.1	
143	-100	100	6.70	6.93	+3.4	0.356	0.357				
144	-100	200	4.40	3.67	-16.6			0.0261	0.0244	-6.5	

TABLE VII (Continued)

Code No.	Temp. °F	Press. psia	Methane			Ethane			Propane		
			K _{BWR}	% Rel. Dev.	K _S	K _{BWR}	% Rel. Dev.	K _S	K _{BWR}	% Rel. Dev.	
145	-100	200	3.67	-13.2	0.187	0.210	+12.3	0.0261	0.0247	-5.4	
146	-100	200	3.62	-5.0	0.201	0.212	+5.5	0.0261	0.0257	-1.5	
147	-100	200	3.60	-3.5	0.205	0.212	+3.4	0.0263	0.0259	-1.5	
148	-100	200	3.47	+8.1	0.249	0.217	-12.9				
149	-100	400	1.95	-5.3				0.0270	0.0234	-13.3	
150	-100	400	1.90	-3.6	0.149	0.160	+7.4	0.0291	0.0248	-14.8	
151	-100	400	1.87	-2.6	0.154	0.162	+5.2	0.0313	0.0256	-18.2	
152	-100	400	1.84	-1.2	0.156	0.164	+5.2	0.0362	0.0267	-26.2	
153	-100	400	1.80	0.0	0.164	0.168	+2.4	0.0481	0.0284	-42.2	
154	-100	400	1.75	+4.8	0.178	0.174	+2.3				
155	-100	600	1.33	+0.8				0.0540	0.0413	-23.5	
156	-100	600	1.31	+0.8	0.229	0.191	-16.6	0.0540	0.0448	-17.0	
157	-100	600	1.25	0.0	0.232	0.214	-7.8	0.0660	0.0572	-13.3	
158	-100	600	1.22	+0.8	0.237	0.238	+0.4				
---	-100	740	1.03	+1.0	0.593	0.485	-18.2				
---	-100	765	1.03	+1.9				0.312	0.203	-35.0	
159	-150	100	3.50	-16.0				0.0080	0.0047	-41.2	
160	-150	100	3.60	-10.0	0.110	0.0810	-26.4	0.0080	0.0047	-41.2	
161	-150	100	3.96	-9.1	0.109	0.0810	-25.7	0.0080	0.0047	-41.2	
162	-150	100	3.82	-5.0	0.103	0.0810	-21.3	0.0097	0.0047	-50.2	
163	-150	100	3.68	-1.4	0.0940	0.0813	-13.5	0.0252	0.0048	-80.8	
164	-150	100	3.61	0.0	0.0920	0.0815	-11.4				
165	-150	200	1.88	-6.5				0.0091	0.0038	-58.2	

TABLE VII (Continued)

Code No.	Temp. °F	Press. psia	K_S	Methane		Ethane		Propane	
				K_{BWR}	% Rel. Dev.	K_{BWR}	% Rel. Dev.	K_{BWR}	% Rel. Dev.
167	-150	200	1.92	1.84	-4.2	0.0860	0.0561	0.0039	-59.8
168	-150	200	1.83	1.82	-0.5	0.0745	0.0569	0.0040	-74.1
169	-150	200	1.76	1.78	+1.1	0.0710	0.0581	0.0043	-88.4
170	-150	200	1.73	1.76	+1.7	0.0702	0.0589		
---	-150	230	1.71	1.65	-3.5			0.0039	-61.4
---	-150	348	1.04	1.05	+1.0			0.0117	-36.4
171	-200	100	1.24	1.18	-4.8			0.0035	-94.3
172	-200	100	1.23	1.15	-6.5	0.0337	0.0100	0.0060	-97.8
173	-200	100	1.22	1.11	-9.0	0.0285	0.0110	0.0155	-98.1
175	-200	100	1.21	1.12	-7.4	0.0245	0.0110		

 K_S smoothed experimental K-value K_{BWR} predicted K-value from BWR equation

TABLE VIII
COMPARISON OF K-VALUES FROM MABP CORRELATION
WITH SMOOTHED EXPERIMENTAL DATA

Code No.	Temp. °F	Press. psia	K=AB	K _S	Methane % Rel. Dev.	Ethane K _S	% Rel. Dev.	K=AB	Propane K _S	% Rel. Dev.
1	50	100	21.5	20.5	+4.9			0.945	0.945	0.0
2	50	100	21.4	20.4	+4.9	3.31	+1.2	0.945	0.947	-0.2
4	50	100				3.30	+1.2	0.945	0.951	-0.6
5	50	200	10.9	10.3	+5.8			0.513	0.540	-5.0
7	50	200	10.6	10.2	+3.9	1.80	0.0	0.513	0.542	-5.4
8	50	200	10.2	10.1	+0.9	1.79	+0.6	0.524	0.545	-3.9
9	50	200	9.81	9.95	-1.4	1.79	+1.1	0.528	0.551	-4.2
10	50	200				1.79	+2.3	0.533	0.587	-9.2
11	50	400	5.50	5.55	-0.9			0.345	0.350	-1.4
12	50	400	5.16	5.12	+0.8	1.02	-4.7	0.355	0.357	-0.6
13	50	400	4.55	4.42	+2.9	1.05	-1.9	0.378	0.374	+1.1
14	50	400	4.47	4.33	+3.2	1.05	-1.9	0.391	0.378	+3.4
15	50	400	4.11	3.94	+4.3	1.05	-1.9	0.400	0.398	+0.5
17	50	400				1.05	-0.9	0.420	0.424	-0.9
18	50	600	3.61	3.46	+4.3			0.304	0.304	0.0
19	50	600	3.38	3.26	+3.7	0.817	-5.0	0.319	0.316	+0.9
20	50	600	3.34	3.23	+3.4	0.817	-5.0	0.319	0.320	-0.3
21	50	600	3.10	2.95	+5.1	0.844	-1.9	0.343	0.343	0.0
22	50	600	2.98	2.88	+3.5	0.845	-1.7	0.348	0.352	-1.1
23	50	600	2.75	2.69	+2.2	0.858	-0.2	0.377	0.374	+0.8
24	50	600	2.69	2.57	+1.2	0.866	+0.7	0.399	0.390	+2.3
25	50	600	2.38	2.43	-2.1	0.871	+1.3			

TABLE VIII (Continued)

Code No.	Temp. °F	Press. psia	Methane		Ethane		Propane		% Rel. Dev.
			K _S	% Rel. Dev.	K _S	% Rel. Dev.	K=AB	K _S	
26	50	800	2.65	+0.8			0.296	0.303	-2.3
27	50	800	2.50	-0.4	0.728	-2.7	0.314	0.312	+0.6
28	50	800	2.21	+1.4	0.753	-3.5	0.354	0.350	+1.1
29	50	800	2.09	+1.0	0.776	-1.8	0.371	0.373	-0.5
30	50	800	1.95	+2.1	0.798	-0.6	0.402	0.415	-3.1
31	50	800	1.63	+3.2	0.839	-1.5			
32	50	1000	1.99	+2.1			0.328	0.332	-1.2
33	50	1000	1.83	+0.5	0.735	+0.4	0.374	0.379	-1.3
34	50	1000	1.76	0.0	0.744	+1.6	0.388	0.397	-2.3
35	50	1000	1.55	-3.7	0.789	+5.9	0.456	0.442	+3.2
36	50	1000	1.33	-3.6	0.856	+0.1	0.595	0.596	-0.2
37	50	1000	1.23	+6.0	0.885	-5.9	0.759	0.776	-2.2
38	50	1100	1.83	+3.4			0.365	0.365	0.0
39	50	1100	1.81	+2.3	0.732	-2.1	0.380	0.370	+2.7
40	50	1100	1.73	+1.2	0.755	+0.8	0.409	0.394	+3.8
41	50	1100	1.58	0.0	0.773	+3.1	0.452	0.445	+1.6
42	50	1100	1.53	+0.7	0.794	+2.7	0.477	0.478	-0.2
43	50	1100	1.47	+3.5	0.817	+0.2	0.519	0.527	-1.5
44	50	1100	1.13	+0.9	0.974	+4.7	0.844	0.830	+1.7
45	50	1200	1.61	+3.2			0.436	0.432	+0.9
46	50	1200	1.53	0.0	0.786	-1.7	0.458	0.458	0.0
47	50	1200	1.31	-2.3	0.844	+3.8	0.609	0.597	+2.0
48	50	1200	1.12	-2.6	0.937	+4.0	0.812	0.810	+0.2
49	0	100	15.7	-1.3			0.440	0.412	+6.8

TABLE VIII (Continued)

Code No.	Temp. °F	Press psia	Methane			Ethane			Propane		
			K=AB	K _S	% Rel. Dev.	K=AB	K _S	% Rel. Dev.	K=AB	K _S	% Rel. Dev.
50	0	100	15.7	15.8	-0.6	1.96	1.95	+0.5	0.440	0.412	+6.8
51	0	100	15.5	15.6	-0.6	1.96	1.95	+0.5	0.444	0.418	+5.9
52	0	100	15.4	15.4	0.0	1.96	1.95	+0.5	0.450	0.421	+6.4
53	0	100	15.0	14.8	+1.4	1.96	1.95	+0.5	0.455	0.437	+4.3
55	0	200	8.40	8.47	-0.8				0.241	0.247	-2.4
57	0	200	8.22	8.04	+2.2	1.06	1.07	-0.9	0.248	0.256	-3.1
58	0	200	7.61	7.51	+1.3	1.07	1.07	0.0	0.258	0.264	-3.0
59	0	200	6.86	6.33	+8.4	1.10	1.07	+2.8	0.270	0.278	-2.9
60	0	200				1.10	1.08	+1.9	0.272	0.283	-3.9
61	0	400	4.33	4.33	0.0				0.173	0.168	+3.0
62	0	400	4.07	4.17	-2.4	0.625	0.626	-0.2	0.186	0.173	+7.5
63	0	400	3.82	3.94	-3.0	0.641	0.648	-1.1	0.196	0.181	+8.3
64	0	400	3.61	3.63	-0.6	0.649	0.662	-2.0	0.199	0.198	+0.5
65	0	400	3.38	3.29	+2.7	0.676	0.680	-0.6			
66	0	600	2.93	2.86	+2.5				0.165	0.158	+4.4
67	0	600	2.70	2.70	0.0	0.522	0.518	+0.8	0.179	0.171	+4.7
68	0	600	2.62	2.64	-0.8	0.533	0.527	+1.1	0.185	0.184	+0.5
69	0	600	2.50	2.50	0.0	0.552	0.549	+0.5	0.195	0.202	-3.5
70	0	600	2.34	2.32	+0.9	0.581	0.575	+1.0	0.208	0.240	-9.4
71	0	600	2.24	2.15	+4.2	0.598	0.596	+0.3			
72	0	800	2.28	2.16	+5.6				0.177	0.173	+2.3
73	0	800	2.04	2.13	-4.2	0.493	0.498	-1.0	0.192	0.191	+0.5
74	0	800	1.92	2.03	-5.4	0.525	0.520	+1.0	0.210	0.210	0.0
75	0	800	1.85	1.97	-6.1	0.539	0.540	-0.2	0.217	0.220	-1.4
76	0	800	1.75	1.81	-3.3	0.569	0.576	-1.2	0.237	0.233	+1.7

TABLE VIII (Continued)

Code No.	Temp. °F	Press psia	Methane		Ethane		Propane			
			K=AB	K _S	% Rel. Dev.	K=AB	K _S	% Rel. Dev.		
77	0	800	1.58	1.58	0.0	0.614	0.621	-1.1		
78	0	1000	1.75	1.71	+2.3				0.220	+2.7
79	0	1000	1.67	1.68	-0.6	0.530	0.548	-3.3	0.235	0.0
80	0	1000	1.58	1.60	-1.3	0.565	0.562	+0.5	0.268	+0.8
81	0	1000	1.52	1.54	-1.3	0.592	0.583	+1.5	0.288	0.0
82	0	1000	1.38	1.40	-1.4	0.664	0.643	+3.3	0.360	+1.4
83	0	1000	1.18	1.15	+2.6	0.784	0.840	-6.7	0.513	-17.0
84	0	1000	1.04	1.09	-4.6	0.973	0.901	+8.0		
85	0	1100	1.57	1.53	+2.6				0.258	-3.7
86	0	1100	1.53	1.50	+2.0	0.591	0.585	+1.0	0.289	+1.8
87	0	1100	1.44	1.46	-1.4	0.624	0.585	+6.7	0.319	+3.9
88	0	1100	1.41	1.41	0.0	0.635	0.602	+5.5	0.326	-1.8
89	0	1100	1.35	1.35	0.0	0.669	0.630	+6.2	0.365	+0.3
90	0	1100	1.32	1.28	+3.1	0.703	0.666	+5.6	0.401	-2.2
91	0	1100	1.27	1.23	+3.3	0.741	0.712	+4.1	0.451	-2.0
92	0	1100	1.24	1.19	+4.2	0.769	0.770	-0.1	0.481	-8.4
93	0	1100	1.20	1.10	+9.1	0.809	0.920	12.1	0.535	-24.7
94	0	1200	1.38	1.37	+0.7			+5.4	0.348	-0.6
95	0	1200	1.29	1.27	+1.6	0.748	0.710	+2.5	0.438	+1.2
96	0	1200	1.23	1.23	0.0	0.738	0.720	+5.0	0.464	-1.5
97	0	1200	1.21	1.20	+0.8	0.777	0.740	+22.0	0.500	-1.4
98	0	1200	0.994	1.00	-0.6	1.22	1.00		1.37	+37.0
99	0	1300	1.19	1.19	0.0				0.540	+1.7
100	0	1300	1.14	1.17	-2.6	0.895	0.828	+8.1	0.622	+11.1

TABLE VIII (Continued)

Code No.	Temp. °F.	Press. psia	Methane		Ethane		Propane		% Rel. Dev.
			K=AB	K _S	K=AB	K _S	K=AB	K _S	
101	0	1300	1.09	1.11	0.947	0.960	0.778	0.630	23.5
102	0	1300	1.05	1.00	1.040	1.00	1.018	1.00	1.8
103	-50	100	11.6	11.5	0.9		0.161	0.160	0.6
104	-50	100	11.4	11.3	0.951	0.950	0.161	0.160	0.6
105	-50	100	11.2	11.2	0.955	0.950	0.161	0.160	0.6
106	-50	100	11.0	11.1	0.955	0.950	0.160	0.160	0.0
107	-50	100	10.9	10.9	0.955	0.950	0.161	0.160	0.6
108	-50	100	10.3	10.8	0.969	0.950	0.161	0.160	0.6
109	-50	100	9.70	10.7	0.975	0.950	0.161	0.160	0.6
110	-50	200	6.21	6.50			0.0889	0.0920	-3.4
111	-50	200	6.02	6.19	0.528	0.530	0.0906	0.0920	-1.5
112	-50	200	5.91	6.00	0.533	0.531	0.0911	0.0922	-1.2
113	-50	200	5.61	5.60	0.546	0.534	0.0929	0.115	-19.2
114	-50	200	5.26	5.00	0.553	0.540			
115	-50	400	3.26	3.20	1.9		0.0709	0.0710	-0.1
116	-50	400	3.19	3.18	0.3	0.304	0.0723	0.0710	1.8
117	-50	400	3.11	3.11	0.0	0.313	0.0741	0.0710	4.4
118	-50	400	2.97	2.97	0.0	0.331	0.0778	0.0750	3.7
119	-50	400	2.90	2.91	-0.3	0.340	0.0790	0.0815	-3.1
120	-50	400	2.88	2.88	0.0	0.343	0.0796	0.0840	-5.2
121	-50	400	2.84	2.83	0.4	0.352	0.0802	0.0950	-15.6
122	-50	400	2.69	2.61	3.1	0.385			
123	-50	600	2.18	2.19	-0.5		0.0744	0.0739	0.7
124	-50	600	2.13	2.11	0.9	0.310	0.0795	0.0795	0.0
126	-50	600	2.04	2.04	0.0	0.317	0.0824	0.0840	1.9
127	-50	600	1.97	1.96	0.5	0.330	0.0890	0.0896	-0.7
128	-50	600	1.84	1.83	0.5	0.356			
129	-50	800	1.63	1.65	-1.2		0.0959	0.0978	-1.9
130	-50	800	1.55	1.55	0.0	0.328	0.114	0.120	-5.0
131	-50	800	1.44	1.44	0.0	0.373	0.145	0.151	-4.0
132	-50	800	1.35	1.34	0.7	0.460			

TABLE VIII (Continued)

Code No.	Temp. OF.	Press. psia.	K=AB	Methane K _S	% Rel. Del.	K=AB	Ethane K _S	% Rel. Del.	K=AB	Propane K _S	% Rel. Del.
159	-150	100	4.19	4.17	0.5				0.0081	0.0080	1.3
160	-150	100	3.98	4.00	-0.5	0.114	0.110	3.5	0.0086	0.0080	7.5
161	-150	100	3.98	3.96	0.5	0.114	0.109	4.6	0.0087	0.0080	8.8
162	-150	100	3.79	3.82	-0.8	0.106	0.103	2.9	0.0096	0.0097	-1.0
163	-150	100	3.64	3.68	-1.1	0.0937	0.094	-0.3	0.0112	0.0252	-55.5
164	-150	100	3.54	3.61	-1.9	0.0869	0.092	-5.5			
165	-150	200	2.13	2.01	6.0				0.0078	0.0091	-14.3
166	-150	200	2.01	1.96	2.6	0.0850	0.112	-14.5	0.0089	0.0092	-3.3
167	-150	200	1.94	1.92	1.0	0.0796	0.086	-7.4	0.0117	0.0097	20.6
168	-150	200	1.85	1.83	1.1	0.0749	0.0745	0.5	0.0156	0.0155	0.6
169	-150	200	1.78	1.76	1.1	0.0704	0.0710	-0.8	0.0370	0.0370	0.0
170	-150	200	1.76	1.73	1.7	0.0688	0.0702	-2.0			
	-150	230	1.74	1.71	1.7				0.0103	0.0101	2.0
	-150	348	1.02	1.04	-1.9						
171	-200	100	1.24	1.24	0.0				0.0036	0.0035	2.9
172	-200	100	1.22	1.23	-0.8	0.0338	0.0337	0.3	0.0060	0.0060	0.0
173	-200	100	1.21	1.22	-0.8	0.0290	0.0285	1.8	0.0155	0.0155	0.0
175	-200	100	1.21	1.21	0.0	0.0248	0.0245	1.2			
		Avg. 2.0% (179)		Avg. 2.8% (140)		Avg. 4.1% (163)					

TABLE IX
COMPARISON OF K-VALUES FROM MABP CORRELATION WITH INDEPENDENT DATA

Component	System	Source	Temp. °F	Press. psia	(MABP) L °F	(MABP) V °F	K corr.	K exp.	% Rel.Dev.
Methane	C1 - C2 =	(25)	-152	147	-190	-247	2.28	2.6	-14.1
	C1 - C2 =	(25)	-152	294	-238	-257	1.18	1.2	- 1.7
	C1 - C2 =	(25)	-128	294	-204	-247	1.70	1.9	-10.5
	C1 - C2 =	(25)	-128	441	-235	-254	1.16	1.2	- 3.3
	C1 - C2 =	(25)	-108	294	-196	-240	2.10	2.1	0.0
	C1 - C2 =	(25)	-108	588	-224	-247	1.19	1.3	- 8.5
	C1 - C2 =	(49)	- 6	282	- 8	-246	6.58	6.7	- 1.8
	C1 - C2 =	(49)	0	429	- 26	-247	4.65	4.8	- 3.1
	C1 - C2 = -C2	(25)	-152	147	-178	-248	2.42	2.75	-12.0
	C1 - C2 = -C2	(25)	-108	147	-159	-227	4.12	4.72	-12.7
	C1 - C2 = -C2	(25)	-108	294	-185	-245	2.16	2.34	- 7.7
	C1 - C2 = -C2	(25)	32	735	-158	-174	1.88	1.92	- 2.1
	C1 - C2 = -C2	(20)	- 60	115	- 24	-234	10.1	10.2	- 1.0
	C1 - C2 = -C2	(20)	- 60	109	- 16	-244	10.5	10.0	+ 5.0
	C1 - C2 = -C2	(20)	- 60	204	- 89	-234	5.60	5.33	+ 5.1
	C1 - C2 = -C2	(20)	- 60	288	-105	-236	4.04	3.74	+ 8.0
	C1 - C2 = -C2	(20)	- 20	100	+ 1	-229	15.2	15.8	- 3.8
	C1 - C2 = -C2	(20)	- 20	200	- 51	-221	7.80	7.50	+ 4.0
	C1 - C2 = -C2	(20)	+ 20	200	- 28	-219	10.2	9.51	+ 7.3
	C1 - C2 = -C2	(20)	+ 20	200	- 83	-148	8.43	8.39	+ 0.5
	C1 - C2 = -C2	(20)	+ 20	200	- 95	-121	no CH ₄	in vapor	-----
	C1 - C2 = -C2	(20)	+ 20	200	- 1	-214	10.6	10.2	+ 3.9
	C1 - C2 = -C2	(20)	+ 20	200	+ 49	-229	11.6	11.0	+ 5.5
	C1 - C2 = -C2	(15)	- 47	500	+ 79	-254	3.38	4.23	-20.1
	C1 - C2 = -C2	(15)	- 42	1000	- 51	-254	2.13	3.08	-30.9

TABLE IX (Continued)

Component	System	Source	Temp. °F	Press. psia	(MABP) _L °F	(MABP) _V °F	K corr.	K exp.	% Rel.Dev.
Methane	C1---C10+	(15)	+ 12	1000	+ 58	-253	3.15	3.07	+ 2.6
	C1---C10+	(15)	- 15	1500	- 16	-252	2.15	1.98	+ 7.9
	C1---C10+	(15)	+ 38	1500	+ 43	-253	3.23	2.47	+30.8
	C1---iC8	(57)	-100	738	-247	-256	0.995	1.063	- 6.4
	C1---iC8	(57)	-105	675	-244	-256	1.04	1.07	- 2.8
	C1---iC8	(57)	- 80	822	-232	-252	1.12	1.13	- 0.9
	C1---iC8	(57)	- 95	648	-220	-255	1.24	1.22	+ 1.6
	C1---C5	(57)	- 80	800	-209	-254	1.23	1.22	+ 0.8
	C1---C5	(57)	- 95	665	-232	-254	1.17	1.13	+ 3.5
Ethane	C2 - C2	(29)	0	255	-133	-136	0.916	0.895	+ 2.3
	C2 - C2	(29)	0	355	-150	-151	0.761	0.746	+ 2.0
	C2 - C2	(29)	- 40	135	-133	-135	0.895	0.864	+ 3.6
	C2 - C2	(29)	- 40	192	-150	-151	0.687	0.691	- 0.6
	C2 - C2	(29)	-100	61	-150	-152	0.548	0.607	- 9.7
	C2 - C3	(45)	10	200	-109	-120	1.19	1.20	- 0.9
	C2 - C3	(45)	40	300	-109	-121	1.22	1.18	- 3.4
	C1 - C2=C2	(25)	-152	147	-178	-248	0.0749	0.103	-24.6
	C1 - C2=C2	(25)	-108	147	-159	-227	0.234	0.256	- 8.6
	C1 - C2=C2	(25)	-108	294	-185	-245	0.155	0.195	-20.5
	C1 - C2=C2	(25)	32	735	-158	-174	0.753	0.795	- 5.6
	C1---iC6	(20)	- 60	115	- 24	-234	0.686	0.67	+ 2.4
	C1---iC6	(20)	- 60	109	- 16	-244	0.716	0.66	+ 8.5
	C1---nC4	(20)	- 60	204	- 89	-234	0.430	0.425	+ 1.2
	C1---nC4	(20)	- 60	288	-105	-236	0.345	0.337	+ 2.4
	C1---nC5	(20)	- 20	100	+ 1	-229	1.47	1.42	+ 3.5
	C2 - C2	(29)	0	255	-133	-136	0.916	0.895	+ 2.3
	C2 - C2	(29)	0	355	-150	-151	0.761	0.746	+ 2.0
	C2 - C2	(29)	- 40	135	-133	-135	0.895	0.864	+ 3.6
	C2 - C2	(29)	- 40	192	-150	-151	0.687	0.691	- 0.6
	C2 - C2	(29)	-100	61	-150	-152	0.548	0.607	- 9.7

TABLE IX (Continued)

Component	System	Source	Temp. °F	Press. psia	(MABP) _L °F	(MABP) _V °F	K corr.	K exp.	% Rel.Dev.
Ethane	C1---iC4	(20)	- 20	200	- 51	-221	0.810	0.804	+ 0.7
	C1---iC4	(20)	+ 20	200	- 28	-219	1.29	1.22	+ 5.7
	C1---iC4	(20)	+ 20	200	- 83	-148	1.34	1.33	+ 0.8
	C1---iC4	(20)	+ 20	200	- 95	-121	1.34	1.31	+ 3.1
	C1---iC4	(20)	+ 20	200	- 1	-214	1.29	1.36	- 5.2
	C1---iC4	(20)	+ 20	200	+ 49	-229	1.29	1.27	+ 1.6
	C1---C10+	(15)	- 47	500	+ 79	-254	0.288	0.334	-13.8
	C1---C10+	(15)	- 42	1000	- 51	-254	0.322	0.280	+15.0
	C1---C10+	(15)	+ 12	1000	+ 58	-253	0.452	0.471	- 4.0
	C1---C10+	(15)	- 15	1500	- 16	-252	0.479	0.500	- 4.2
	C1---C10+	(15)	+ 38	1500	+ 43	-253	0.569	0.381	+49.3
	C1---iC8	(57)	-100	738	-247	-256	0.389	0.313	+24.3
	C1---iC8	(57)	-105	675	-244	-256	0.330	0.287	+15.0
	C1---iC8	(57)	- 80	822	-232	-252	0.432	0.368	+17.4
	C1---iC8	(57)	- 95	648	-220	-255	0.243	0.222	+ 9.5
	C1---C5	(57)	- 80	800	-209	-254	0.289	0.285	+ 1.4
	C1---C5	(57)	- 95	665	-232	-254	0.281	0.318	-11.6
	C1---iC6	(20)	- 60	115	- 24	-234	0.119	0.145	-17.9
	C1---iC6	(20)	- 60	109	- 16	-244	0.126	0.096	+31.3
	C1---nC4	(20)	- 60	204	- 89	-234	0.0718	0.108	-32.6
Propane	C1---nC4	(20)	- 60	288	-105	-236	0.0680	0.115	-40.8
	C1---nC5	(20)	- 20	100	+ 1	-229	0.302	0.280	+ 7.9
	C1---iC4	(20)	- 20	200	- 51	-221	0.167	0.175	- 4.6
	C1---iC4	(20)	20	200	- 28	-219	0.326	0.318	+ 2.5
	C1---iC4	(20)	20	200	- 83	-148	0.352	0.352	0.0

TABLE IX (Continued)

Component	System	Source	Temp. °F	Press. psia	(MABP) _L °F	(MABP) _V °F	K corr.	K exp.	% Rel.Dev.
Propane	C1---iC4	(20)	20	200	- 95	-121	0.366	0.354	+ 3.4
	C1---iC4	(20)	20	200	- 1	-214	0.326	0.338	- 2.4
	C1---iC4	(20)	20	200	+ 49	-229	0.321	0.324	- 0.9
	C1---C10+	(15)	- 47	500	+ 79	-254	0.0845	0.0553	+52.8
	C1---C10+	(15)	- 42	1000	- 51	-254	0.114	0.0493	+131.
	C1---C10+	(15)	+ 12	1000	+ 58	-253	0.178	0.113	+57.5
	C1---C10+	(15)	- 15	1500	- 16	-252	0.240	0.127	+89.0
	C1---C10+	(15)	+ 38	1500	+ 43	-253	0.231	0.165	+40.0
	C1---iC8	(57)	-100	738	-247	-256	0.295	0.143	+106.
	C1---iC8	(57)	-105	675	-244	-256	0.212	0.124	+71.
	C1---iC8	(57)	- 80	822	-232	-252	0.365	0.178	+105.
	C1---iC8	(57)	- 95	648	-220	-255	0.079	0.073	+ 8.5
	C1---iC8	(57)	- 80	800	-209	-254	0.127	0.112	+13.4
	C1---nC5	(57)	- 95	665	-232	-254	0.108	0.142	-23.9

TABLE X

COMPARISON OF K-VALUES FROM CORRESPONDING STATES CORRELATION WITH EXPERIMENTAL RESULTS

Component	System	Source	Temp. °F	Press. psia	K exp.	K corr.	% Rel. Dev.	$\frac{Pr_L}{Pr_i}(\psi_L - \psi_c)$	$\ln \Delta$
Methane	C1 - C3	(62)	160	1000	1.27	1.25	-1.89	0.337	0.0149
	C1 - C3	(62)	100	500	4.21	4.40	+4.5	2.18	-0.0591
	C1 - C4	(62)	250	1000	1.97	1.88	-4.6	1.12	0.0463
	C1 - C4	(62)	100	500	5.45	5.45	0	3.52	0.1011
	C1 - iC4	(49A)	100	500	4.92	4.08	-17.1	3.02	0.2409
	C1 - C5	(62)	160	2000	1.57	1.598	+1.8	1.42	-0.0194
	C1 - C5	(62)	280	1500	1.47	1.438	-2.2	0.774	0.0119
	C1 - C10	(62)	460	2000	2.06	1.593	-21.1	2.29	0.2719
	C1 - C10	(62)	100	2000	2.23	2.33	+4.48	6.27	0.3642
	C1 - C4 - C10	(62)	160	400	8.59	9.95	+15.85	7.92	0.5613
	C1 - C4 - C10	(62)	160	2000	1.70	1.665	-1.76	1.82	0.0157
	C1 - C4 - C10	(62)	160	2000	2.29	1.975	-13.51	4.79	0.351
	C1 - C3 - C5	(17) (19)	100	500	5.74	5.73	-0.2	4.57	0.1204
	C1 - C3 - C5	(17) (19)	160	1000	3.22	3.27	+5.3	3.06	0.0351
	C1 - C3 - C5	(8A)	100	1000	2.45	2.65	+8.16	2.09	-0.0770
	C1 - C2 = -iC4	(3A)	100	500	5.15	4.24	-17.68	2.57	0.2221
	C1 - C2 = -iC4	(3A)	160	500	5.04	4.47	-11.3	2.48	0.1422
	C1 - C2 = -iC4	(3A)	160	500	4.93	4.44	-9.95	2.37	0.1242
	C1 - C2 - C3	This work	-150	100	4.00	4.17	+4.3	4.12	0.0950
	C1 - C2 - C3	This work	-150	100	3.83	3.86	0.8	3.52	0.0744
	C1 - C2 - C3	This work	-150	100	3.69	3.63	-1.6	2.77	0.0541
	C1 - C2 - C3	This work	-150	200	1.99	1.69	-15.0	2.74	0.2021
	C1 - C2 - C3	This work	-150	200	1.91	1.528	-19.9	2.38	0.2392
	C1 - C2 - C3	This work	-150	200	1.75	1.67	-4.6	1.60	0.0435
	C1 - C2 - C3	This work	50	1000	1.77	1.97	10.0	1.20	-0.1189

TABLE X (Continued)

Component	System	Source	Temp. °F	Press. psia	K exp.	K corr.	% Rel. Dev.	$\frac{P_{RL}(\psi_L - \psi_e)}{P_{Ri}}$	$\ln \Delta$
Methane	C1-C6	(29)	100	1419	1.98	2.15	+ 8.6	2.20	-0.0655
	C1-C6	(29)	100	1822	1.37	1.36	- 0.7	0.991	-0.002
Ethylene	C2-C7	(35A)	185	1000	1.59	1.55	- 2.5	1.89	0.1627
	C2-C7	(35A)	350	1000	1.94	1.925	- 0.8	1.86	0.1430
	C1-C2-C5	(8A)	100	1000	0.912	0.907	- 0.55	0.929	0.0689
	C1-C2=iC4	(3A)	100	500	1.73	1.654	- 4.4	1.55	0.1504
	C1-C2=iC4	(3A)	160	500	2.10	2.190	+ 4.2	1.65	0.0763
	C1-C2=iC4	(3A)	160	500	2.26	2.16	- 4.4	1.48	0.1463
	C1-C2-C3	This work	-150	100	0.109	0.1122	+ 2.9	0.585	0.0217
Ethane	C1-C2-C3	This work	-150	100	0.0971	0.1093	+ 1.25	0.052	-0.0787
	C1-C2-C3	This work	-150	100	0.101	0.0917	- 9.2	-0.512	0.1427
	C1-C2-C3	This work	-150	200	0.123	0.0641	-47.2	-0.574	0.6992
	C1-C2-C3	This work	-150	200	0.0803	0.0634	-21.1	-0.858	0.3013
	C1-C2-C3	This work	-150	200	0.0735	0.0843	-14.7	-1.46	-0.0100
	C1-C2-C3	This work	50	1000	0.729	0.726	- 0.4	0.156	0.0499
	C1-C2-C3	This work	0	1000	0.586	0.543	- 7.3	-0.111	0.1168
	C1-C2-C3	This work	- 50	1000	0.671	0.645	- 3.9	-0.342	0.0836
	C1-C2-C3	This work	-100	600	0.229	0.212	- 7.4	-0.932	0.1404
	C1-C2-C3	This work	-150	200	0.0733	0.0706	- 3.7	-1.17	0.1187
	C1-C2-C3	This work	-200	100	0.0157	0.01324	-15.9	-2.96	0.4556
	C1-C2-C3	This work	- 50	800	0.332	0.202	-39.2	-0.897	0.5651
	C1-C2-C3	This work	-200	100	0.0234	0.0277	+18.4	-3.14	0.1377
	C1-C2-C3	This work	0	1300	0.933	0.788	-15.6	-0.121	0.2096
	C1-C2-C3	This work	- 50	1000	0.565	0.509	- 9.9	-0.443	0.1715
	C1-C2-C3	This work	-100	400	0.150	0.1675	+11.7	-0.495	-0.0668
	C1-C2-C3	This work	-150	100	0.109	0.1122	+ 2.9	0.585	0.0217
	C1-C2-C3	This work	-150	100	0.0971	0.1093	+ 1.25	0.052	-0.0787
	C1-C2-C3	This work	-150	100	0.101	0.0917	- 9.2	-0.512	0.1427
	C1-C2-C3	This work	-150	200	0.123	0.0641	-47.2	-0.574	0.6992
	C1-C2-C3	This work	-150	200	0.0803	0.0634	-21.1	-0.858	0.3013
	C1-C2-C3	This work	-150	200	0.0735	0.0843	-14.7	-1.46	-0.0100

TABLE X (Continued)

Component	System	Source	Temp. °F	Press. psia	K exp.	K corr.	% Rel. Dev.	$\frac{P_{R_i}}{P_{R_i}}(\psi_L - \psi_G)$	$\ln \Delta$
Ethane	C1-C2-C3	This work	-150	100	0.112	0.0678	-39.5	0.001	0.5418
	C1-C2-C3	This work	-50	600	0.297	0.266	-10.4	-0.0928	0.1535
	C1-C2-C3	This work	-100	200	0.193	0.197	+2.0	0.153	0.0233
	C1-C2-C3	This work	-100	600	0.227	0.228	+0.4	-1.138	0.0679
	C1-C2-C3	This work	0	1200	0.708	0.622	-12.1	-0.164	0.1735
	C1-C2-C3	This work	-50	100	0.356	0.342	-3.9	-0.602	0.0974
	C1-C2-C3	(8A)	100	2000	0.864	0.880	+1.85	0.347	0.0277
	C1-C2-C5	(28)	100	517	1.51	1.271	-15.9	2.56	0.3937
	C1-C2-C5	(28)	100	946	0.873	0.887	+1.6	1.72	0.0674
	C1-C2-C5	(28)	100	1431	0.872	0.783	-10.2	1.097	0.1822
	C1-C2-C5	(28)	100	1736	0.838	0.688	-16.7	0.512	0.2434
	C1-C2-C6	(28)	100	1235	0.784	0.819	+4.5	1.254	0.0407
	C1-C2-C6	(28)	100	1419	0.890	0.808	-9.2	1.10	0.1716
	C1-C2-C6	(28)	100	1822	0.836	0.738	-15.6	0.314	0.1686
	C1-C2-C6	(62)	100	500	0.547	0.534	-2.4	-0.155	0.0779
	C1-C2-C6	(62)	160	1000	0.894	1.381	+54.5	0.018	-0.3866
Propane	C1-C2-C3	(62A)	220	500	1.18	1.192	+0.85	0.262	0.0485
	C1-C2-C3	(17)(19)	100	500	0.514	0.507	-1.4	1.357	0.1580
	C1-C2-C3	(17)(19)	160	1000	0.548	0.537	-2.0	0.781	0.1044
	C1-C2-C3	This work	-150	100	0.0064	0.01225	+92.2	-1.682	-0.4490
	C1-C2-C3	This work	-150	100	0.00984	0.01282	+30.0	-2.10	0.0054
	C1-C2-C3	This work	-150	100	0.0265	0.0346	+30.6	-2.47	0.0827
	C1-C2-C3	This work	-150	200	0.00456	0.00953	+109.0	-2.54	-0.3639
	C1-C2-C3	This work	-150	200	0.00971	0.01005	+3.5	-2.72	0.3892
	C1-C2-C3	This work	-150	200	0.0342	0.0405	+18.4	-3.12	0.3687
	C1-C2-C3	This work	50	1000	0.400	0.353	-11.7	-0.539	0.1890
	C1-C2-C3	This work	0	1000	0.279	0.241	-13.6	-0.847	0.2110

TABLE X (Continued)

Component	System	Source	Temp. °F	Press. psia	K exp.	K corr.	% Rel. Dev.	$\frac{PR_L(\psi_L - \psi_G)}{PR_i} \ln \Delta$	
Propane	C1-C2-C3	This work	- 50	1000	0.548	0.435	- 20.6	-0.680	0.3072
	C1-C2-C3	This work	-100	600	0.0522	0.0619	+ 18.6	-2.12	0.1043
	C1-C2-C3	This work	-150	200	0.0157	0.0119	- 24.2	-2.96	0.7474
	C1-C2-C3	This work	-200	100	0.0143	0.00431	- 70.0	-5.11	2.561
	C1-C2-C3	This work	- 50	800	0.124	0.0522	- 58.0	-2.20	1.1379
	C1-C2-C3	This work	-200	100	0.0175	0.01382	- 21.2	-5.22	2.7048
	C1-C2-C3	This work	0	1300	0.680	0.590	- 13.2	-0.382	0.1986
	C1-C2-C3	This work	- 50	100	0.325	0.277	- 14.8	-0.980	0.2785
	C1-C2-C3	This work	-100	400	0.0283	0.0176	- 37.6	-1.92	0.7111
	C1-C2-C3	This work	-150	100	0.00804	0.00761	- 5.4	-1.71	0.2490
	C1-C2-C3	This work	- 50	600	0.0854	0.0894	+ 4.7	-1.15	0.0719
	C1-C2-C3	This work	-100	200	0.0269	0.0310	+ 15.2	-1.60	-0.0367
	C1-C2-C3	This work	-100	600	0.0691	0.0785	+ 13.6	-2.13	0.1511
	C1-C2-C3	This work	0	1200	0.453	0.347	- 23.4	-0.633	0.3381
	C1-C2-C3	This work	- 50	800	0.152	0.1232	- 18.9	-1.54	0.3807
	C1-C3-C5	(17)(19)	220	1000	0.897	0.869	- 3.1	0.201	0.0860
	C1-C3-C5	(17)(19)	160	1000	0.696	0.668	- 4.0	0.0815	0.1132
	C1-C3-C5	(17)(19)	100	1000	0.400	0.359	- 10.2	0.600	0.1173
	C1-C3-C5	(28)	100	517	0.407	0.422	+ 3.7	1.110	0.0739
	C1-C3-C5	(28)	100	946	0.368	0.372	+ 1.1	0.587	0.0571
	C1-C3-C5	(28)	100	1431	0.419	0.385	- 8.1	0.214	0.1836
	C1-C3-C5	(28)	100	1736	0.482	0.447	- 7.25	0.0187	0.1287
	C1-C3-C5	(28)	100	1235	0.370	0.357	- 3.5	0.2735	0.0924
	C1-C3-C5	(28)	100	1419	0.476	0.397	- 16.6	0.241	0.2560
	C1-C3-C5	(28)	100	1822	0.569	0.465	- 18.3	-0.1872	0.2508

TABLE X (Continued)

Component	System	Source	Temp. °F	Press. psia	K exp.	K corr.	% Rel. Dev.	$\frac{PR_L(\psi_L - \psi_G)}{PR_i} \ln \Delta$
Butane	C ₄ - C ₇	(35A)	400	248.5	0.738	0.775	+ 5.0	1.21 0.0772
	C ₄ - C ₇	(35A)	200	127.3	0.140	0.126	-10.0	0.703 0.1969
	C ₄ - C ₇	(35A)	300	164.4	0.399	0.342	-14.4	1.137 0.1783
	C ₁ - C ₄	(62)	100	500	0.180	0.190	+ 5.6	-0.314 0.0460
	C ₁ - C ₄	(62)	250	1500	0.727	0.726	- 0.1	-0.049 0.0809
	C ₁ - C ₄ - C ₁₀	(62)	160	400	0.293	0.364	+24.2	2.49 0.1027
	C ₁ - C ₄ - C ₁₀	(62)	160	2000	0.405	0.376	- 7.15	0.00 0.1576
	C ₁ - C ₄ - C ₁₀	(62)	160	2000	0.250	0.217	-13.2	1.34 0.2816
	C ₁ - C ₅	(28)	100	517	0.175	0.157	-10.3	0.030 0.1898
	C ₁ - C ₅	(28)	100	946	0.122	0.169	+38.5	-0.250 -0.2266
	C ₁ - C ₅	(28)	100	1431	0.196	0.185	- 5.6	-0.47 0.1597
	C ₁ - C ₅	(28)	100	1736	0.332	0.274	-17.5	-0.455 0.2959
Isobutane	C ₁ - iC ₄	(49A)	100	500	0.254	0.257	+ 1.2	-0.300 0.0840
	C ₁ - C ₂ - iC ₄	(3A)	100	500	0.281	0.259	- 7.8	-0.553 0.1790
	C ₁ - C ₂ - iC ₄	(3A)	160	500	0.499	0.495	- 0.8	-0.209 0.0981
	C ₁ - C ₂ - iC ₄	(3A)	160	500	0.521	0.513	- 1.5	-0.284 0.1093
Pentane	C ₁ - C ₅	(62)	160	2000	0.317	0.284	-10.4	-0.433 0.2055
	C ₁ - C ₅	(62)	280	1500	0.674	0.712	+ 5.6	-0.125 0.0168
	C ₃ - C ₅	(62A)	220	500	0.427	0.425	- 0.5	-0.507 -0.1090
	C ₁ - C ₃ - C ₅	(17)(19)	100	500	0.069	0.0776	+12.5	-0.613 -0.0086
	C ₁ - C ₃ - C ₅	(17)(19)	160	1000	0.150	0.1371	- 8.7	-0.601 0.1932
	C ₁ - C ₂ - C ₅	(8A)	100	1000	0.141	0.1180	-16.3	-1.06 0.3914
	C ₁ - C ₂ - C ₅	(8A)	100	2000	0.444	0.388	-12.6	-0.416 0.2297
	C ₁ - C ₃ - C ₅	(17)(19)	100	1000	0.0858	0.0767	-11.8	-0.911 0.2849
	C ₁ - C ₃ - C ₅	(17)(19)	160	1000	0.298	0.268	-10.1	-0.710 0.245

TABLE X (Continued)

Component	System	Source	Press. psia	Temp. °F	K exp.	K corr.	% Rel. Dev.	$\frac{P_{Ri}}{P_{Ri}}(\psi_L - \psi_e) \ln \Delta$
Pentane	C1-C3-C5	(17)(19)	1000	220	0.488	0.456	- 6.55	-0.400 0.1590
	C1-C-C5	(28)	517	100	0.0593	0.690	+16.3	-0.759 -0.0164
	C1-C-C5	(28)	946	100	0.0886	0.0840	- 5.2	-0.855 0.2100
	C1-C-C5	(28)	1431	100	0.124	0.1028	-16.9	-0.851 0.3489
	C1-C-C5	(28)	1736	100	0.214	0.1714	-20.1	-0.781 0.3439
	C1-C-C6	(28)	1235	100	0.0868	0.0944	+ 8.75	-1.115 0.1299
	C1-C-C6	(28)	1419	100	0.148	0.1168	-21.0	-0.954 0.3917
	C1-C-C6	(28)	1822	100	0.363	0.221	-40.3	-0.882 0.6577
>Hexane	C2 - C7	(35A)	1000	350	0.369	0.271	-26.5	-0.517 0.3725
	C2 - C7	(35A)	1000	185	0.0990	0.0748	-24.4	-1.17 0.4922
	C4 - C7	(35A)	248.5	400	0.738	0.755	+ 2.3	-0.138 0.0111
	C4 - C7	(35A)	127.3	200	0.140	0.189	+35.0	-1.13 -0.100
	C4 - C7	(35A)	164.4	300	0.399	0.466	+16.8	-0.480 -0.0934
	C1 - C10	(35A)	2000	460	0.207	0.149	-28.0	-0.710 0.4318
	C1 - C10	(35A)	2000	100	0.0034	0.00596	+75.3	-1.062 -0.390
	C1-C4-C10	(35A)	400	160	0.0032	0.00582	+82.0	-1.88 -0.1299
	C1-C4-C10	(35A)	2000	160	0.061	0.0507	-16.9	-1.12 0.4041
	C1-C4-C10	(35A)	2000	160	0.0093	0.01172	+26.0	-1.30 0.0440
	C1-C-C6	(28)	1235	100	0.0477	0.0554	+ 9.3	-1.52 0.1788
	C1-C-C6	(28)	1419	100	0.0831	0.0725	-12.75	-1.30 0.3901
	C1-C-C6	(28)	1822	100	0.247	0.1535	-37.6	-1.07 0.6528

TABLE A-I
INFRARED CALIBRATION DATA FOR ETHANE (SMOOTHED)

Partial Pressure mm Hg	Pure C ₂ H ₆ *	Optical Density (Log 100/% Transmission)						
		C ₂ in C ₁ (0% in C ₃)	C ₂ in C ₁ + 10% C ₃	C ₂ in C ₁ + 20% C ₃	C ₂ in C ₁ + 30% C ₃	C ₂ in C ₁ + 40% C ₃	C ₂ in C ₁ + 50% C ₃	C ₂ in C ₃
0	0.000	0.000	0.015	0.027	0.042	0.052	0.065	0.129
50	0.258	0.307	0.320	0.333	0.348	0.363	0.376	0.419
100	0.484	0.551	0.571	0.587	0.601	0.617	0.632	0.662
150	0.693	0.768	0.791	0.808	0.825	0.840	0.854	0.871
200	0.891	0.964	0.987	1.007	1.032	1.049	1.063	1.063
250	1.082	1.139	1.172	1.200	1.223			1.242
300	1.276	1.313	1.351	1.381				1.398
350	1.466	1.482	1.522					1.530
400	1.645	1.645						1.645

* Partial Pressure = Total Pressure

TABLE A-II

INFRARED CALIBRATION DATA FOR PROPANE (SMOOTHED)

Partial Pressure (mm Hg)	Pure Propane	Optical Density (Log 100/% Transmission) C ₃ in C ₁ (0% in C ₂)	C ₃ in C ₁ + 25% C ₂	C ₃ in C ₁ + 50% C ₂	C ₃ in C ₂
0	0.000	0.000	0.003	0.005	0.011
50	0.106	0.106	0.109	0.111	0.115
100	0.210	0.210	0.213	0.215	0.220
150	0.310	0.310	0.313	0.317	0.321
200	0.410	0.410	0.412	0.415	0.417
250	0.504	0.504	0.509	0.511	0.513
300	0.597	0.597	0.603	0.605	0.605
350	0.689	0.689	0.696		0.698
400	0.777	0.777	0.787		0.789
450	0.860	0.860	0.874		0.874
500	0.944	0.944			0.957
550	1.029	1.029			1.038
600	1.115	1.115			1.115

TABLE B-I

TABULATION OF BWR PREDICTED DATA SUPPLEMENTARY TO TABLE VI

Code No.	Initial f_i/y_i (psia)		Final f_i/y_i (psia)		f_i/x_i (psia)		Density (# mol/ft ³)	
	CH ₄	C ₂ H ₆	CH ₄	C ₂ H ₆	CH ₄	C ₂ H ₆	Liq.	Vap.
1	106.6		86.4		1962.1		81.1	0.7133
2	106.6	95.6	86.4	95.6	1960.9	312.3	81.1	0.7141
3	107.1	95.8	86.4	95.7	1958.8	312.1	81.1	0.7157
4		95.8	86.4	95.7		312.0	81.1	0.7158
5	204.1		153.5		1950.7		83.3	0.7217
7	204.3	175.6	153.4	175.6	1940.8	316.6	83.3	0.7274
8	206.8	175.7	151.9	175.8	1925.1	315.6	83.4	0.7358
9	209.9	176.2	150.5	176.2	1905.5	314.6	83.5	0.7455
10		177.0	149.0	176.7		313.4	83.6	0.7551
11	391.8		251.7		1926.1		88.1	0.7369
12	395.7	307.1	246.7	307.0	1886.1	325.6	88.5	0.7517
13	409.6	303.8	234.0	303.7	1800.1	322.2	89.8	0.7745
14	411.1	303.6	232.9	303.4	1787.0	321.8	90.0	0.7769
15	426.1	302.5	224.0	302.5	1715.1	320.0	91.7	0.7858
17		302.5	217.5	302.5		319.0	93.5	0.7880
18	569.4		311.7		1897.9		93.9	0.7495
19	576.9	404.8	300.1	405.9	1851.3	337.5	94.7	0.7603
20	577.1	404.7	299.8	404.9	1845.2	337.2	94.8	0.7615
21	590.5	397.6	284.1	397.9	1777.3	335.4	96.4	0.7717
22	594.2	396.1	280.4	395.6	1749.8	334.9	97.2	0.7738
23	610.6	390.7	266.9	389.8	1671.1	334.1	99.9	0.7745
24	629.6	386.3	254.4	386.3	1612.6	334.2	102.4	0.7693
25	645.9	383.3		382.3	1532.8	335.0		0.7545

TABLE B-I (Continued)

Code No.	Initial f_i/y_i CH ₄	f_i/y_i C ₂ H ₆	f_i/y_i C ₃ H ₈	Final f_i/y_i CH ₄	f_i/y_i C ₂ H ₆	f_i/y_i C ₃ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈	Density Liq.	Density (#mol/ft ³) Vap.
26	742.0		335.2	740.2		338.3	1865.8		101.1	0.7583	0.1949
27	750.2	473.2	322.6	748.8	474.3	324.6	1823.3	351.5	102.2	0.7638	0.2021
28	772.5	458.6	296.7	772.9	458.4	296.4	1714.4	350.7	106.2	0.7654	0.2209
29	785.8	452.0	284.8	786.3	451.8	284.4	1666.3	351.1	108.4	0.7612	0.2310
30	809.0	442.7	267.4	808.0	443.0	268.1	1602.9	352.3	111.9	0.7506	0.2471
31	868.6	425.5		877.7	423.4		1393.3	361.9		0.6709	0.2991
32	906.9		337.3	907.5		336.4	1807.0		111.0	0.7593	0.2619
33	931.4	505.3	306.2	931.5	505.2	306.0	1725.4	369.1	114.9	0.7558	0.2837
34	939.0	500.1	298.4	940.3	499.2	297.1	1690.5	369.9	116.9	0.7509	0.2914
35	972.4	481.4	270.6	973.6	480.9	269.8	1592.9	373.7	123.9	0.7279	0.3197
36	1050.0	451.9	227.6	1051.1	451.5	227.2	1460.3	382.9	136.8	0.6751	0.3837
37	1113.8	434.6	203.6	1113.5	434.7	203.6	1308.2	399.8	157.9	0.5810	0.4339
38	991.6		326.1	992.7		324.7	1782.0		116.9	0.7565	0.3017
39	1001.5	527.8	313.7	1001.2	528.1	314.1	1769.9	378.1	117.6	0.7567	0.3097
40	1014.3	517.9	299.9	1014.5	517.7	299.7	1729.9	379.0	120.0	0.7524	0.3221
41	1029.5	507.6	285.8	1031.7	506.3	283.9	1654.3	382.1	125.3	0.7361	0.3378
42	1044.8	498.7	273.5	1045.4	498.4	273.1	1624.1	383.8	127.8	0.7275	0.3498
43	1070.4	485.8	256.0	1064.4	488.7	259.8	1608.5	384.6	129.2	0.7238	0.3662
44	1212.3	439.1	195.4	1187.0	445.5	203.5	1439.1	400.0	148.6	0.6468	0.4677
45	1090.2		297.1	1086.5		300.8	1748.8		124.5	0.7490	0.3524
46	1105.0	520.4	283.6	1097.2	525.7	290.5	1724.0	390.3	126.2	0.7450	0.3625
47	1147.0	496.4	253.2	1148.4	495.8	252.4	1574.6	400.6	140.3	0.6987	0.4091
48	1257.1	455.5	203.4	1236.4	461.7	210.8	1488.8	410.1	151.6	0.6581	0.4826

TABLE B-I (Continued)

Code No.	Initial f_i/y_i (psia)		Final f_i/y_i (psia)		f_i/x_i (psia)			Density (# mol/ft ³)	
	CH ₄	C ₂ H ₆	C ₂ H ₆	CH ₄	CH ₄	C ₂ H ₆	C ₃ H ₈	Liq.	Vap.
---	1194.3		267.9	1190.0	271.2	1702.2	134.8	0.7332	0.4143
---	1321.6		221.7	1282.1	240.9	1655.3	145.2	0.7125	0.4757
49	100.0		84.3	99.8	84.6	1589.5	35.3	0.7725	0.0218
50	100.0	91.5	84.4	99.9	84.5	1588.1	179.4	0.7746	0.0218
51	100.6	91.4	83.8	100.6	83.7	1578.0	178.9	0.7880	0.0222
52	100.9	91.4	83.5	101.0	83.4	1573.2	178.9	0.7940	0.0223
53	101.9	91.5	82.8	101.9	82.8	1561.9	178.2	0.8067	0.0227
55	194.4		149.9	194.2	150.6	1577.0	36.3	0.7860	0.0444
57	196.5	167.8	145.8	196.4	145.8	1545.8	181.2	0.8170	0.0458
58	199.4	166.6	141.7	199.5	141.7	1508.5	180.0	0.8461	0.0475
59	205.5	165.9	136.5	205.5	136.4	1439.9	178.5	0.8856	0.0505
60		165.9	135.0		135.1		178.2	0.8959	0.0515
61	372.2		236.3	371.7	238.1	1550.1	38.7	0.8114	0.0938
62	376.3	284.8	223.7	376.7	222.8	1487.0	187.5	0.8514	0.0986
63	380.1	280.8	215.6	380.8	214.4	1440.3	186.8	0.8720	0.1019
64	386.3	276.3	205.8	386.6	205.3	1384.4	186.6	0.8901	0.1063
65	391.0	273.7		392.5		1333.0	187.2	0.8999	0.1106
66	535.8		274.9	535.3	277.3	1519.0	41.7	0.8339	0.1501
67	541.9	360.8	255.1	541.1	257.5	1452.9	196.1	0.8613	0.1578
68	543.3	358.7	251.8	543.5	251.3	1428.6	196.1	0.8685	0.1607
69	548.8	298.3	240.0	548.6	240.4	1386.5	196.4	0.8781	0.1663
70	556.7	343.5	226.7	556.1	227.7	1330.4	197.6	0.8835	0.1741
71	562.5	338.7		563.9		1275.4	199.9	0.8800	0.1819

TABLE B-I (Continued)

Code No.	Initial f_i/y_i CH ₄	f_i/y_i C ₂ H ₆	(psia) C ₃ H ₈	Final CH ₄	f_i/y_i C ₂ H ₆	(psia) C ₃ H ₈	CH ₄	f_i/x_i C ₂ H ₆	(psia) C ₃ H ₈	Density (# mol/ft ³) Liq.	Vap.
72	687.4		275.3	686.3		279.5	1482.7		45.6	0.8515	0.2163
73	695.0	401.6	253.4	693.0	405.2	258.5	1423.7	206.8	47.2	0.8654	0.2275
74	700.2	393.3	242.2	701.6	391.3	239.4	1363.1	208.4	29.4	0.8705	0.2401
75	706.7	384.6	230.3	707.0	384.2	229.8	1331.5	209.8	50.8	0.8693	0.2475
76	716.7	373.5	215.4	716.9	373.4	215.3	1281.1	212.9	53.6	0.8609	0.2605
77	732.3	359.6		732.8	359.2		1206.4	219.8		0.8307	0.2809
78	830.4		245.8	828.1		252.0	1439.6		51.2	0.8603	0.2988
79	835.5	416.5	234.2	832.9	421.1	239.8	1407.5	219.8	52.6	0.8621	0.3083
80	844.9	401.4	216.8	842.5	405.0	220.9	1357.6	222.5	55.1	0.8590	0.3254
81	851.0	393.3	207.5	849.3	395.4	210.0	1328.2	224.7	57.0	0.8536	0.3369
82	876.5	366.2	177.9	868.2	374.0	186.3	1261.6	231.5	62.2	0.8300	0.3672
83	928.1	329.1	140.7	918.1	335.1	146.5	1147.9	250.5	76.0	0.7472	0.4434
84	1061.6	272.8		1061.8	272.7		1101.8	261.4		0.6979	0.6474
85	901.2		221.5	897.2		229.9	1413.3		55.2	0.8588	0.3494
86	907.3	406.9	210.7	902.6	414.5	218.9	1386.8	228.3	56.6	0.8571	0.3603
87	914.6	396.3	199.4	909.2	403.9	207.5	1357.8	230.5	58.5	0.8522	0.3728
88	915.2	395.6	198.7	915.8	394.7	197.8	1314.2	234.8	61.8	0.8383	0.3849
89	928.1	380.0	182.6	925.0	383.5	186.2	1301.1	236.3	63.0	0.8345	0.4008
90	938.5	369.2	171.9	935.2	372.5	175.1	1272.8	240.0	65.7	0.8210	0.4182
91	946.1	362.2	165.1	943.2	364.8	167.6	1249.4	243.6	68.3	0.8073	0.4316
92	948.3	360.2	163.2	948.5	360.0	163.0	1234.7	246.1	70.1	0.7975	0.4403
93	977.3	338.0	142.4	960.0	350.6	154.0	1219.7	248.8	72.0	0.7868	0.4588
94	977.2		188.5	967.8		202.2	1384.8		60.3	0.8512	0.4109
95	998.6	369.6	164.8	986.4	382.8	177.3	1325.3	243.2	65.2	0.8333	0.4465

TABLE B-I (Continued)

Code No.	Initial CH ₄	Initial f _i /y _i C ₂ H ₆	Initial f _i /y _i C ₃ H ₈	Final CH ₄	Final f _i /y _i C ₂ H ₆	Final f _i /y _i C ₃ H ₈	f _i /x _i (psia)			Density Liq.	Density (# mol/ft ³) Vap.
							CH ₄	C ₂ H ₆	C ₃ H ₈		
96	999.1	369.1	164.3	991.6	376.9	171.7	1308.2	245.6	67.0	0.8255	0.4559
97	1016.4	353.3	150.0	997.2	370.9	166.1	1299.7	246.8	67.9	0.8214	0.4659
98	1098.8	302.9	108.3	1006.8	361.6	157.6	1241.5	257.4	75.4	0.7834	0.4834
99	1069.2		147.2	1045.8		167.9	1346.2		68.0	0.8311	0.4926
100	1075.1	351.4	143.0	1056.2	368.6	157.8	1320.3	254.9	70.9	0.8186	0.5119
101	1098.2	334.1	128.8	1061.3	363.6	153.5	1311.4	256.5	72.0	0.8138	0.5208
102	1110.1	326.4	122.7	1064.9	360.2	150.5	1304.7	257.8	72.9	0.8097	0.5272
103	97.5		82.8	97.4		83.3	1124.1		12.4	0.8315	0.0239
104	97.7	89.0	81.9	97.7	89.1	82.0	1122.8	82.6	12.4	0.8584	0.0242
105	98.1	88.6	80.8	98.1	88.7	81.0	1119.5	82.5	12.5	0.8801	0.0244
106	98.4	88.4	80.2	98.4	88.4	80.3	1115.7	82.4	12.5	0.8961	0.0246
107	98.5	88.3	79.9	98.5	88.3	80.0	1113.3	82.4	12.5	0.9044	0.0247
108	99.6	87.8	78.2	99.7	87.8	78.2	1093.1	82.1	12.6	0.9527	0.0254
109	101.2	87.6		101.2	87.6		1062.1	82.0		1.0000	0.0261
110	188.9		142.5	188.9		142.7	1113.4		12.8	0.8541	0.0495
111	189.6	160.2	138.1	189.6	160.2	138.2	1102.7	84.3	12.9	0.8967	0.0504
112	190.1	159.1	136.1	190.0	159.3	136.4	1095.3	84.2	12.9	0.9147	0.0508
113	191.3	157.2	132.0	191.2	157.3	132.2	1070.5	84.0	13.1	0.9585	0.0521
114	193.2	155.2		193.1	155.3		1030.8	84.1		1.0060	0.0535
115	355.5		203.5	355.4		204.8	1088.1		13.8	0.8971	0.1071
116	355.8	261.0	200.2	355.8	261.0	200.2	1076.6	88.7	13.9	0.9167	0.1083
117	356.5	258.0	195.3	356.6	257.3	194.3	1057.4	88.7	14.1	0.9424	0.1102

TABLE B-I (Continued)

Code No.	Initial CH ₄	f _i /y _i		(psia)		Final CH ₄	f _i /y _i		(psia)		CH ₄	f _i /x _i		(psia)		C ₃ H ₈	Density		# mol/ft ³ Vap.
		C ₂ H ₆	C ₂ H ₆	C ₃ H ₈	C ₃ H ₈		C ₂ H ₆	C ₂ H ₆	C ₃ H ₈	C ₃ H ₈		Liq.							
118	357.8	253.3	187.9	357.8	253.4	188.0	1033.5	88.8	14.3	0.9683	0.1123								
119	358.3	252.1	185.9	358.3	251.9	185.6	1021.8	88.9	14.5	0.9780	0.1132								
120	358.5	251.5	185.0	358.5	251.4	184.8	1018.0	89.0	14.5	0.9810	0.1135								
121	358.9	250.4	183.2	359.0	250.4	183.2	1009.5	89.1	14.6	0.9873	0.1142								
122	361.4	245.3		360.9	246.2		973.1	90.1		1.0087	0.1171								
123	500.9		209.9	500.8		211.0	1057.2		15.3	0.9345	0.1771								
124	502.3	304.7	199.4	501.9	306.7	201.9	1029.9	94.5	15.7	0.9567	0.1813								
125	502.4	304.4	198.9	501.9	306.7	202.0	1030.0	94.5	15.7	0.9565	0.1812								
126	503.1	301.0	194.5	502.9	301.8	195.5	1009.5	95.0	16.0	0.9699	0.1845								
127	504.7	295.2	186.9	504.6	295.5	187.2	981.0	96.0	16.6	0.9837	0.1892								
128	509.3	282.9		508.9	284.0		924.6	99.6		0.9930	0.1991								
129	626.9		179.2	626.8		180.0	1017.6		17.6	0.9608	0.2687								
130	629.3	304.7	166.0	628.5	307.7	169.2	984.5	103.4	18.6	0.9701	0.2777								
131	632.5	293.2	153.9	632.7	292.6	153.3	932.5	108.0	20.8	0.9673	0.2938								
132	640.8	272.2		641.0	271.9		872.4	117.8		0.9284	0.3213								
---	725.9	226.6		723.1	230.7		837.0	140.6		0.8278	0.4622								
133	738.9		119.6	737.3		124.3	961.5		22.7	0.9550	0.4086								
134	743.1	259.2	109.3	741.7	262.9	112.3	931.9	120.5	25.0	0.9402	0.4323								
135	749.8	243.3	96.8	744.3	256.0	106.7	918.4	123.3	26.2	0.9292	0.4450								
136	755.7	231.9	88.4	749.8	243.3	96.9	895.3	129.2	28.9	0.9033	0.4704								
137	765.4	216.4	77.6	756.4	230.7	87.6	873.8	136.2	32.2	0.8691	0.4989								
138	783.4	194.3	63.3	782.9	194.8	63.6	785.7	191.9	61.8	0.6138	0.6036								
---	823.3		58.4	792.7		88.9	927.0		28.5	0.9160	0.5284								

TABLE B-I (Continued)

Code No.	Initial CH ₄	f _i /y _i (psia)		Final f _i /y _i (psia)		f _i /x _i (psia)			Density Liq.	Density (# mol/ft ³) Vap.
		C ₂ H ₆	C ₃ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈	CH ₄	C ₂ H ₆		
139	95.7		78.8	95.7		79.1	676.0	2.94	0.9036	0.0273
140	95.8	86.0	78.1	95.7	86.1	78.3	680.2	30.1	0.9295	0.0274
141	95.8	85.6	77.3	95.8	85.6	77.4	683.2	30.1	0.9637	0.0276
142	95.9	85.4	76.9	96.0	84.9	76.0	681.9	30.1	1.0183	0.0279
143	96.4	84.1		96.4	84.1		668.1	30.3	1.0932	0.0283
144	182.9		124.5	182.9		124.9	670.8	3.05	0.9462	0.0575
145	182.9	148.6	123.6	182.9	148.6	123.6	670.5	31.1	0.9691	0.0578
146	183.1	146.7	120.3	183.2	146.5	120.0	662.4	31.0	1.0333	0.0586
147	183.2	146.1	119.3	183.2	146.1	119.4	659.7	31.0	1.0446	0.0588
148	183.8	143.3		183.6	144.1		636.8	31.2	1.1089	0.0597
149	332.4		144.8	332.4		146.1	646.4	3.42	1.0285	0.1312
150	332.6	210.3	140.7	332.5	211.0	141.5	631.3	33.8	1.0633	0.1332
151	332.6	209.6	139.8	332.6	209.7	139.8	623.3	33.9	1.0771	0.1340
152	332.8	207.8	137.3	332.8	208.2	137.9	613.9	34.2	1.0907	0.1349
153	333.0	206.0	135.0	333.0	206.4	135.4	600.1	34.7	1.1064	0.1361
154	333.3	204.1		333.3	204.2		584.2	35.6	1.1201	0.1376
155	449.2		105.9	449.1		109.3	598.2	4.51	1.0848	0.2406
156	449.4	205.3	104.2	449.2	207.6	106.5	587.6	39.6	1.0887	0.2437
157	450.0	198.8	98.0	449.8	200.8	99.9	562.7	43.1	1.0812	0.2516
158	450.2	197.0		450.3	195.9		547.5	46.7	1.0587	0.2579
---	514.0	137.9		513.1	143.6		536.2	69.7	0.8714	0.4451
xx	520.7		49.1	520.3		51.9	547.9	10.6	0.9526	0.0442

TABLE B-I (Continued)

Code No.	Initial f_i/y_i C_2H_6	Initial f_i/y_i C_3H_8	Final f_i/y_i C_2H_6	Final f_i/y_i C_3H_8	CH_4	f_i/x_i (psia) C_2H_6	f_i/x_i (psia) C_3H_8	Density Liq.	Density (# mol/ft ³) Vap.
159	93.2	69.0	93.2	69.2	326.4	0.325	0.325	1.0215	0.0325
160	93.2	68.3	93.2	68.6	335.1	6.43	0.321	1.0789	0.0326
161	93.2	68.2	93.2	68.6	335.5	6.42	0.321	1.0829	0.0326
162	93.2	67.8	93.2	68.2	338.7	6.41	0.320	1.1259	0.0327
163	93.2	67.1	93.2	67.7	338.2	6.41	0.322	1.1894	0.0328
164	93.2	78.6	93.2	78.7	336.7	6.41		1.2103	0.0328
165	172.9	90.9	172.9	91.5	324.3		0.344	1.1228	0.0713
166	172.9	89.8	172.9	90.8	322.2	6.88	0.347	1.1565	0.0715
167	172.9	89.6	172.9	90.5	319.5	6.90	0.352	1.1777	0.0717
168	173.0	88.9	172.9	89.9	314.0	6.97	0.363	1.2099	0.0718
169	173.0	88.5	172.9	89.4	307.4	7.10	0.382	1.2375	0.0720
170	172.9		173.0	122.1	304.1	7.19		1.2498	0.0721
---	194.2	91.0	194.2	91.7	319.6		0.357	1.1539	0.0849
---	266.1	72.7	266.1	73.2	278.6		0.859	1.2135	0.1252
171	88.3	49.8	88.3	49.9	104.1		0.0095	1.3791	0.0413
172	88.3	49.6	88.3	49.6	101.7	0.645	0.0111	1.3930	0.0414
173	88.3	49.6	88.3	49.8	100.2	0.689	0.0127	1.4122	0.0413
175	88.4		88.3	65.6	99.3	0.734		1.4208	0.0413

TABLE C-I

METHANE-ETHANE DATA FROM BLOOMER AND OTHERS (9)

Temp. °F	Press. psia	Liquid Composition		Vapor Composition		K-Value	
		CH ₄	C ₂ H ₆	CH ₄	C ₂ H ₆	CH ₄	C ₂ H ₆
50	600	0.0875	0.9125	0.206	0.794	2.35	0.870
50	800	0.207	0.793	0.325	0.675	1.58	0.852
0	400	0.123	0.877	0.410	0.590	3.33	0.673
0	600	0.256	0.744	0.561	0.439	2.18	0.591
0	800	0.390	0.610	0.619	0.381	1.59	0.621
- 50	100	0.006	0.994	0.066	0.934	9.61	0.940
- 50	200	0.096	0.904	0.512	0.488	5.34	0.540
- 50	400	0.283	0.717	0.731	0.269	2.58	0.375
- 50	600	0.455	0.545	0.796	0.204	1.75	0.374
- 50	800	0.619	0.381	0.828	0.172	1.34	0.451
-100	100	0.096	0.904	0.676	0.324	7.04	0.358
-100	200	0.248	0.752	0.837	0.163	3.38	0.217
-100	400	0.524	0.456	0.916	0.084	1.75	0.177
-100	600	0.784	0.216	0.953	0.047	1.22	0.218
-150	100	0.264	0.736	0.928	0.072	3.52	0.098
-150	200	0.561	0.439	0.970	0.030	1.73	0.068
-200	100	0.855	0.145	0.996	0.001	1.17	0.007

TABLE C-II

METHANE-PROPANE DATA FROM SAGE & LACEY (62)

Temp. °F	Press. psia	Liquid Composition		Vapor Composition		K-Value	
		CH ₄	C ₃ H ₈	CH ₄	C ₃ H ₈	CH ₄	C ₃ H ₈
100	189	0.000	1.000	0.000	1.000		1.000
100	200	0.0049	0.9951	0.0521	0.9749	10.63	0.952
100	250	0.0257	0.9743	0.2184	0.7816	8.50	0.803
100	300	0.0460	0.9540	0.3255	0.6745	7.07	0.707
100	400	0.0845	0.9155	0.4472	0.5528	5.29	0.603
100	600	0.1630	0.8370	0.5714	0.4286	3.51	0.512
100	800	0.2418	0.7582	0.6321	0.3679	2.62	0.485
100	1000	0.3271	0.6729	0.6635	0.3365	2.03	0.500
100	1100	0.3731	0.6269	0.6738	0.3262	1.81	0.520
100	1200	0.4226	0.5774	0.	0.3221	1.60	0.558
100	1300	0.4889	0.5111	0.6643	0.3357	1.36	0.657
100	1353	0.5882	0.4118	0.5882	0.4118	1.00	1.000
160	384	0.000	1.0000	0.0000	1.0000		1.000
160	400	0.0063	0.9937	0.0276	0.9724	4.38	0.979
160	600	0.0813	0.9187	0.2392	0.7608	2.94	0.828
160	800	0.1618	0.8382	0.3414	0.6586	2.11	0.787
160	1000	0.2800	0.7200	0.3558	0.6442	1.27	0.895
160	1020	0.3228	0.6772	0.3228	0.672	1.00	1.000

TABLE C-III

METHANE-PROPANE DATA FROM AKERS, BURNS, & FAIRCHILD (1)

Temp. °F	Press. psia	Liquid Composition		Vapor Composition		K-Value	
		CH ₄	C ₃ H ₈	CH ₄	C ₃ H ₈	CH ₄	C ₃ H ₈
0	400	0.196	0.804	0.879	0.121	4.49	0.151
0	600	0.303	0.697	0.890	0.110	2.94	0.158
0	800	0.411	0.589	0.894	0.106	2.18	0.180
0	1000	0.522	0.478	0.893	0.107	1.71	0.224
0	1100	0.574	0.426	0.883	0.117	1.54	0.273
0	1200	0.640	0.360	0.873	0.127	1.36	0.353
0	1300	0.718	0.282	0.847	0.153	1.18	0.543
- 50	200	0.154	0.846	0.919	0.081	5.97	0.0957
- 50	400	0.288	0.712	0.943	0.057	3.28	0.0800
- 50	600	0.440	0.560	0.957	0.043	2.18	0.0767
- 50	800	0.593	0.407	0.961	0.039	1.62	0.0958
- 50	1000	0.777	0.223	0.944	0.056	1.215	0.251
-100	200	0.249	0.751	0.977	0.023	3.93	0.0306
-100	400	0.463	0.537	0.989	0.011	2.14	0.0205
-100	600	0.730	0.270	0.976	0.024	1.34	0.0889

APPENDIX DSAMPLE CALCULATIONSI. Calculation of AnalysesA. Infrared Method1. Measured Absorption Data: (Measurement No.T-108-L)Ethane: Wave length: 9.43 micronsSlit opening: 2.26 mm.Shutter: glassPressure: 400 mm HgOptical Density: 0.542Propane: Wave length: 12.34 micronsSlit opening: 1.30 mmShutter: glassPressure: 600 mm HgOptical Density: 0.2412. Calculation of Composition

From accurately constructed graphs similar to Figures 7 and 8, the following "partial pressures" were obtained corresponding to the optical densities recorded above:

Ethane: 91.0 mm HgPropane: 114.2 mm Hg

Dividing by the appropriate total pressures to obtain mol fractions,

$$\text{Ethane: } \frac{91.0}{400} = \underline{0.228} \text{ mol fraction}$$

Propane: $\frac{114.2}{600} = \underline{0.190}$ mol fraction

Methane (obtained by difference) $\frac{0.582}{1.000}$ " "

B. Chromatographic Method

1. Measured Data on unknown sample (from No.T-58-L)

<u>Component</u>	<u>Break-through Time</u> (minutes)	<u>Peak Area</u> (cm ²)
CH ₄	9.17	33.4
C ₂ H ₆	12.42	11.1
C ₃ H ₈	23.67	3.31

Barometric pressure = 30.356 in. Hg.

2. Reference Data

<u>Component</u>	<u>Break-through Time</u> (minutes)	<u>Reference Peak Area</u> (cm ²)
CH ₄	9.40	42.9
C ₂ H ₈	12.70	65.7
C ₃ H ₈	24.07	85.1

Barometric pressure = 30.000 in. Hg.

3. Calculation of Correction Factors of Equation 22

a. Flow Rate Correction: $\frac{Q_s}{Q_R}$ factor

As observed by the difference in break-through times, the flow rate for the unknown sample was slightly higher than that for the reference samples. The correction factor, $\frac{Q_s}{Q_R}$, is therefore calculated as the ratio of the corresponding break-through times.

<u>Component</u>	<u>Flow Rate Correction Factor, $\frac{Q_S}{Q_R}$</u>		
CH ₄	$\frac{9.40}{9.17}$	=	1.024
C ₂ H ₆	$\frac{12.70}{12.42}$	=	1.022
C ₃ H ₈	$\frac{24.07}{23.67}$	=	1.017

b. Barometric Pressure Correction: $\frac{P_R}{P_S}$ factor

To account for differences in atmospheric pressure during the unknown and reference measurements, the following factors are calculated:

<u>Component</u>	<u>Barometric Pressure Correction Factor</u>
CH ₄	$\frac{30.000}{30.356} = 0.989$
C ₂ H ₆	$\frac{30.000}{30.356} = 0.989$
C ₃ H ₈	$\frac{30.000}{30.356} = 0.989$

c. Compressibility Factor Correction

For this correction, an approximate analysis is needed to enable calculation of a pseudo compressibility factor. For this purpose, the two preceding factors are applied in the manner of Equation 22. The approximate mol fractions are then used with the pure component z factors to obtain the pseudo z factor. The corresponding correction factors follow from this. The example is continued below:

Component	Approximate Mol Fraction ($\bar{m}$)	Corrected ($\bar{m}^*$)	Pure Comp. z_R	$\bar{m}^* z$	$\frac{z_s}{z_R}$
CH ₄	$\frac{33.4}{42.9}(1.024)(0.989)=0.789$	0.790	0.998	0.789	0.999
C ₂ H ₆	$\frac{11.1}{65.7}(1.022)(0.989)=0.171$	0.171	0.991	0.170	1.006
C ₃ H ₈	$\frac{3.31}{85.1}(1.017)(0.989)=\underline{0.0390}$	<u>0.0390</u>	0.983	<u>0.938</u>	1.016
Total		0.9990	1.000	$z_S = 0.997$	

4. Calculation of Mol Fractions

Applying the compressibility correction to $\bar{m}$ of the preceding table:

Component	Mol Fraction	Adjusted Mol Fraction
CH ₄	$(0.789)(0.999)=0.788$	0.7884
C ₂ H ₆	$(0.171)(1.006)=0.172$	0.172
C ₃ H ₈	$(0.0390)(1.016)=\underline{0.0396}$	<u>0.0396</u>
	0.9996	1.0000

II. Calculations with the Benedict-Webb-Rubin Equation of State

An example calculation was included in the original articles (6) for the ternary system methane-ethane-n-pentane. The same procedure was followed in this study except the complete form of the vapor phase fugacity equation was used (identical to liquid equation).

As the authors explain, however, just one time through the equation is not adequate if the calculated equilibrium compositions differ much from the experimental values. For this reason, a flash calculation is made using the predicted

K-values and the overall composition discussed on page 67. With the new phase compositions thus obtained, the BWR calculation is repeated, yielding new K-values. Another flash is made, and the process is repeated until the K-values cease to change by more than 1%.

Numerical examples will be omitted since both the BWR and flash calculations are described in the literature (6)(58).

III. Calculations Used in the MABP Correlation

The following are based on the data for the experimental investigation corresponding to "Code No. 33" (see Table V, VII and Table I, Appendix B).

A. Calculation of Molal Average Boiling Points

1. Measured equilibrium phase compositions:

<u>Component</u>	<u>Liquid</u>	<u>Vapor</u>
CH ₄	0.389	0.707
C ₂ H ₆	0.169	0.126
C ₃ H ₈	0.442	0.167

2. Normal Boiling Points:

CH ₄ :	-258.7°F
C ₂ H ₆ :	-127.5°F
C ₃ H ₈ :	- 43.7°F

3. Calculations

<u>Component</u>	<u>Liquid Phase</u>	<u>Vapor Phase</u>
CH ₄	$(-258.7)(0.389) = -101$	$(-258.7)(0.707) = -183$
C ₂ H ₆	$(-127.5)(0.169) = - 22$	$(-127.5)(0.126) = - 16$
C ₃ H ₈	$(- 43.7)(0.442) = - 19$	$(- 43.7)(0.167) = - 7$
Molal Average Boiling Point	-142°F	-206°F

Note: Absolute temperature should be used if the signs of normal boiling points are not all the same.

B. Calculation of Liquid and Vapor Factors (A and B)

The following table shows the steps involved in the calculation.

Component	Initial f_i/y from BWR Calculation (psia)	$\frac{1}{f_i/Py} = B$	Smoothed K	$A = \frac{K_s}{B}$
CH ₄	931.4	1.073	1.82	1.70
C ₂ H ₆	505.3	1.980	0.732	0.370
C ₃ H ₈	306.2	3.27	0.379	0.116

C. Calculation of K-Value from Figures 34 - 39

1. Assume equilibrium phase compositions and calculate MABP for each phase (-142°F and -206°F for "Code No. 22")

2. On the proper A and B charts, read across to the correct temperature line, vertically to the correct pressure line, and horizontally again to obtain A and B. For this example, the above MABP's, the temperature (50°F), and the pressure (1000 psia) are used. The following results are obtained:

<u>Component</u>	<u>A</u>	<u>B</u>	<u>K=AB</u>	<u>K actual</u>
CH ₄	1.69	1.082	1.83	(1.82)
C ₂ H ₆	0.371	1.98	0.735	(0.732)
C ₃ H ₈	0.117	3.20	0.374	(0.379)

IV. Calculation of K-Values from the Generalized Correlation

K-Values for the methane-propane system at 100°F and 500 psia are calculated below:

A. Critical Data

Component 1
Methane

$$(z_c)_1 = 0.290$$

$$(T_c)_1 = 343.3^\circ\text{R}$$

$$(P_c)_1 = 673.1 \text{ psia}$$

$$\beta_{11} = \left(\frac{z_c T_c}{P_c} \right)_{11}$$

$$\beta_{11} = \frac{(0.290)(343.3)}{(673.1)}$$

$$\beta_{11} = 0.1479$$

$$\alpha_{11} = (T_c \beta)_{11}$$

$$= (0.1479)(343.3) = 50.78$$

Component 2
Propane

$$(z_c)_2 = 0.278$$

$$(T_c)_2 = 665.95^\circ\text{R}$$

$$(P_c)_2 = 617.4 \text{ psia}$$

$$\beta_{22} = \left(\frac{z_c T_c}{P_c} \right)_{22}$$

$$\beta_{22} = \frac{(0.278)(665.98)}{617.4}$$

$$\beta_{22} = 0.2999$$

$$\alpha_{22} = (T_c \beta)_{22}$$

$$= (0.2999)(665.95) = 199.69$$

The interaction criticals for unlike pairs:

$$\beta_{12} = \left[\frac{1}{2} \beta_{11}^{1/3} + \frac{1}{2} \beta_{22}^{1/3} \right]^3 = \left[\frac{1}{2} (0.1479)^{1/3} + \frac{1}{2} (0.2999)^{1/3} \right]^3 = 0.2151$$

$$\alpha_{12} = \sqrt{\alpha_{11} \alpha_{22}} = \sqrt{(50.78)(199.69)} = 101.0$$

B. Experimental Data: (62)

Vapor

$$y_1 = 0.5209$$

$$y_2 = \frac{0.4791}{1.0000}$$

Liquid

$$x_1 = 0.1235$$

$$x_2 = \frac{0.8765}{1.0000}$$

C. Pseudo Critical Calculation:

1. Gas Phase

$$(T_c')_G = \frac{\sum \sum y_i y_j \alpha_{ij}}{\sum \sum y_i y_j \beta_{ij}}$$

$$= \frac{(0.5209)^2(50.78) + 2(0.5209)(0.4791)(101.0) + (0.4791)^2(199.69)}{(0.5209)^2(0.1479) + 2(0.5209)(0.4791)(0.2151) + (0.4791)^2(0.2999)}$$

$$= \frac{109.9}{0.216} = 510^\circ\text{R}$$

$$(z_c')_G = \sum y_i Z_{c,i} = \left[(0.5209)(0.290) + (0.4791)(0.278) \right]$$

$$= 0.284$$

$$P_c' = \frac{z_c' T_c'}{\sum \sum x_i x_j \beta_{ij}} = \frac{(0.284)(9510)}{(0.216)} = 670 \text{ psia}$$

2. Liquid Phase

$$T_c' = \frac{\sum \sum x_i x_j \alpha_{ij}}{\sum \sum x_i x_j \beta_{ij}} = 631^\circ\text{R}$$

$$(z_c')_L = 0.279$$

$$(P_c')_L = 631 \text{ psia}$$

D. Pseudo Reduced Conditions

<u>Vapor</u>	<u>Liquid</u>
$(T_R')_G = 1.103$	$(T_R')_L = 0.889$
$(P_R')_G = 0.749$	$(P_R')_L = 0.792$
$(z_c')_G = 0.284$	$(z_c')_L = 0.279$

E. Thermodynamic Properties:

By interpolating in the generalized tables of

Lydersen and co-workers (43):

<u>Vapor</u>	<u>Liquid</u>
$\left(\frac{f}{p}\right)_G = 0.839$	$\left(\frac{f}{p}\right)_L = 0.487$
$\left(\frac{\Delta H}{T_c}\right)_G = 1.42$	$\left(\frac{\Delta H}{T_c}\right)_L = 9.62$
$Z_G = 0.792$	$Z_L = 0.127$

F. Calculation of Ψ values:

1. Evaluation of $(\Psi_G)_1$ for CH_4 in the gas phase:

$$(\Psi_G)_1 = \left(\frac{\Delta H}{T_c}\right)_G \left[\frac{2}{RT_R'} \frac{\sum y_i \beta_{i,j}}{\sum \sum y_i y_j \beta_{i,j}} - \frac{\sum y_i \alpha_{i,j}}{\sum \sum y_i y_j \alpha_{i,j}} \right] + Z_G \left[\frac{4 \sum y_i \beta_{i,j}}{\sum \sum y_i y_j \beta_{i,j}} - \frac{2 \sum y_i \alpha_{i,j}}{\sum \sum y_i y_j \alpha_{i,j}} - \frac{Z_{c1}}{\sum y_i Z_{c,i}} - 1 \right]$$

$$\frac{\sum y_i \beta_{i,j}}{\sum \sum y_i y_j \beta_{i,j}} = \frac{(0.5209)(0.1479) + (0.4791)(0.2151)}{0.216} = 0.833$$

$$\frac{\sum y_i \alpha_{i,j}}{\sum \sum y_i y_j \alpha_{i,j}} = \frac{(0.5209)(50.78) + (0.4791)(101.0)}{109.9} = 0.681$$

$$\frac{Z_{c1}}{\sum y_i Z_{c,i}} = \frac{0.290}{0.284} = 1.020$$

$$\begin{aligned} (\Psi_G)_1 &= (1.42) \left[\frac{2}{(1.987)(1.103)} (0.833 - 0.681) \right] + \\ &\quad (0.793) \left[4(0.833) - 2(0.681) - 2.020 \right] \\ &= (0.1980 - 0.0396) = 0.1584 \end{aligned}$$

2. Evaluation of $(\Psi_L)_1$ is carried out in the same manner for CH_4 in the liquid phase. The result is:

$$(\Psi_L)_1 = (9.62)(0.2305) + (0.127)(-0.1508) = 2.20$$

G. K-value for CH_4

$$\begin{aligned}\ln K_1 &= \ln \frac{f_L}{f_G} + (\psi_L - \psi_G)_1 + \ln \Delta_1 \\ &= \ln \frac{0.487}{0.839} + (2.20 - 0.16) + \ln \Delta_1\end{aligned}$$

If $\ln \Delta_1$ is neglected:

$$\begin{aligned}\ln (K_1)_{\text{theo.}} &= \ln \frac{0.487}{0.839} + (2.20 - 0.16) = 1.49 \\ K_{1\text{theo.}} &= 4.43\end{aligned}$$

From Equation 92:

$$\ln \Delta_1 = 0.0150 \left[\frac{(P_R')_L}{P_{R1}} (\psi_L - \psi_G) - 1 \right]^2 - 0.010$$

$$(P_R)_1 = \frac{500}{673} = 0.743$$

$$\begin{aligned}\ln \Delta_1 &= 0.0150 \left[\frac{0.792}{0.743} (2.20 - 0.16) - 1 \right]^2 - 0.010 \\ &= -0.006\end{aligned}$$

$$\Delta_1 = 0.994$$

$$K_1 = (0.994)(4.43) = 4.40$$

The experimental K-value is 4.21

$$\% \text{ Error} = \left(\frac{4.40 - 4.21}{4.21} \right) (100) = 4.5\%$$

H. K-Value for C_3H_8

The calculations for C_3H_8 are carried out similarly:

For the liquid phase

$$\Phi_{2L} = \frac{2}{R(T_R')_L} \left(\frac{\sum x_j \beta_{2j}}{\sum \sum x_i x_j \beta_{ij}} - \frac{\sum x_j \alpha_{2j}}{\sum \sum x_i x_j \alpha_{ij}} \right) = -0.0325$$

$$\Theta_{2L} = \left(\frac{4 \sum x_i \beta_{2i}}{\sum \sum x_i x_j \beta_{ij}} - \frac{2 \sum x_i \alpha_{2i}}{\sum \sum x_i x_j \alpha_{ij}} - \frac{Z_{C2}}{\sum x_i Z_{Ci}} - 1 \right) = 0.02125$$

For the vapor phase

$$\Phi_{2G} = -0.1516$$

$$\Theta_{2G} = 0.0542$$

$$\begin{aligned} [\Psi_L - \Psi_G]_2 &= \left[\left(\frac{\Delta H}{T_C'} \right) \Phi_{2L} + Z_L \Theta_{2L} \right]_L - \left[\frac{\Delta H}{T_C'} \Phi_2 - Z \Theta_2 \right]_G \\ &= [9.62(-0.0325) + (0.127)(0.02125)] \\ &\quad - [1.42(-0.1516) + (0.792)(0.0542)] \\ &= -0.138 \end{aligned}$$

$$\ln K_{2, \text{theo.}} = \ln \frac{f_L}{f_G} + [\Psi_L - \Psi_G]_2 = \left[\ln \frac{0.487}{0.839} - 0.138 \right]$$

$$K_{2, \text{theo.}} = 0.506$$

Equation 94:

$$\ln \Delta_2 = 0.050 \left[\frac{(P_R')_G}{P_{R2}} (\Psi_L - \Psi_G)_2 \right]^2 + 0.050$$

$$= 0.050 \left[\frac{0.792}{0.810} (-0.138) \right]^2 + 0.050 = 0.0509$$

$$\Delta_2 = 1.052$$

$$K_2 = (\Delta_2)(K_2)_{\text{theo.}} = (1.052)(0.506)$$

$$K_2 = 0.533$$

The experimental value is $K_2 = 0.547$

$$\% \text{ Error} = \left[\frac{0.533 - 0.547}{0.547} \right] (100) = -2.6\%$$

APPENDIX EDEVELOPMENT OF COMBINING RULES
FOR
PSEUDOCRITICAL CONSTANTS

The derivation given here follows a development by Dr. T. W. Leland. It is a modification of the statistical derivation of pseudocriticals by Dr. Z. W. Salsburg (64) for a mixture of simple molecules.

I. Assumptions

The law of corresponding states has been expressed in a modified form by Equation 42 as

$$z = f(P_R, T_R, z_C) \quad (1-E)$$

This may be considered an equation of state in which P_C , T_C and z_C are three constants. Therefore, developing pseudocritical expressions to represent a mixture is analogous to the combining of constants in an equation of state. The latter problem can be treated theoretically only for very simple molecules under restricted conditions. In this development, a molecular model obeying the following conditions is assumed:

(1) The molecules are spherical and are distributed in a random manner.

(2) The intermolecular potential energy of the system can be represented as the sum of the intermolecular potentials between pairs of molecules.

(3) The intermolecular potential is a function only of the distance between molecular centers and two parameters

characteristic of the substance. This function may be represented as

$$U_r = f(r, \epsilon, \sigma) \quad (2-E)$$

Where U_r = intermolecular potential energy between a pair of like molecules.

r = distance between molecular centers

ϵ = an energy parameter representing the maximum possible attractive potential between two molecules.

σ = a length parameter representing the closest approach distance between two molecular centers.

The Lennard-Jones "6-12" relation given below is an example of this type function.

$$U_r = 4\epsilon \left[\left(\frac{r}{\sigma} \right)^{12} - \left(\frac{r}{\sigma} \right)^6 \right] \quad (3-E)$$

It is represented graphically as:

II. Second Virial Coefficients of Mixture

Before developing combination rules for pseudocriticals, a discussion of the virial coefficients of mixtures is desirable.

The virial equation of state is usually written in the form

$$\frac{PV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \dots \quad (4-E)$$

where $B(T)$, $C(T)$, $D(T)$, ... = second, third, fourth, etc.,
virial coefficients

The problem of combining these pure component virial coefficients to represent actual mixtures is very complicated. For systems obeying the restrictions imposed above, however, the second virial coefficient for mixtures can be shown to be

$$B(T)_m = \sum_{i=1}^n \sum_{j=1}^n x_i x_j B(T)_{ij} \quad (5-E)$$

where x = concentration of a component

n = number of components

The development of this relation given below is based on work by Kirkwood (38), Scatchard (65), and Hildebrand (31). Although presented for a binary system, it can be extended to any number of components.

A. The first step is to determine the probability of finding a molecule somewhere within a spherical shell of volume dV surrounding a reference molecule.

Consider a system of n_1 moles of component 1 and n_2 moles of component 2. Select the center of any molecule as a reference point. Then it is assumed that the probability of finding another molecule within a sphere of volume $\frac{\bar{V}}{N}$ about the reference point is unity, where

$\bar{V}$ = molal volume of the system

N = Avogadro's number

The volumes being discussed are shown below.

In the simplest case, the probability, $P(V)$, of finding the center of another molecule somewhere within the spherical shell is given by the ratio of the volumes, i.e.

$$P(V) = \frac{dV}{V/N} \quad (6-E)$$

This relation is sufficient for large values of r , but another function must be included for smaller radii. This is due to two factors:

(1) Molecular size imposes a physical limitation on the number of molecules which can be put into dV at very small r values.

(2) Intermolecular forces become important, causing the location of molecules at some radii to be more probable than others. Therefore, let $P(r)$ be the ratio of the number of ways the element dV may be filled at any given radius to the total possible ways at a very large radius. Thus $P(r)$ is the probability of finding a molecule at any radius,

approaching unity at large radii.

Then, the product of the two probability functions, $P(V) P(r)$, represents the total probability of a molecule's being in the shell bounded by spheres of radii r and $r+dr$. This is given by

$$P(V) P(r) = P(r) \frac{N dV}{V} = P(r) \frac{(N)(4\pi r^2) dr}{V} \quad (7-E)$$

B. The second step is to determine the probability that the molecular pair described above belongs to a particular species.

In a random system the probability that the reference molecule with center at $r=0$ is a molecule of component 1 is

$$\frac{n_1}{n_1 + n_2} = x_1 \quad (8-E)$$

Similarly, the probability that the molecule at any other location in the system belongs to species 1 is also x_1 . Thus the probability that the molecules at two specified locations both are component 1 is $(x_1)^2$. Including the probability that the second molecule lies in a spherical shell dV , (Equation 7-E), the following relation is obtained:

$$P(11) = (x_1)^2 \left[\frac{4\pi N P(r)_{11} r^2 dr}{V} \right] \quad (9-E)$$

$P(11)$ is the probability that a molecule in dV is also a molecule of component 1.

A similar development for a pair of component 2 molecules gives

$$P(22) = (x_1)^2 \left[\frac{4\pi N P(r)_{22} r^2 dr}{V} \right] \quad (10-E)$$

Also, the probability that the reference molecule is component 1 and the other is component 2 is

$$P(12) = x_1 x_2 \left[\frac{4\pi N P(r)_{12} r^2 dr}{\bar{V}} \right] \quad (11-E)$$

Finally, the possibility of finding a component 2 molecule at the center and a component 1 molecule in the shell is

$$P(21) = x_1 x_2 \left[\frac{4\pi N P(r)_{21} r^2 dr}{\bar{V}} \right] \quad (12-E)$$

In the system considered here, Equations 11-E and 12-E are identical.

Now, the total possible number of pairs of any type is

$$1/2 (n_1 + n_2)N \quad (13-E)$$

Therefore the probable pairs of any particular type are obtained by multiplying the proper equation (from 9-E through 12-E) by the above factor. For example, the total number of pairs expected between molecules of component 1 within a distance r and $r + dr$ from each other is

$$P_T(11) = (n_1 + n_2)(x_1)^2 \left[\frac{2\pi N^2 P(r)_{11} r^2 dr}{\bar{V}} \right] \quad (14-E)$$

C. Now consider the potential energy described in assumption (3). The contribution of pairs of component 1 molecules to the total intermolecular potential energy of the system is the product of the probable number of pairs of these molecules and the potential energy of interaction between each pair. This is expressed as

$$E_{11} = P_T(11) U(r)_{11} = (n_1 + n_2)(x_1)^2 \left[\frac{2\pi N^2 U(r)_{11} P(r)_{11} r^2 dr}{\bar{V}} \right] \quad (15-E)$$

where E_{11} = total intermolecular potential energy of all pairs of component 1 molecules

$U(r)_{11}$ = potential energy of interaction between two component 1 molecules

Dividing by total number of mols, $(n_1 + n_2)$:

$$\bar{E}_{11} = (x_1)^2 \left[\frac{2\pi N^2 U(r)_{11} P(r)_{11} r^2 dr}{\bar{V}} \right] \quad (16-E)$$

where $\bar{E}_{11}$ = molal intermolecular potential energy of all pairs of component 1 molecules.

Similar expressions result for $\bar{E}_{22}$, $\bar{E}_{12}$, and $\bar{E}_{21}$.

It is now possible to obtain an expression for the total intermolecular potential per mole of the system. This is accomplished by summing the molal potentials between all types of pairs (Equation 16-E and related expressions) and integrating over all possible values of r . This gives

$$\bar{E}_m = \frac{2\pi N^2}{\bar{V}} \left[(x_1)^2 \int_0^\infty U(r)_{11} P(r)_{11} r^2 dr + 2x_1 x_2 \int_0^\infty U(r)_{12} P(r)_{12} r^2 dr + (x_2)^2 \int_0^\infty U(r)_{22} P(r)_{22} r^2 dr \right] \quad (17-E)$$

D. The final step is to show the relation of $\bar{E}_m$ above to the second virial coefficient.

This molal intermolecular potential energy, $\bar{E}_m$, can be represented as a function of the internal energy of the system, U . Consider the isothermal change of internal energy with volume from $V = \infty$ (where the intermolecular potential is zero) to $V = \bar{V}$. An integration of this change should

yield the intermolecular potential of a molal volume of the system. Mathematically,

$$\bar{E}_m = \int_{\infty}^{\bar{V}} \left(\frac{\partial U}{\partial V} \right)_T d\bar{V} \quad (18-E)$$

But $\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P$

Therefore, $\bar{E}_m = \int_{\infty}^{\bar{V}} \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] d\bar{V} \quad (19-E)$

The virial equation of state can be written as

$$P = RT \left[\frac{1}{\bar{V}} + \frac{B(T)_m}{\bar{V}^2} \right] \quad (20-E)$$

neglecting terms involving higher than the second virial coefficient. Performing the differentiation indicated in Equation (19-E),

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{RT}{\bar{V}^2} \left(\frac{\partial B(T)_m}{\partial T} \right)_V + R \left[\frac{1}{\bar{V}} + \frac{B(T)_m}{\bar{V}^2} \right] \quad (21-E)$$

Substituting (21-E) into (19-E):

$$\bar{E}_m = \int_{\infty}^{\bar{V}} \left[\frac{RT^2}{\bar{V}^2} \left(\frac{\partial B(T)_m}{\partial T} \right)_V \right] d\bar{V} \quad (22-E)$$

Integrating,

$$\bar{E}_m = - \frac{RT^2}{\bar{V}} \left(\frac{\partial B(T)_m}{\partial T} \right)_V \quad (23-E)$$

A similar analysis for component 1 molecules, assuming the intermolecular potential to be uninfluenced by the presence of other molecules, gives

$$(\bar{E}_{11})_{\text{total}} = - \frac{RT^2}{\bar{V}} \left(\frac{\partial B(T)_{11}}{\partial T} \right)_V \quad (24-E)$$

$$\text{also, } (\bar{E}_{22})_{\text{total}} = -\frac{RT^2}{V} \left(\frac{\partial B(T)_{22}}{\partial T} \right)_V \quad (25-E)$$

It is next assumed that an interaction virial coefficient, $B(T)_{12}$, accounting for attraction between unlike molecules, is defined by

$$(\bar{E}_{12})_{\text{total}} = -\frac{RT^2}{V} \left(\frac{\partial B(T)_{12}}{\partial T} \right)_V \quad (26-E)$$

Substituting Equation 23-E through 26-E into Equation 17-E,

$$\left(\frac{\partial B(T)_m}{\partial T} \right)_V = (x_1)^2 \left(\frac{\partial B(T)_{11}}{\partial T} \right)_V + 2x_1x_2 \left(\frac{\partial B(T)_{12}}{\partial T} \right)_V + x_2^2 \left(\frac{\partial B(T)_{22}}{\partial T} \right)_V \quad (27-E)$$

Solution of the partial differential equation gives:

$$B(T)_m = x_1^2 B(T)_{11} + 2x_1x_2 B(T)_{12} + x_2^2 B(T)_{22} + f(V) \quad (28-E)$$

Imposing the boundary conditions:

$$\begin{aligned} B(T)_m &= B(T)_{11} \text{ at } x_1 = 1 \\ \text{and } B(T)_m &= B(T)_{22} \text{ at } x_2 = 1, \\ \text{then } f(V) &= 0 \end{aligned}$$

Therefore

$$B(T)_m = x_1^2 B(T)_{11} + 2x_1x_2 B(T)_{12} + x_2^2 B(T)_{22} \quad (29-E)$$

$$\text{or } B(T)_m = \sum_{i=1}^m \sum_{j=1}^m x_i x_j B(T)_{ij} \quad (30-E)$$

III. Pseudocriticals from the Reduced Dieterici Equation of State

The Dieterici equation given below is considered the most accurate of the classical two-constant equations of state.

$$P = \left(\frac{RT}{V-b} \right) e^{-\frac{a}{RTV}} \quad (31-E)$$

The constants, a and b , can be related to the critical constants by applying the critical point criteria:

$$\left(\frac{\partial P}{\partial V} \right)_T = 0 \quad (32-E)$$

$$\left(\frac{\partial^2 P}{\partial V^2} \right)_T = 0 \quad (33-E)$$

Solving Equations 32-E and 33-E simultaneously yields

$$a = 2 RT_c V_c \quad (34-E)$$

$$b = \frac{V_c}{2} \quad (35-E)$$

Rearranging the two preceding equations to include z_c gives

$$a = (2R^2) \left(\frac{z_c T_c^2}{\rho_c} \right) \quad (36-E)$$

$$b = \left(\frac{R}{2} \right) \left(\frac{z_c T_c}{\rho_c} \right) \quad (37-E)$$

The second virial coefficient of Equation 31-E is $\left(b - \frac{a}{RT} \right)$. Recall that the second virial for a mixture of substances following the assumed model can be written

$$B(T)_m = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} x_i x_j B(T)_{ij} \quad (\text{Equation 30-E})$$

Since the second virial for this equation of state is a linear combination of a and b , these constants in the equation for a mixture can be expected to be

$$a_m = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} x_i x_j a_{ij} \quad (38-E)$$

$$b_m = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} x_i x_j b_{ij} \quad (39-E)$$

Then by analogy, using relations 36-E and 37-E,

$$\left(\frac{Z_c T_c^2}{P_c}\right)' = \sum_{i=1}^n \sum_{j=1}^n \chi_i \chi_j \left(\frac{Z_c T_c^2}{P_c}\right)_{ij} \quad (40-E)$$

$$\left(\frac{Z_c T_c}{P_c}\right)' = \sum_{i=1}^n \sum_{j=1}^n \chi_i \chi_j \left(\frac{Z_c T_c}{P_c}\right)_{ij} \quad (41-E)$$

where the primed functions are for mixtures.

For brevity, the following notation will be used:

$$\alpha_{ij} = \left(\frac{Z_c T_c^2}{P_c}\right)_{ij} \quad (42-E)$$

$$\beta_{ij} = \left(\frac{Z_c T_c}{P_c}\right)_{ij} \quad (43-E)$$

Dividing 40-E by 41-E gives

$$T_c' = \frac{\sum \sum \chi_i \chi_j \alpha_{ij}}{\sum \sum \chi_i \chi_j \beta_{ij}} \quad (44-E)$$

Rearranging Equation 41-E,

$$P_c' = \frac{Z_c' T_c'}{\sum \sum \chi_i \chi_j \beta_{ij}} \quad (45-E)$$

In the discussion thus far, no mention has been made of evaluating $B(T)_{ij}$ (and related functions a_{ij} , b_{ij} , and α_{ij} , β_{ij}) when i and j are not equal. These interaction terms will be considered now for the simple model assumed here.

The first step is to relate the constants a and b of the equation of state to the parameters ϵ and σ of the potential function. Referring to Equation 31-E, it is seen that

b must have the dimensions of volume, hence it bears some relation to the cube of the length parameter, σ . This is written as

$$b = k_1 \sigma^3 \quad (46-E)$$

where k_1 = a constant of proportionality

Similarly, a must have the dimensions of RTV. Therefore a is related to the product of the energy parameter (ϵ) and the cube of the length parameter (σ):

$$a = k_2 \epsilon \sigma^3 \quad (47-E)$$

where k_2 = constant of proportionality

Considering the physical picture for two spherical molecules of types 1 and 2,

$$\sigma_{12} = \frac{1}{2} (\sigma_{11} + \sigma_{22}) \quad (48-E)$$

or

$$(\sigma_{12}^3)^{\frac{1}{3}} = \frac{1}{2} \left[(\sigma_{11}^3)^{\frac{1}{3}} + (\sigma_{22}^3)^{\frac{1}{3}} \right] \quad (49-E)$$

Therefore, applying Equation 46-E,

$$b_{12}^{\frac{1}{3}} = \frac{1}{2} b_{11}^{\frac{1}{3}} + \frac{1}{2} b_{22}^{\frac{1}{3}} \quad (50-E)$$

Then, recalling relations 36-E and 37-E,

$$\beta_{12}^{\frac{1}{3}} = \frac{1}{2} \beta_{11}^{\frac{1}{3}} + \frac{1}{2} \beta_{22}^{\frac{1}{3}} \quad (51-E)$$

or

$$\beta_{12} = \left[\frac{1}{2} \beta_{11}^{\frac{1}{3}} + \frac{1}{2} \beta_{22}^{\frac{1}{3}} \right]^3 \quad (52-E)$$

The interaction term for the energy parameter, ϵ , is of a more empirical nature, and is usually taken as (31A)

$$\epsilon_{12} = \sqrt{\epsilon_{11} \epsilon_{22}} \quad (53-E)$$

The differences in values of ϵ for various substances is usually much greater than the differences in σ , therefore the interaction term $(\epsilon \sigma^3)_{12}$ can be represented approximately as

$$(\epsilon \sigma^3)_{12} = \sqrt{(\epsilon \sigma^3)_{11} (\epsilon \sigma^3)_{22}} \quad (54-E)$$

Note that $(\epsilon \sigma^3)_{12}$ is not the same as $(\epsilon_{12})(\sigma^3)_{12}$.

Applying 47-E,

$$a_{12} = \sqrt{a_{11} a_{22}} \quad (55-E)$$

and from 36-E,

$$\alpha_{12} = \sqrt{\alpha_{11} \alpha_{22}} \quad (56-E)$$

On the basis of Equations 52-E and 56-E, relations 44-E and 45-E may be rewritten as

$$T_c' = \frac{\sum \sum \kappa_i \kappa_j \alpha_i^{1/2} \alpha_j^{1/2}}{\sum \sum \kappa_i \kappa_j \left[\frac{1}{2} \beta_i^{1/3} + \frac{1}{2} \beta_j^{1/3} \right]^3} \quad (57-E)$$

$$P_c' = \frac{Z_c' T_c'}{\sum \sum \kappa_i \kappa_j \left[\frac{1}{2} \beta_i^{1/3} + \frac{1}{2} \beta_j^{1/3} \right]^3} \quad (58-E)$$

where

$$\alpha_i^{1/2} = \left(\frac{Z_c T_c^2}{P_c} \right)_i^{1/2} \quad \beta_i^{1/2} = \left(\frac{Z_c T_c}{P_c} \right)_i^{1/2}$$

Because the variation of z_c is small, the following rule is assumed:

$$z_c' = \sum x_i (z_c)_i \quad (59-E)$$

The above equations (57-E, 58-E and 59-E) were used to express the pseudocritical constants of mixtures of light hydrocarbons.

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