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INVESTIGATION OF THE DENSITIES OF COEXISTING LIQUID AND VAPOR FOR LIGHT HYDROCARBONS AND THEIR MIXTURES NEAR THE CRITICAL REGION

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INVESTIGATION OF THE DENSITIES OF COEXISTING LIQUID AND VAPOR

FOR LIGHT HYDROCARBONS AND THEIR MIXTURES

NEAR THE CRITICAL REGION

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ABSTRACT

A new equation of state has been proposed for coexisting vapor and liquid phases of pure hydrocarbons and their mixtures. This equation is based on a modified theorem of corresponding states and utilizes a new third parameter to account for the nonideality of the system. The proposed third parameter is the molecular refraction determined by the sodium D-line, expressed in terms of density ρ, molecular weight M, and the refractive index n, as follows:

$$(R)_D = \frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho}$$

It is superior to the existing parameters because: 1) it can be measured directly and more accurately for pure as well as complex mixtures of hydrocarbons; 2) among other things, it is a direct measure of London dispersion forces which are believed to be the dominating cause of nonideality in nonpolar systems; 3) its value varies over a wide range, from 3.350 for methane to 48.481 for decane, thus allowing very accurate interpolation of properties between reference substances.

This parameter bears a linear relationship to the critical compressibility factor Z_c introduced by Meissner and Seferian and successfully used as a third parameter for pure compounds by Lydersen-Greenkorn-Hougen.

Since the molecular refraction is an additive quantity, the molal

average molecular refraction can be used as a third parameter for mixtures. The heptanes-plus in a mixture may be separated from a small portion of the sample by fractionation. Then ordinary atmospheric measurement of the density, molecular weight, and the refractive index of this sample yields the molecular refraction of heptanes-plus required to calculate the molar average molecular refraction of the mixture.

The relative ease and accuracy with which this technique can be applied to natural hydrocarbon mixtures such as gas condensates and volatile oils is in direct contrast to the use of other third parameters for mixtures where the measurement of the third parameter, say, critical compressibility factor or Pitzer's acentric factor for heptane-plus is a very difficult if not an impossible task.

The literature data on binary and ternary systems were used to make the preliminary test of the proposed equation of state. Experimental data were then obtained on seven different hydrocarbon systems of liquid mixtures in coexistence with vapor to make further test of the proposed method. These systems were synthesized to simulate gas condensate and highly volatile oil reservoirs with a temperature range of 100 - 310^{o}F and pressures to about 7000 psi.

An entirely new P-V-T equipment was designed and built for this study comprising a high-low temperature bath (range -40^{o}F to 350^{o}F), P-V-T variable volume, visual cell (1100 cc capacity, 20,000 psi working pressure) and stainless steel spherical pycnometers (5 cc for liquid, 22 cc for vapor) and other auxiliary equipment. A multicolumn thermal conductivity chromatograph was used to determine the composition of the multicomponent systems.

To my wife, Loretta, and my parents

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CHAPTER I

INTRODUCTION

The determination of the economics and feasibility of many contemporary recovery techniques such as high pressure gas drive, enriched gas drive, and CO_2 combination drive hinges upon a knowledge of the volumetric behavior of the fluids under study. Detailed phase behavior studies are also required for recovery predictions of the ever increasing number of deep reservoirs which often contain highly volatile oil or gas condensate, because the conventional bottom hole analysis can lead to drastically misleading results for such cases. For instance, in the case of volatile oil reservoirs, the conventional method can underestimate the recovery by a factor of two or more.

Many empirical equations of state are available to predict the density of pure substances.[1,5,6,29,31,32,41,49] The corresponding state principle has also been applied to determine the density of pure substances in gaseous phase. The corresponding state principle has been improved for the gaseous phase and extended to liquid phase by introduction of a third parameter accounting for the degree of nonideality of the pure substances under study. Among the more successful third parameters are the critical compressibility factor Z_c of Meissner[65] and his

co-workers and the slope of the vapor pressure curve near the critical temperature as introduced by Pitzer.[74] The equation used to determine the density by the corresponding state principle is the same as the ideal gas law equation in terms of molal volume $\underline{V}$, absolute pressure P, absolut temperature T, and gas constant R; but the compressibility factor Z is introduced to account for the nonideality as follows:

$$P\underline{V} = ZRT \tag{1}$$

Since the molal volume is the same as the ratio of molecular weight M to density ρ or $\underline{V} = \frac{M}{\rho}$, then a variation of equation (1) in terms of density becomes:

$$\frac{P}{\rho} = \frac{Z}{M} RT \tag{2}$$

A widely used correlation for liquid hydrocarbon mixtures is given by Brown, Katz, and Oberfell.[13] This correlation which is in fact a combination and extension of several other correlations is sometimes referred to as NGAA correlation. In this technique, the density of propane-plus is calculated at $60^{o}F$ and atmospheric pressure assuming the volumes are additive. This density is then corrected for methane and ethane content, pressure, and temperature using four different empirical charts. When used in conjunction with phase behavior programs at Sinclair Research, Inc., this technique lead to some inconsistancy near the critical region. This was later proved to be due to the inaccuracy of the liquid density prediction around the critical region.

Another technique for the determination of the density of liquid hydrocarbon mixtures has recently been presented by Alani.[1] In this technique van der Waals equation of state is used. The constants for the equation are given in terms of temperature for pure substances. A

general equation for the constants of heptanes-plus is given in terms of molecular weight and specific gravity of the heptanes-plus fraction and the temperature. This general equation is obtained through regression analysis using a number of density-composition data representing a limited range of specific gravity and molecular weight. For the mixture, the molal average of the constants is proposed to be used in the van der Waals equation. However, Alani does not recommend the use of his method for gas condensate systems.

The theory of corresponding state has been extended to the mixtures by many investigators[20,41,48,63,72,81,83,91] based on the justifications presented by Guggenheim.[32] Many mixing rules have been proposed from the simple molal average critical properties presented by Kay[51] to a more complex empirical form analogous to statistical mechanics treatment presented by Leland and Mueller.[57] The use of the third parameter in the theorem of corresponding states for mixture has been advanced by Leland and Mueller.[57] In fact, these investigators have shown that a combination of their proposed mixing rule and the molal average critical compressibility factor for a third parameter to determine a reference substance yields good density prediction. But this method breaks down when used for liquid hydrocarbon mixtures containing heavy ends such as heptanes-plus because the critical compressibility factor of the heptanes-plus cannot be accurately and easily evaluated. Even Pitzer's third parameter cannot be readily determined for the heptanes-plus.

Although the modified theorem of corresponding states works well for the pure substances and simple mixtures, it cannot be applied to complex hydrocarbon mixtures because there is no available third parameter

that can be directly and accurately measured for such complex portions of the mixture as the heptanes-plus.

Thus, there is a need for a third parameter for characterizing the nonideality of complex hydrocarbon mixtures which can be measured directly, accurately, and with relative ease which also varies enough between reference substances as to allow for accurate interpolation of P-V-T properties between the reference substances.

The objective of this research project was twofold: First, to develop a technique and method for the prediction of the P-V-T properties of hydrocarbons and their complex mixtures near the critical region. Second, to design and develop an apparatus and technique to obtain accurate density-composition data on various natural hydrocarbon mixtures near the critical region to test out the proposed density prediction techniques.

For the first objective, since the modified theorem of corresponding state has been shown to be promising for the pure and simple systems, it was attempted to extend this theorem to complex hydrocarbon mixture through the development of a new third parameter which can characterize such systems with regard to nonideality. After extensive screening, it was found that the molecular refraction of a substance can be used as a third parameter for characterizing the system with regard to nonideality because it is related to refractive index, molecular weight, and the density of the substance. It is ironic that the "London dispersion forces" which have been shown to be the dominating forces in determining the nonideality of nonpolar substances was coined because of the intimate relation between light dispersion, which is manifested

in the refractive index, and the London dispersion forces. On the more applied aspects, the molecular refraction bears a linear relationship to the critical compressibility factor Z_c which has already been found to be an excellent parameter for pure substances and simple mixtures.[57,63] Molecular refraction is inherently superior to Z_c even for pure substances and simple mixtures since it can be expressed accurately in more significant figures than Z_c and varies from 3.530 for methane to 48.481 for normal decane[82] while the values of Z_c are reported to vary only from .290 for methane to .247 for normal decane.[63] The wide variation of the molecular refraction over the reference substances allows for more accurate interpolation of the P-V-T properties between the reference substances. What is more important is the fact that the molecular refraction can be easily measured by standard laboratory equipment at atmospheric conditions for pure substances as well as complex hydrocarbon mixtures.

Since the molecular refraction is an additive quantity, the molal average molecular refraction may be used as a third parameter for mixtures. In equation form the molecular refraction may be expressed in terms of the refractive index n as measured by sodium D-line, density ρ, and the molecular weight M, as follows:

$$(R)_D = \frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho} \qquad (3)$$

This parameter together with Leland's empirical mixing rule for the critical properties was used for a number of binary and ternary data available in literature and on a number of samples of multicomponent liquid mixtures determined experimentally on seven different systems. The

percentage deviation was found to be 3.54 for C_1 - nC_5, 2.65 for nC_4 - nC_{10}, 2.22 for C_1 - nC_4 - nC_{10}, and 3.79 for the hydrocarbon liquid mixtures containing good portions of heptanes-plus (excluding the first system). When applied to the same complex hydrocarbon liquid mixtures, the average error was 7.98 per cent for the NGAA method and 15.8 per cent for the Alani method.

Leland and Mueller used a combination of arithmetic and geometric averaging for interaction distance and energy parameters of unlike molecules in the potential function to arrive at their pseudocritical equations. Since according to Magasanik[64] the distance and energy parameters are internally related, Leland's mixing rule was modified by using the same averaging technique for both energy and distance parameters. The use of arithmetic average for energy parameters has been widely questioned in the literature, thus Leland's equations were modified so that the geometric average was used in the first case and harmonic average was used in the second case for both energy and distance parameters of unlike molecules. These modifications were applied to predict the density of 11 multicomponent, one ternary, and two binary samples, again using the molar average molecular refraction as the third parameter, with the following results:

	Method 1	Method 2	Method 3
	Geometric-Arithmetic (Leland-Mueller Equation)	Geometric-Geometric	Harmonic-Harmonic
Percentage Deviation	3.70	2.86	5.15

An entirely new P-V-T equipment was designed and built for this study comprising a high-low temperature bath (range -40°F to 350°F), P-V-T variable volume, visual cell (1100 cc capacity, 20,000 psi working pressure), stainless steel spherical pycnometers (5 cc for liquid, 22 cc for vapor), and other auxiliary equipment. A multicolumn chromatograph was used to determine the composition of the multicomponent systems.

The accuracy of the experimental measurements are believed to be as follows:

Accuracy	Variable
1:2000	Density
1:2000	Temperature
1:2000	Pressure
3.0%	Composition

CHAPTER II

THEORETICAL BACKGROUND

For many centuries the P-V-T properties of gases have been a matter of considerable interest. Since the discovery of petroleum reservoirs in the present century, the knowledge of the P-V-T properties of both gases and liquids have become necessary information for the prediction of oil and gas recoveries. In volatile oil and gas condensate reservoirs, the knowledge of the P-V-T properties of liquid and vapor in coexistence have also become of importance. In order to understand the complexity of the P-V-T properties of the liquid and vapor in coexistence in a multicomponent system, we must start with the discussion of the P-V-T properties of an ideal system then extend the development to real and complex systems.

A. Ideal Gas System

The ideal gas can be treated by either macroscopic or microscopic thermodynamics.

1. Treatment by Macroscopic Thermodynamics

An ideal gas is defined as one for which the laws of Boyle-Gay-Lussac, and Avogadro are applicable at all temperatures. The generalization reached by R. Boyle (1662) has been known as Boyle's law (also known as Mariotte's law) which states: "At constant temperature the

volume of a definite mass of gas is inversely proportional to the pressure:

$$PV = \text{Constant} \tag{4}$$

It will be shown later that the Equation (4) holds only if the molecules are point masses with no attraction for one another. Therefore, the applicability of this equation may be regarded as one of the criteria of ideal gas law. Gay-Lussac's law, published in 1802, refers to the generalization of the variation of the volume of gas with temperature, at constant pressure. Analagous conclusions, which remained unpublished, had been reached by J. A. C. Charles (1787). Mathematically, Charles' law may be expressed as:

$$V_t = V_0(1 + \alpha_v t) \tag{5}$$

If absolute temperature is represented by $T = t + 273.15$, then Charles' law can be expressed as:

$$V_t = \frac{V_0}{T_0} T_t \quad \text{or} \quad \frac{V_t}{T_t} = \frac{V_0}{T_0} = \text{Constant} \tag{6}$$

Now since $PV = \text{Constant}$ according to Boyle's law and $\frac{V}{T} = \text{Constant}$ according to Gay-Lussac's law, then we can write the following relation for an ideal gas.

$$\frac{PV}{T} = \text{Constant} \tag{7}$$

This relationship is frequently used in various forms in P-V-T studies.

Avogadro made the assumption that equal volumes of all gases under the same conditions of pressure and temperature contain equal numbers of molecules. Avagadro's law leads to the conclusion that in Equation (7) the constant is a function of the number of molecules; and if one mole is considered, it should be independent of the nature of the gas and be the

same for all gases. Therefore, the following relation should hold for ideal gases if molal volume $\underline{V}$ is considered

$$P\underline{V} = RT \tag{8}$$

where R is the universal gas constant.

Equation (8) embodies the three laws applicable to an ideal gas, namely Gay-Lussac, Boyle, and Avogadro laws; and it is consequently called the ideal gas equation.

2. Treatment by Microscopic or Statistical Thermodynamics

In the microscopic treatment of ideal gas, the potential energy of the system of molecules is assumed to be negligible so that the total energy of the system is equal to the kinetic energy of the gas molecules alone. That is:

$$E = PE + KE = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) \tag{9}$$

Where: E = total energy
PE = potential energy
KE = kinetic energy
m = mass of a molecule
p = momentum
x,y,z = spacial coordinates

The partition function for one molecule, f, may be expressed as follows:

$$f = \sum_i g_i e^{-E_i/kT} = \frac{1}{h^3}\int_{-\infty}^{\infty} e^{-E/kT} dA = \underline{V}\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \tag{10}$$

Where: $dA = dxdydzdp_x dp_y dp_z$

The partition function for N molecules of nonlocalized independent system is given as follows:

$$Z = \frac{f^N}{N!} \tag{11}$$

and

$$P = \frac{kTd\ln Z}{d\underline{V}} = \frac{RT}{\underline{V}} \tag{12}$$

Equation (9) is the statement of equation of state for ideal gas.

B. Real Pure System

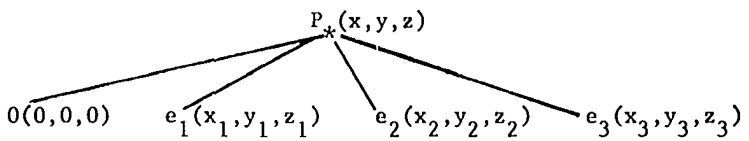
In the real system, the potential energy of the molecules can no longer be neglected and must be introduced in the evaluation of P-V-T properties. Hence it is of interest to disclose the nature of the potential energy or intermolecular interaction before the available techniques of P-V-T relations for real systems are discussed.

1. Nature of Intermolecular Forces

Considering only one molecule, the potential produced by charge distribution at point P in Figure 1 is given as follows:

$$\Phi = \sum_i \Phi_i = \sum_i \frac{e_i}{R_i} = \sum_i \frac{e_i}{[(x - x_i)^2 + (y - y_i)^2 + (Z - Z_i)^2]^{1/2}} \tag{13}$$

Figure 1
Charge Distribution



Taylor expansion of expression (13) about $\frac{1}{R}(0,0,0)$ gives:

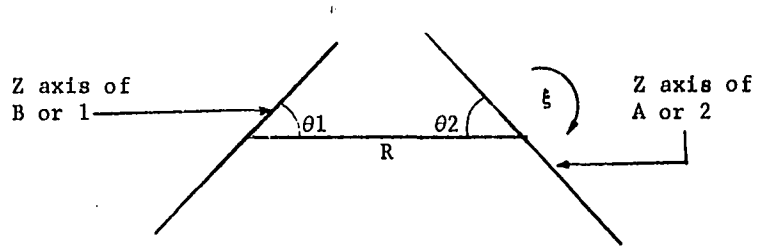
$$\Phi = \frac{q}{R} + \frac{\mu_\alpha R_\alpha}{R^3} + \frac{\theta_{\alpha\beta}}{3R^5}(3R_\alpha R_\beta - R^2\delta_{\alpha\beta}) + \frac{\Omega_{\alpha\beta\gamma}}{5R^7} 3R_\alpha R_\beta R_\gamma$$
$$- R^2 (R_\alpha \delta_{\beta\gamma} + R_\beta \delta_{\alpha\gamma} + R_\gamma \delta_{\alpha\beta}) \tag{14}$$

where α, β, γ take the values of 1, 2, and 3 and δ is a unit tensor defined as follows:

$$\delta = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{15}$$

Now to determine the interaction between two molecules A and B with their respective orientation as shown in Figure 2, the interaction between their respective potentials Φ_1 and Φ_2 should be considered.

Figure 2
Interaction between Two Molecules



After much algebra this interaction potential U_{12} takes the following form:

Charge-Charge Charge-Dipole

$$U_{12} = \frac{q_1 q_2}{R} + \frac{1}{R^2}\left[(q_1\mu_2 \mathrm{Cos}\theta_2 + q_2\mu_1 \mathrm{Cos}\theta_1)\right]$$

Charge-Quadrupole

$$+ \frac{1}{2R^3}\left[q_1\theta_2(3\mathrm{Cos}^2\theta_2 - 1) + q_2\theta_1(3\mathrm{Cos}^2\theta_1 - 1)\right]$$

Dipole-Dipole

$$+ \frac{\mu_1\mu_2}{R^3}\left[2\mathrm{Cos}\theta_1\mathrm{Cos}\theta_2 + \mathrm{Sin}\ \theta_1\ \mathrm{Sin}\ \theta_2\ \mathrm{Cos}\xi\right]$$

Charge-Octapole

$$+ \frac{1}{2R^4}\left[q_1\Omega_2(5\mathrm{Cos}^3\theta_2 - 3\mathrm{Cos}\theta_2) q_2\Omega_1(5\mathrm{Cos}^3\theta_1 - 3\mathrm{Cos}\theta_1)\right]$$

Dipole-Quadrupole

$$+ \frac{3}{2R^4}\left[\mu_1\theta_2\left[\mathrm{Cos}\theta_1(3\mathrm{Cos}^2\theta_2 - 1) + 2\ \mathrm{Sin}\ \theta_1\ \mathrm{Sin}\ \theta_2\ \mathrm{Cos}\theta_2\ \mathrm{Cos}\xi\right]\right]$$

Dipole-Quadrupole

$$+ \mu_2\theta_2\left[\mathrm{Cos}\theta_2(3\mathrm{Cos}^2\theta - 1) + 2\ \mathrm{Sin}\ \theta_1\ \mathrm{Sin}\ \theta_2\ \mathrm{Cos}\theta_1\ \mathrm{Cos}\xi\right]$$

Quadrupole - Quadrupole

$$+ \frac{3\theta_1\theta_2}{4R^5}\left[1 + 5\mathrm{Cos}^2\theta_1 - 5\mathrm{Cos}^2\theta_2 + 17\ \mathrm{Cos}^2\theta_1\ \mathrm{Cos}^2\theta_2 + 2\ \mathrm{Sin}^2\theta_1\ \mathrm{Sin}^2\partial_2\ \mathrm{Cos}^2\xi + 16\ \mathrm{Sin}\ \theta_1\ \mathrm{Sin}\ \theta_2\ \mathrm{Cos}\ \theta_1\ \mathrm{Cos}\ \theta_2\ \mathrm{Cos}\xi\right] + \cdots. \qquad (16)$$

2. Explanation of Nonideality by Interaction between Molecules

W. H. Keesom[41] (1912) attempted to explain molecular attraction in terms of dipole-dipole interaction in the molecules. He stated that magnitude and sign, i.e., whether it results in attraction or repulsion, of the interaction energy depends on the relative orientation of the dipoles; and hence the phenomenon is known as orientation effect. If all orientations were equally possible, the resultant energy would be zero; but from statistical consideration he concluded that the orientation energy U_o between two dipolar molecules is given as follows for high temperature:

$$U_o = -\frac{2}{3}\mu^4/r^6kT \qquad (17)$$

The negative sign of the potential energy means that the work has to be done on the molecules to separate them, i.e., there is a

resultant attraction. As temperature is increased, U_o decreases rapidly in contrast to experimental findings; thus Debye[28] (1920) showed that there exists an induced dipole moment caused by permanent moment which is actually independent of temperature and gives rise to the induction potential energy based on polarizability α and dipole moment μ and distance between molecules r as follows:

$$U_I = -2\alpha\mu^2/r^6 \tag{18}$$

This suggestion met with two serious difficulties. First, the interaction energies being applicable only to a pair of molecules are not additive for all molecules and may cancel out and there may be no attraction force to account for cohesion. Besides many nonpolar molecules exhibit appreciable attraction on each other such as H_2, O_2, CH_4. The suggestion of the existence of quadrupole moment partly overcame these difficulties. However, when London (1930) introduced what is now known as London dispersion forces, many of these difficulties were alleviated. London's theory was quantum mechanical, based on Heisenberg's uncertainty principle, that is, all molecules must possess energy even in their lowest energy status. He stated that at any instant the charge distribution in a molecule may cause an instantaneous dipole moment, although on the average the molecule does not have any dipole moment. The temporary dipoles are capable of inducing dipoles in other molecules in phase with themselves. So, as a result, there is a net attraction between molecules. The dispersion potential energy caused by this attraction is approximated by the following equation:

$$U_D = -\frac{3}{2} h\nu_o^2/r^6 \tag{19}$$

where h is Planck's constant and ν_0 is the characteristic frequency of the molecule which is the same as the one used for dispersion of light by a molecule;[41] hence the source of the word "dispersion forces."

TABLE 1

RELATIVE MAGNITUDES OF MOLECULAR INTERACTION EFFECTS

Molecule	Dipole Moment	Orientation Effect	Induction Effect	Dispersion Effect
H_2	-	-	-	11.3
A	-	-	-	57
N_2	-	-	-	62
CH_4	-	-	-	117
CL_2	-	-	-	461
CO	.12D	.0034	.057	67
HCL	1.03	18.6	5.4	105
NH_3	1.5	84.0	10.0	93
H_{20}	1.8	190.0	10.0	47

Table 1 gives the relative magnitude of various molecular interaction effects for a number of polar and nonpolar compounds. It is seen that the dispersion effect seems to be able to produce considerable molecular interaction. For the polar molecules, the orientation effect is most important while the induction effect may be neglected. The attractive forces are the integrals of Equations (17), (18), and (19) and hence proportional to $1/r^7$. In the dispersion forces the quadrupole-quadrupole

attractions have a $1/r^8$ term.

When molecules are brought together, they will not separate without a repulsive force. Therefore, a repulsive force must exist for separating molecules. This force as given by wave mechanics equals $be^{-r/n}$ where b and n are adjustable parameters. The following equation gives the overall potential energy for a pair of molecules:

$$U = be^{-r/n} - \frac{c}{r^6} - \frac{d}{r^8} \tag{20}$$

The first term at right is due to repulsion forces. The second term is due to dipole-dipole interaction, and the third term is due to quadrupole-quadrupole interactions.

2. General Empirical Equations of State

Many empirical equations of state have been proposed for gaseous regions. Some of these equations are also valid for the unsaturated liquid regions. A rather complete list of these references was recently published by Opfell and Co-workers.[66] Most of these equations do not, however, apply to the two phase region where a discontinuity between the vapor and liquid densities exist. The mere existence of this discontinuity is the reason for the lack of accuracy of the empirical equations of state around the region of coexistent phases.

The forms of the equations of state are generally picked to match a physical model for the system. For instance, in the van der Waals equation, a correction is made for the volume occupied by a molecule and another correction is made for the attraction force between the molecules generally referred to as London dispersion forces, so that:

$$V_{eff} = \underline{V} - b$$

$$P_{eff} = P + \frac{a}{\underline{V}^2}$$

$$V_{eff}\, P_{eff} = (P + \frac{a}{\underline{V}^2})\,(\underline{V} - b) = RT \qquad (21)$$

Note that the pressure correction for the London dispersion forces is proportional to $(\frac{1}{\underline{V}^2})$ or $(\frac{1}{r^6})$ which is in agreement with the attraction term of Lennard-Jones potential. Thus, apparently no correction due to the quadrupole-quadrupole attraction and repulsion of the molecules as they collide is made. Dieterici's[28] equation makes an exponential correction for the London dispersion forces so that the equation of state takes the form:

$$P = \frac{RT}{\underline{V} - b}\, e^{-a/RT\underline{V}} \qquad (22)$$

Dieterici reasoned that the molecules at the wall of a container have less potential energy than the ones in the interior; and, therefore, according to the Boltzman distribution law, there will be fewer molecules per unit volume at the wall than in the interior. If ΔE is the excess potential energy at the wall per mole, then:

$$\frac{n}{n_1} = e^{-\Delta E/RT} \qquad (23)$$

Where n and n_1 are the number of molecules in unit volume at the walls and the bulk of the gas, respectively. Since the pressure is proportional to molecular concentration, it follows that:

$$\frac{P}{P_1} = e^{-A/RT} \qquad (24)$$

where P is the observed pressure and P_1 is the pressure in the interior. Using van der Waals volume and Equation (24), he arrived at the following equation of state:

$$P_1 = (V - b)RT = \frac{P(\underline{V} - b)}{e^{-A/RT}} \tag{25}$$

or

$$P(\underline{V} - b)e^{A/RT} = RT \tag{26}$$

However, this was modified by replacing A by $\frac{a}{V}$ to obtain a better fit with experimental data to arrive at the following equation:

$$P(\underline{V} - b)e^{\frac{a}{RT\underline{V}}} = RT \tag{27}$$

Dieterici's equation is usually approximated as follows:[29]

$$P = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}^2} \tag{28}$$

Another version of van der Waals equation was proposed by Clausius[29,41] who accounted for the temperature dependence of the constant a. He assumed that the molecular attraction factor is inversely proportional to temperature; thus, his proposed equation took the following form:

$$\left[P + \frac{a}{T(\underline{V} + c)^2}\right]\left[\underline{V} - b\right] = RT \tag{29}$$

but for simplicity it is generally assumed that c = c(a,b). This was first done by Berthelot who arrived at the following modification of equation:

$$(P + \frac{a}{T\underline{V}^2})\ (\underline{V} - b) = RT \tag{30}$$

Still another modification to van der Waals equation was brought about by F. G. Keyes[29] who reasoned that the van der Waals factor b was influenced by the surrounding molecules. He made allowance for this in the equation, reserving the Dieterici's version of pressure correction.

Thus he obtained the following relationship:

$$P = \frac{RT}{\underline{V} - \beta e^{-\alpha/\underline{V}}} - \frac{A}{(\underline{V} - 1)^2} \tag{31}$$

where A,α,β, and 1 are constants depending on the nature of the gas.

Another modification of van der Waals equation was proposed by Alani[1] who obtained an equation for van der Waals constants as a function of temperature for pure hydrocarbon liquids and gases from C_1 to nC_{10}.

Many other equations of state have been proposed which include multiple constants that need empirical evaluation. Among these perhaps Benedict, Benedict-Webb-Rubin, Beattie-Bridgeman, and virial equation of state seem to stand out. The virial equation of state is usually represented in terms of inverse volume as follows:

$$\frac{P\underline{V}}{RT} = 1 + \frac{B}{\underline{V}} + \frac{C}{\underline{V}^2} + \frac{D}{\underline{V}^3} + \cdots. \tag{32}$$

where B, C, D, etc., are second, third, fourth virial coefficients denoting interaction between two, three, four, etc., molecules.

Thus, there already exist numerous equations of state, and no doubt many more will be proposed. In reality the form of all these equations is governed by the degree of understanding of interaction between molecules and the ability of choosing an empirical equation whose form will give the best fit to the experimental data.

3. Equation of State for Coexistent Vapor and Liquid Phases

The equations of state for gases if applicable to liquids have an abrupt discontinuity at the region of liquid-vapor coexistence. Other equations of state have been proposed which consider the sum or the difference between the vapor and liquid densities at coexistence. Cailletet

and Mathias[18,28,41] proposed that the sum of the vapor and liquid densities must be a function of temperature in the following form:

$$\rho_l + \rho_v = a + bT + CT^2 + \cdots \tag{33}$$

Later this was referred to as the rectilinear diameter law when the terms higher than T were neglected. Eyring[23] explained this linear relationship using his fluid vacancy model. He claimed that as molecules escape from liquid into vapor they leave a vacancy behind which is fluidized. Therefore, the same concentration of vacancies in liquid as of molecules in the vapor is expected, and the sum of the two densities must be constant except that lattice expansion causes the mean density of the liquid to decrease slightly with temperature. Using Eyring's conclusions, Benson[7] arrived at the following equation of state:

$$\rho_l = 2\rho_c + \frac{T_c - T}{T_c - T_b}(\rho_{lb} - 2\rho_c) - \rho_v \tag{34}$$

Thus the liquid density at coexistence with vapor is expressed in terms of ρ_c, ρ_v, T_c, ρ_{lb}, T_b, T, critical density, vapor density, liquid density at bubble point, boiling temperature, and temperature, respectively.

Another equation involving ρ_l and ρ_v is needed, or an equation of state for ρ_v, to calculate ρ_l.

Hammermacher[32] proposed the following equation of state:

$$\frac{1}{\rho_v} - \frac{1}{\rho_l} = V_v - V_l = \frac{RT}{MP}\left(1 - \frac{Pr}{Tr^3}\right)^{1/2} = \Delta V \tag{35}$$

However, the accuracy of Equation (35) breaks down as $Tr > .85$ is considered. Goldhammer[29] proposed the following relationship between the density and temperature at a given pressure:

$$\frac{(\rho_l - \rho_v)_2}{(\rho_l - \rho_v)_1} = \left(\frac{T_c - T_2}{T_c - T_1}\right)^{1/3} \tag{36}$$

At temperatures below normal boiling point the reference density of vapor ρ_{vl} may be neglected as compared to liquid density ρ_l, then:

$$\frac{(\rho_l - \rho_v)_2}{\rho_l^1} = \left(\frac{T_c - T}{T_c - T_1}\right)^{1/3} = G(T) \tag{37}$$

the exponent 1/3 is not constant actually and varies for various compounds from .237 to .343 and must be evaluated empirically. Table 2 gives some values of this exponent, n, for various substances.

TABLE 2

GOLDHAMMER EXPONENTS FOR VARIOUS SUBSTANCES

Compound Group	n
Alcohol and water	.25
Hydrocarbons and ethers	.29
All other organic compounds	.31
All other inorganic compounds	.333

From the simultaneous solution of Equations (35) and (37), an equation of state for coexistent vapor and liquid is then derived. The overall percentage error is reported to be 1.7 for saturated liquid and 3.3 for saturated vapor by this method.[24]

The calculations of molal volume at atmospheric boiling temperature was suggested by Schroeder[81] as follows: The number of atoms of carbon, hydrogen, oxygen, and nitrogen are counted. One is added for

each double bond; then the sum is multiplied by seven. This gives molal volume in cc/g mole. The prediction by this technique is reported to be within three to four per cent of experimental values.

Benson[81] proposed the following equation for the calculation of molal volume at the boiling point:

$$\frac{1}{\underline{V}b} = \frac{.422 \ln P_c + 1.981}{\underline{V}c} \tag{38}$$

Watson[81] proposed a generalized method whereby the volume of liquid is related to empirical expansion factor, w:

$$\underline{V}_1 w_1 = \underline{V}_2 w_2 = \underline{V} w \tag{39}$$

where

$$w = f(Pr, Tr) \tag{40}$$

Charts of w as a function of T_r and P_r are available for $P_r = 0 - 5$ and $T_r = .6 - 1.0$. An average accuracy of 2.3 per cent is reported for this method, but for some liquids it gives large error. For instance, for ethylene at -40^0F an error of 8.7 per cent is reported.

Kurtz[81] and associates proposed the following expression for the determination of molal volume of high molecular weight hydrocarbons which is reported to have an average deviation of .6 per cent.

$$\underline{V} = F_1 K_1 N_1 + F_1 K_2 N_2 + F_1 K_3 N_3 - F_1 K_4 N_4 + F_5 K_5 \tag{41}$$

where $\underline{V}$ = molal volume cc/g mole

N_1 = number of chain of carbon atoms

N_2 = number of carbon atoms in rings

N_3 = number of carbon atoms at ring junctions

N_4 = number of double bonds

K_1----K_5 = temperature dependent constants given graphically as a function of temperature

F_1, F_5 = pressure dependent constants given graphically as a function of pressure -F_5 is also a function of temperature

4. Theorem of Corresponding State

a. Classical approach. The theorem of corresponding state is not a new idea. It has been known and used to various degrees for many years. It implies that different chemical substances have similar thermodynamic properties if compared at the same values of reduction parameters. More directly, the compressibility factor $Z = \frac{PV}{RT}$, which is a measure of the deviation of P-V-T behavior of a pure fluid from ideal gas law, can be expressed as a universal function of some dimensionless groups referred to as reduced parameters. That is:

$$Z = f_r \text{ (reduced parameters)} \tag{42}$$

where f_r is a universal function.

Since the constants of any two parameter equation of state may be evaluated by the critical constants, because the critical point is always the point of inflection where $\frac{\delta P}{\delta V} = \frac{\delta^2 P}{\delta V^2} = 0$, then such equations can be written in terms of reduced properties defined as follows:

$$Pr = \frac{P}{Pc}, \quad Tr = \frac{T}{Tc}, \quad Vr = \frac{V}{Vc} \tag{43}$$

Van der Waals equation is a two-constant equation of state; and, hence, it can be written in terms of reduced parameters. In terms of critical constants, van der Waals constants are:

$$a = 3P_cV_c^2, \quad b = \frac{V_c}{3}, \quad \text{and} \quad R = \frac{8}{3}\frac{P_cV_c}{T_c} \tag{44}$$

Applying Equations (43) and (44) to van der Waals equation yield:

$$\left(P_r + \frac{3}{V_r^2}\right)\left(V_r - \frac{1}{3}\right) = \frac{8}{3}T_r \tag{45}$$

In reduced form, van der Waals equation expresses any one of the reduced properties in terms of the other two. For instance

$$Vr = \Phi(Pr, Tr) \tag{46}$$

since

$$Z_c = \frac{P_c V_c}{RT_c} \quad \text{and} \quad \frac{PV}{RT} = Z, \quad \text{then} \quad Z = \frac{Z_c T_c PV}{P_c V_c T} = \frac{P_r}{T_r} Z_c \Phi(Pr, Tr) \tag{47}$$

and hence, if Z_c is taken to be constant, then

$$Z = f_r(Pr, Tr) \tag{48}$$

where f_r is again a universal function. Thus, as early as 1873 van der Waals had demonstrated the principle of corresponding state.

Extensive generalized charts for the Z factor as a function of P_r and T_r have been published by Cope, Lewis, Weber,[15] Brown, Souder,[12,13] and Smith, Katz, Brown, and Associates,[13] and many others. Sarem[90] developed a method for computing Z factors requiring 36 coefficients which is well suited to small- and medium-sized computers where the computer memory storage limitation may be a serious factor as follows:

$$Z = \sum_{m=0}^{5} \sum_{n=0}^{5} A_{mn} P_m(x) P_n(y) \tag{49}$$

where

$$x = \frac{2Pr - 15}{14.8}, \quad y = \frac{2Tr - 4}{1.9}, \quad P_m, P_n = \text{Legendre polynomials of degree m and n} \tag{50}$$

A more general treatment of the theorem of corresponding states requires the introduction of molecular parameters to form the reduction parameters. From the study of interactions between molecules and the parameters involved in the potential function, it can be deduced that the compressibility factor may depend on parameters in the potential

function: length and energy, dipole moment μ, quadrupole moment θ, octapole moment Ω, acentricity of molecules ω, molar polarization Π, Plancks constant h, molecular mass m, and two of the three state variables.

$$Z = Z(\epsilon, \sigma, \mu, \theta, \Omega, \omega, \Pi, P, V, h, m) \tag{51}$$

A possible functional relationship between these various quantities is the dimensionless relationship

$$Z = f(\frac{V}{\sigma^3}, \frac{RT}{\epsilon}, \frac{\mu^2}{\epsilon\sigma^3}, \frac{Q^2}{\epsilon\sigma^5}, \frac{\alpha}{\sigma^3}, \frac{h}{\sigma\sqrt{\epsilon m}}, \omega, \frac{\Omega}{\sigma^3}) \tag{52}$$

Because of lack of information on molecular parameters and electrical properties, it is not possible to use the relationship expressed in Equation (52). For simple molecules where μ, Q, α, and ω are negligible, this reduces to a quantum mechanical principle of corresponding state which has been used to predict many of the properties of H^3 by De Boer.[41] This is where the group containing h is used at very low temperatures.

Because of lack of information about molecular parameters, macroscopic quantities V_c and RT_c are used for volume and energy parameters instead of σ^3 and ϵ leading to the following relationship

$$Z = f(\frac{V}{V_c}, \frac{T}{T_c}, \frac{\mu^2}{V_c RT_c}, \frac{Q^2}{V_c^{5/3} RT_c}, \frac{\alpha}{V_c}, \omega) \tag{53}$$

The choice of σ^3 for V_c and ϵ for RT_c is mostly taken for granted in literature. Although the former is rather logical, since σ is the collision diameter whose cube must be related to V_c, the latter is not quite obvious other than the fact that both have energy units. However, since ϵ is the depth of the minimum polential well signifying the maximum possible potential energy between the molecules, it sets an upper

limit to the kinetic energy of the molecules before they can be separated far enough on the average to be considered gaseous. This is based on the assumption that so long as the average attraction potential between molecules is greater than their kinetic energy, the molecules can exist as a liquid phase; but when the average kinetic energy exceeds the maximum attraction potential energy, then the molecules can no longer exist in a liquid phase no matter how closely they are brought together. Thus the minimum potential is related to the maximum kinetic energy required to reach the critical point. Since kinetic energy can be taken to be a function of temperature alone, then the temperature at which the kinetic energy of the system becomes equal to the maximum attraction potential energy, represented by ϵ, can be defined as critical temperature. Thus the choice of ϵ to substitute for RT_c appears to be rather logical. Maybe this is why others have taken it for granted!

Nelson and Obert[71] have used the molecular principle of corresponding state to develop generalized charts of Z factor in terms of Lennard-Jones constants

$$Z = f\left(\frac{P\,b_o}{R(\frac{\epsilon}{k})}, \frac{T}{\epsilon/k}\right) \tag{54}$$

where $b_o = 2/3\ N\sigma^3$, σ = collision diameter, ϵ = maximum attraction energy. However, as mentioned before, the drawback of this relationship is the lack of uniqueness for the values of ϵ and σ, aside from the fact that no corrections due to other parameters shown in (52) are considered. Still another relationship was proposed by Pitzer[74] on the basis of his derivation for the partition function f:

$$f = (2\pi mk\epsilon\sigma^2)^{2m/2}\ F\left(\frac{V}{\sigma^3}, \frac{\epsilon}{T}\right) \tag{55}$$

To arrive at Equation (55), Pitzer made the following assumptions:

1) Classical statistical mechanics will be used. As an example, this assumption for a harmonically vibrating solid gives the DuLong and Petit value of the heat capacity. Since most solids attain this condition before melting, this assumption should be acceptable for their liquids.

2) Molecules are spherically symmetrical either actually or by virtue of rapid rotation.

3) The nature of intermolecular vibrations is assumed to be the same whether the molecules are in liquid or gas states.

4) The potential energy of an assemblage of molecules will be taken as a function only of the various intermolecular distances. This assumption is consistent with the properties of saturated molecules where only attractive forces are of the van der Waals-London type.

5) The potential energy for a pair of molecules can be written $U = \epsilon[f(\sigma/r)]$ with (σ) and (ϵ) being distance and energy parameters. Probably no group of substances follow this assumption precisely, but at least the heavier rare gases satisfy it to a high degree of accuracy. The exact nature of the function f is not of any concern, the only assumption is its universality.

b. Introduction of a third parameter. In recent years there has been a flurry of activity in connection with a modified principle of corresponding state in which a single characterizing parameter is used in addition to the reduced state variables. The reduced form of van der Waals equation had given a big hint that since Z_c was assumed to be

constant and it actually varies from .2 to .3, then Z_c could be a good third parameter. This was suggested by Meissner and Seferian[65] and used to prepare extensive tables by Lyderson and associates.[63] A summary of other third parameters as listed by Lyderson and co-workers[63] is as follows:

1) From Stockmayer potential for polar molecules as a dimensionless dipole.
2) Kihara's investigation indicates a shape factor as significant.
3) Riedel introduced a temperature derivative of the vapor pressure at critical point, α_c, as a third parameter for generalized vapor pressure and liquid density data, where

$$\alpha_c = \frac{T_c}{P_c} \left(\frac{\partial P}{\partial T}\right)_c$$

4) Lightfoot suggested the use of latent heat of vaporization at normal boiling point as a third parameter, inasmuch as latent heat is a measure of the intermolecular forces of attraction in a liquid.
5) Bloomer and Peck chose $\partial P_r/\partial T_r$ at constant value of psP_r, where $\rho_c = P_c/.29\ RT_c$, $.29 = Z_c$ for N_2 taken arbitrarily as reference substance in plotting Z as a function of P_r and T_r.
6) Pitzer, Lippman, et. al., introduce a third parameter $\omega = (1. + \log P_r^{o})$, P_r measured at $T_r = .7$. Then $Z = Z^o + \omega Z^1$, where Z^o and Z^1 are tabulated as functions of P_r and T_r. This is very similar to the factor introduced by Riedel.

These investigators[63] report that Z_c is an excellent third parameter for liquid and vapor phases in coexistence. The basis for this

assertion is given to be the linear relationship of the compressibility factor at saturation pressure Z_s to the critical compressibility Z_c as found on 82 different compounds at $P_r = .2$ and .8 (See Figure 3). To discount the use of any other third parameter, plots of Z_c vs all other available third parameters were made by the same researchers[63] and reported to give considerable scatter in all cases (See Figures 4-7). The influence of Z_c on the compressibility factor Z in two phase region is shown in Figure 8.[63]

5. Treatment by Microscopic or Statistical Thermodynamics

For the treatment of the real systems by statistical mechanics, it is necessary to include the potential energy of the molecules which is the source of the interaction between the molecules. Then the total energy is used in the partition function as in the case of ideal gas to obtain all other thermodynamics properties. Since the potential function is too complex to be described explicitly, it is generally expressed in a form compatible with physical realities in terms of some parameters. The parameters are then determined empirically based on experimental data for various substances. Lennard-Jones and Devonshire[41,43] (1932) proposed the following potential function for spherically symmetric molecule. (See Figure 9)

$$U(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}] \qquad (56)$$

Kihara[52] presented a potential function for globulal molecules by introducing a "core" in the center of the molecule. In his model the distance between the molecules is taken to be the distance between the cores of the molecules. For molecules with dipole moment, Stockmeyer[93] introduced

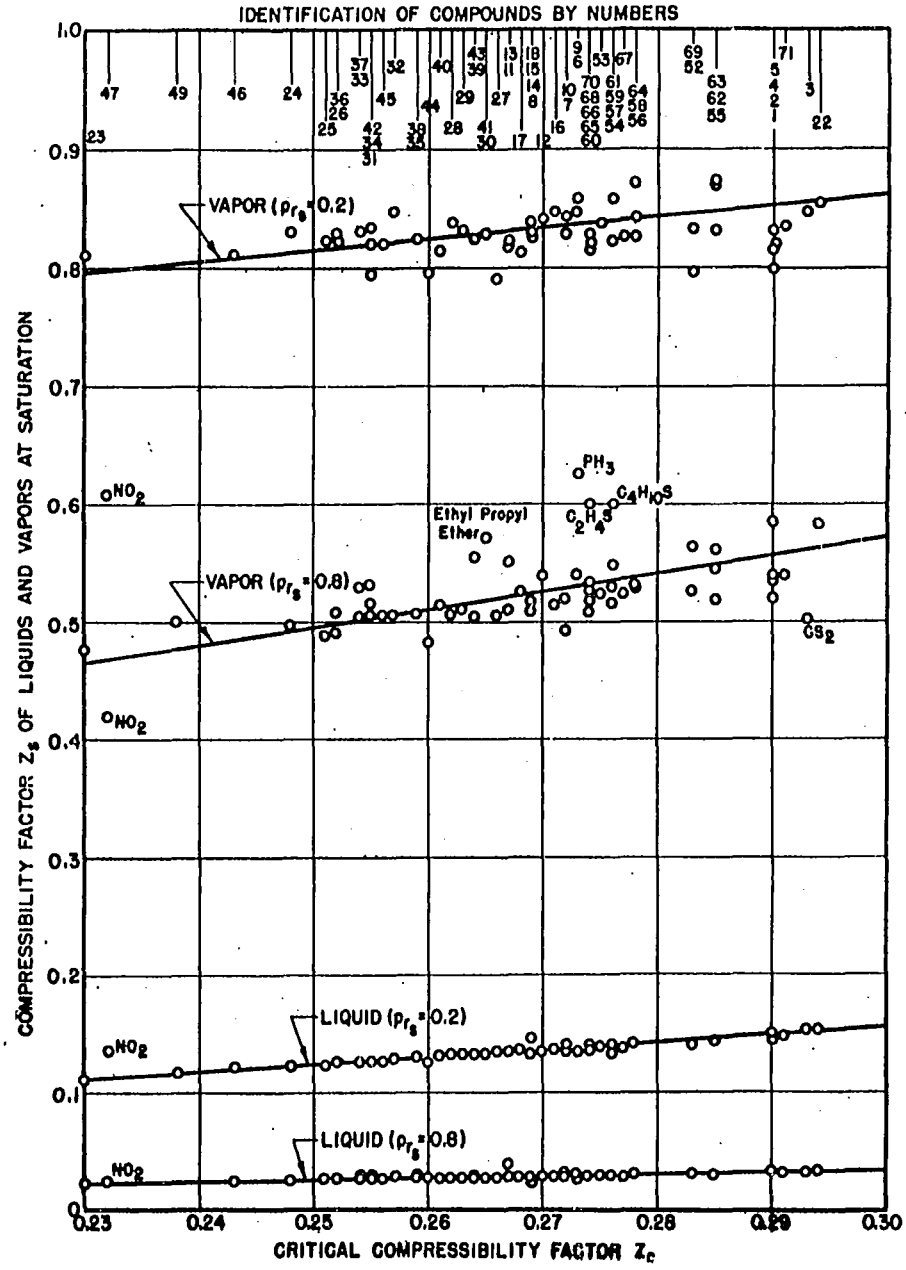
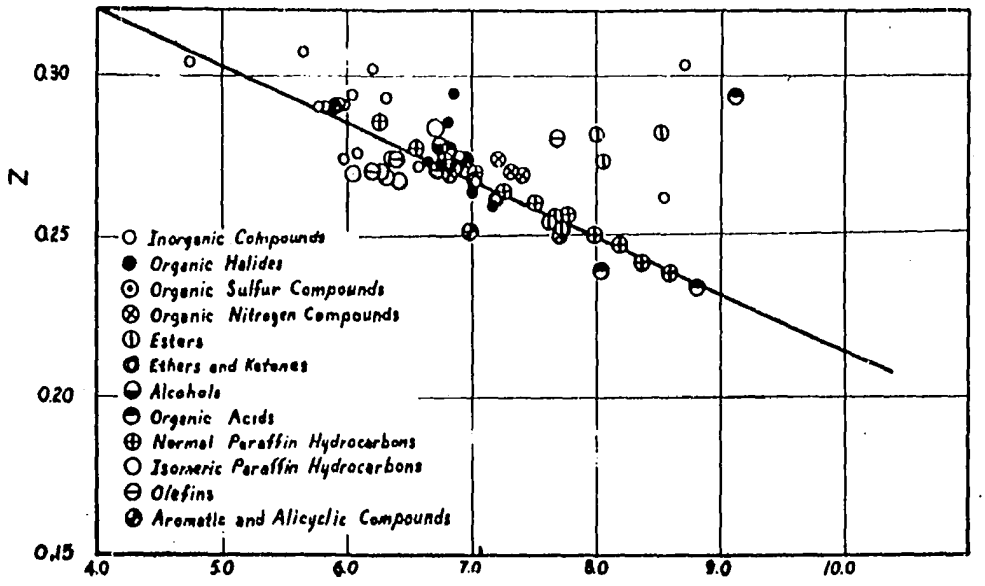
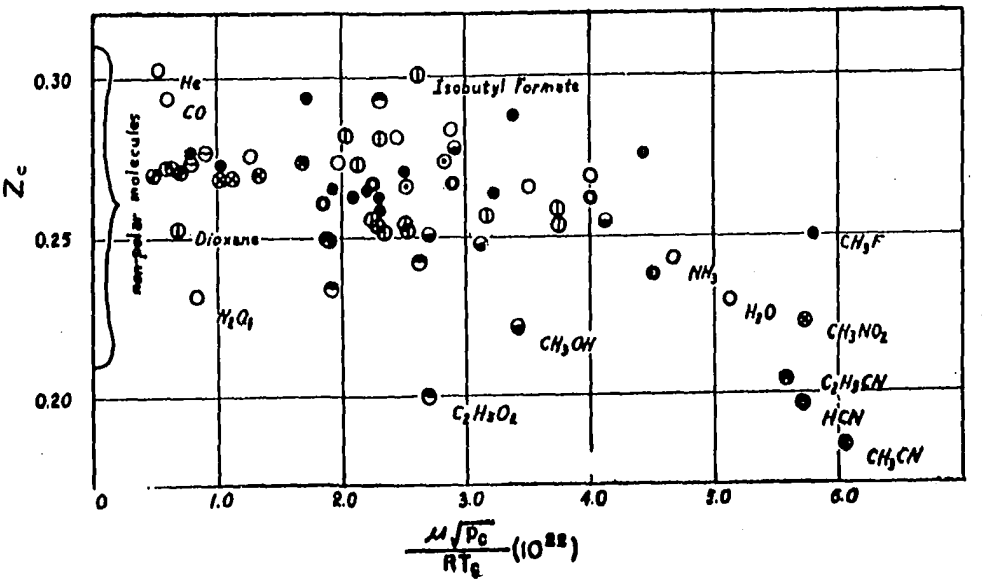


Figure 3

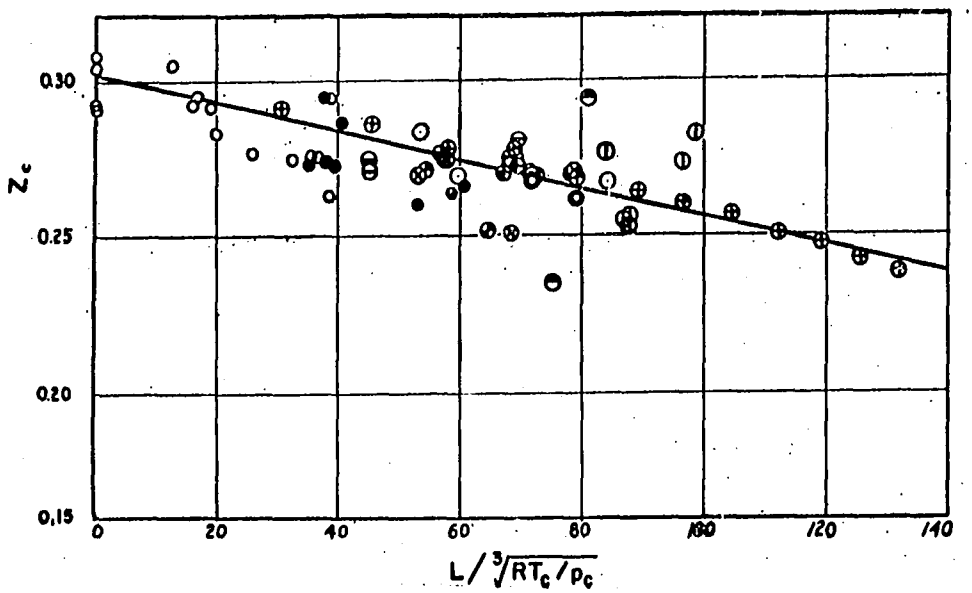
CORRELATION OF COMPRESSIBILITY FACTORS OF LIQUIDS AND VAPORS WITH THE CRITICAL COMPRESSIBILITY FACTOR Z_c
TAKEN FROM REFERENCE 63



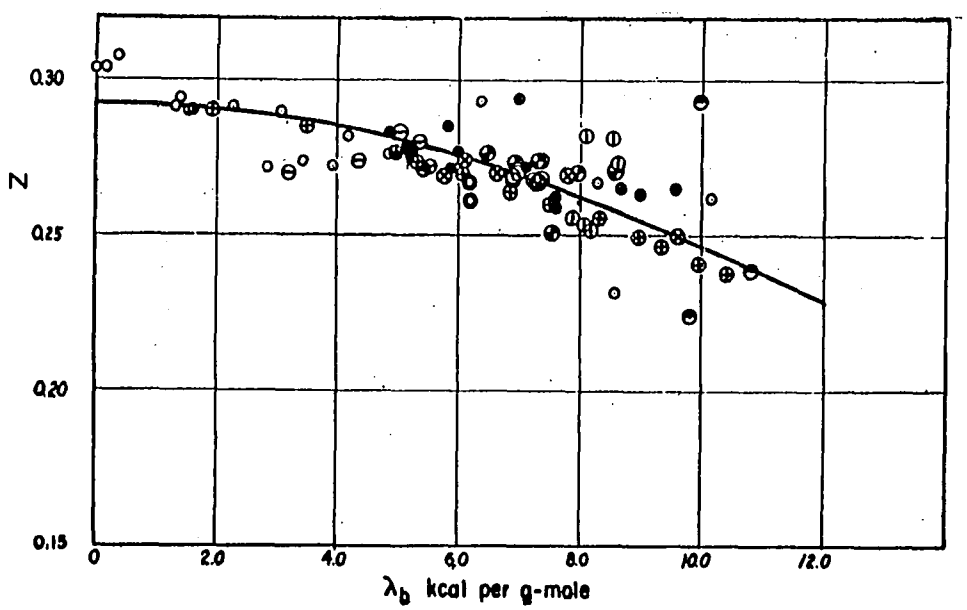
PLOT OF Z_c VERSUS RIEDEL MODULUS



Figures 4, 5
PLOT OF Z_c VERSUS STOCKMAYER POTENTIAL
TAKEN FROM REFERENCE 63



PLOT OF Z_c VERSUS BOND LENGTH FACTOR



Figures 6, 7
PLOT OF Z_c VERSUS NORMAL HEAT OF VAPORIZATION
TAKEN FROM REFERENCE 63

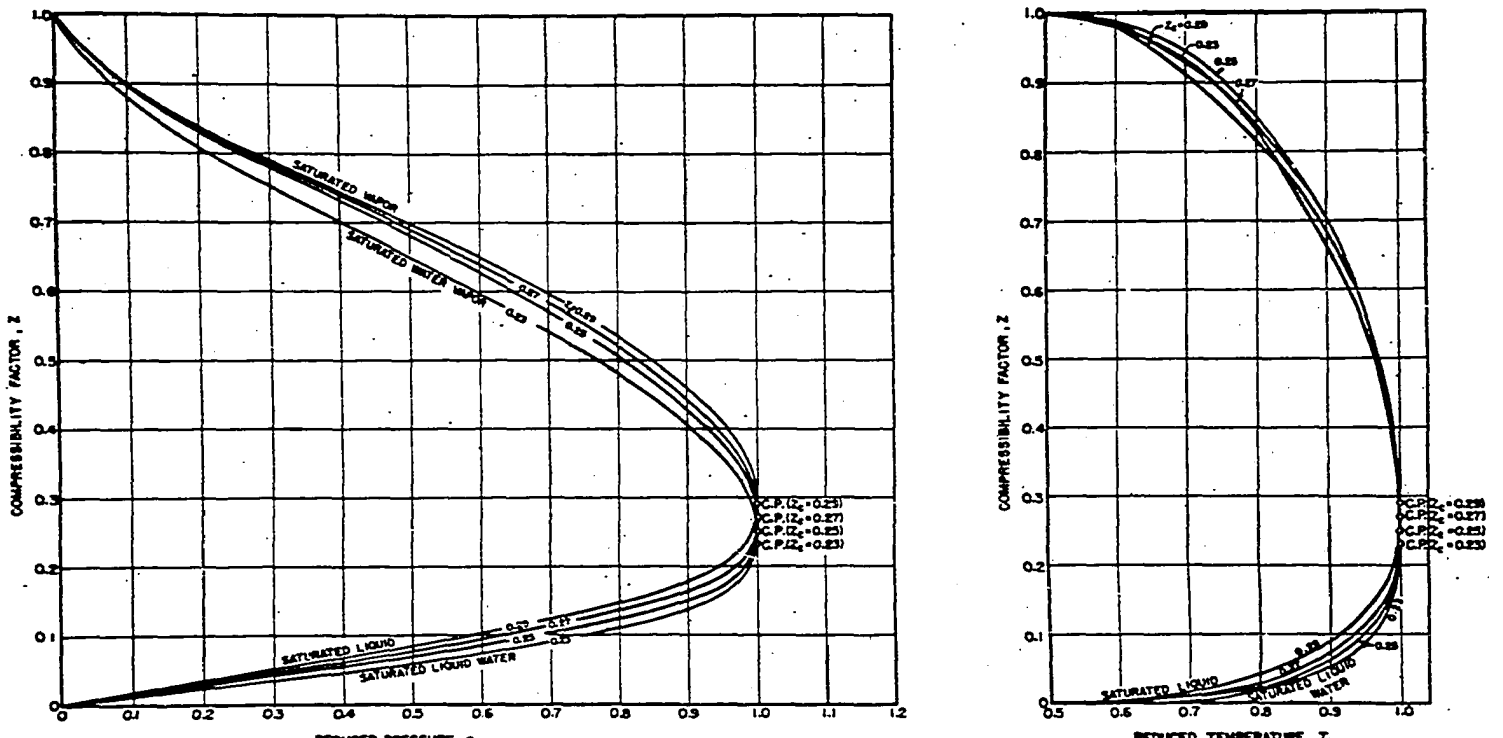
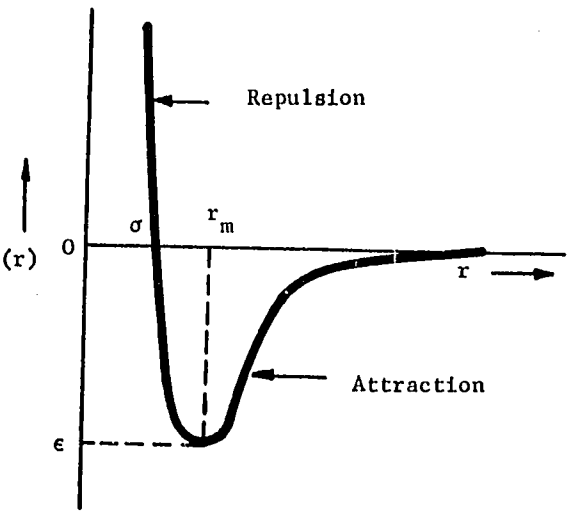


FIG. 3 COMPRESSIBILITY FACTORS OF SATURATED LIQUIDS AND VAPORS

Figure 8
COMPRESSIBILITY OF SATURATED LIQUIDS AND VAPORS
TAKEN FROM REFERENCE 63

Figure 9
Lennard-Jones Potential Energy of Molecular Interaction
as a Function of Distance r Between
the Two Molecules



a potential function with a dipole moment term.

C. Binary and Multicomponent Mixtures

In mixtures the interaction between unlike molecules dominate the theoretical developments for P-V-T properties. Therefore, these forces will be reviewed before various P-V-T prediction techniques are discussed.

1. Nature of Intermolecular Forces

The nature of intermolecular forces can be classified into two categories: First, the interaction between like molecules. This interaction is essentially the same as was encountered and discussed in a previous section for pure substances. The second and more important one is the interaction between unlike molecules. This interaction is essentially what causes the nonideal behavior in the mixtures. In the statistical mechanics treatment of pure substances, it is not hard to find a two or more parameter potential function which will work adequately well for the system based on whether the substance may be considered neutral and spherically symmetric, globular, or even polar. Once the potential function is postulated, the parameters of this function may be empirically determined from experimental data. However, in binary or multicomponent systems the interaction parameter between two unlike molecules must somehow be averaged. Many investigators have arbitrarily chosen the arithmetic average for the distance parameter of unlike molecules and geometric average for the energy parameter of the unlike molecules for the potential function. Magasaink[64] shows that the interaction length and energy parameters are internally related so that when one is determined the

other can be calculated. He also presents a new averaging technique which is in fact a weighted arithmetic average with the weighting factor being determined from experimental data by the method of least squares. Unfortunately, due to the nature of its complexity, the constants necessary for the use of Magasanik's correlation are only determined on a few compounds; and the correlations cannot at present be applied to complex hydrocarbon mixtures.

2. Empirical Equations of State

The equations of state may be extended to multicomponent systems if the constants for the mixtures can be determined.

Satter[91] reports the various available combining rules for most of the available equations of state. The combining rules for the constants of the equation of state have been treated much in the same manner as the interaction parameter of the potential function.

3. Theorem of Corresponding State

The theorem of corresponding state may be extended to mixtures based on the theoretical justification presented by Guggenheim.[32] In this manner, the hypothetical or pseudocritical properties are obtained for both liquid and vapor mixture. These values are then used to calculate reduced conditions at which the thermodynamic properties of the system may be found either from a generalized chart or from a reference substance chosen by a third parameter indicative of the nonideality of the system under study.

The original approach to calculate pseudocritical properties was the molal average critical method by Kay[51] who proposed the following

equations for pseudocritical pressure and temperature based on molal average.

$$P_{pc} = \sum_i X_i \, Pc_i \tag{57}$$

$$T_{pc} = \sum_i X_i \, Tc_i \tag{58}$$

where X_i represents the mole fraction of component i and Tc_i and Pc_i are critical temperature and pressure, respectively. When applied to non-polar hydrocarbon gaseous mixtures, Kay's method is reported to yield an average error of 2.5 per cent and maximum error of 10 per cent.

Joffe[48,49] improved upon Kay's method and obtained a slightly better average error of 2 per cent and a maximum error of 8.8 per cent.

Leland and Mueller[57] arrived at an empirical mixing rule which originates from the analogy to the method of obtaining interaction second and third virial coefficients of a mixture from the second and third virial coefficient of pure substances.

Kilpatrick[53] shows the relation of the virial coefficients of the mixture to those of the pure components to be:

Second Virial Coefficient

$$B_m = \sum_i \sum_j X_i \, X_j \, B_{ij} \tag{59}$$

Third Virial Coefficient

$$C_m = \sum_i \sum_j \sum_k X_i \, X_i \, X_j \, C_{ijk} \tag{60}$$

Taking the expression for second virial coefficient as[41]

$$B = 2\pi N \int_0^\infty (1 - e^{-U(r)kt}) r^2 dr \tag{61}$$

and using the Lennard-Jones 6-12 potential, the following expression can be written for the second virial coefficient.[41]

$$B = \sum_{\gamma=0}^{\infty} f_\gamma (T)\sigma^3 \epsilon^{\frac{2\gamma+1}{4}} \tag{62}$$

and for the mixture

$$B_m = \sum_i \sum_j X_i X_j \sum_\gamma f_\gamma(T) \sigma_{ij}^3 \epsilon_{ij}^{\frac{2\gamma+1}{4}} \tag{63}$$

Leland[57] states that if the pseudocritical concept is valid according to Pitzer's assumptions[74] mentioned earlier, then for each constant composition of the mixture, there must exist a hypothetical pure substance with criticals P_c', T_c', V_c', which has thermodynamic properties idential with those of the mixture at the same P-V-T conditions. If the corresponding state principle is to be upheld, this hypothetical pure substance must also have a potential function in the form

$$U(r) = \bar{\epsilon} f(\frac{\bar{\sigma}}{r}) \tag{64}$$

where $\bar{\epsilon}$ and $\bar{\sigma}$ are two potential parameters. Thus from the combination of Equations (61), (62), (63), and (64) he gets

$$\sum_{\gamma=0}^{\infty} f_\gamma(T)\bar{\sigma}^3 \bar{\epsilon}^{\frac{2\gamma+1}{4}} = \sum_{i=1}^{n} \sum_{j=1}^{n} X_i X_j \sum_{\gamma=0}^{\infty} f(T)\sigma_{ij}^3 \sigma_{ij}^{\frac{2\gamma+1}{4}} \tag{65}$$

or

$$f_o(T)\left[\bar{\sigma}^3\,\bar{\epsilon}^{1/4} - \sum_{i=1}^{n}\sum_{j=1}^{n} X_i X_j \sigma_{ij}^{1/4}\sigma_{ij}^{3}\right] + f_1(T)\left[\bar{\sigma}^3\,\bar{\epsilon}^{3/4} - \sum_{i=1}^{n}\sum_{j=1}^{n} X_i X_j \epsilon_{ij}^{5/4}\sigma_{ij}^{3} + \ldots = 0\right] \tag{66}$$

Then, when the theory of corresponding state is valid, he expresses the pseudocritical properties in the following form.[57]

$$T_c' = \left[\frac{\sum_{i=1}^{n}\sum_{j=1}^{n} X_i X_j \left(\frac{Z_c T_c}{P_c}\right)_i^{\alpha+1/2} \left(\frac{Z_c T_c}{P_c}\right)_j^{\alpha+1/2}}{\sum_{i=1}^{n}\sum_{j=1}^{n} X_i X_j \left[\frac{1}{2}\left(\frac{Z_c T_c}{P_c}\right)_i^{1/3} + \frac{1}{2}\left(\frac{Z_c T_c}{P_c}\right)_j^{1/3}\right]^3}\right]^{1/\alpha} \tag{67}$$

$$P_c' = \frac{T_c' \sum_{i=1}^{n} X_i (Z_c)_i}{\sum_{i=1}^{n}\sum_{j=1}^{n} X_i X_j \left[\frac{1}{2}\left(\frac{Z_c T_c}{P_c}\right)_i^{1/3} + \frac{1}{2}\left(\frac{Z_c T_c}{P_c}\right)_j^{1/3}\right]^3} \tag{68}$$

where α is empirically determined to be a function of temperature and pressure as follows:

$$\alpha = -.75\left(\frac{P\sum_i X_i T_{ci}}{T\sum_i X_i P_{ci}}\right) + 2.44 \quad \text{for} \quad .4 < F = \frac{P\sum_i X_i T_{ci}}{T\sum_i X_i P_{ci}} < 2 \tag{69}$$

$\alpha = 2.2$ for $F \leq .4$, $\alpha = 1.0$ for $F \geq 2.0$

There are several points of interest in this derivation and its use:

1) The choice of only the second virial coefficient rather than higher virial coefficients is just incidental and as good as others as demonstrated by Equation (14) of Reference 57.

2) The choice of Lennard-Jones potential is a good one because it is the simplest of all potential functions to handle and furthermore, any other two parameter potential function would result in the same critical property expressions. Any deviation due to nonidealty must be dealt with empirically.

3) There is a need for a yardstick to choose the reference substance. Lyderson, Greenkorn, and Hougen[32] show that the molal average compressibility factor Z_c is an excellent third parameter for use in the theory of corresponding states. Leland and co-workers [57] use Z_c as a third parameter in conjunction with their empirical mixing rule on a number of binary mixtures of vapor and liquid in coexistence. However, this third parameter can not be directly evaluated for complex mixtures especially where a lumped heptanes-plus fraction needs to be considered as in reservoir fluid samples.

4) Possible empirical improvement on this theory could be the manipulation with the temperature dependence of the second virial coefficient of the mixture.[59] That is, a correction factor can be devised as a multiplier for the critical properties that would make the temperature dependence of the second virial coefficients of the individual components in the mixture match a common curve.

5) In their derivation of pseudocritical temperature and pressure, Leland and Mueller made the following assumptions for the

interaction distance and energy parameters:

$$\sigma_{ij} = \frac{1}{2} (\sigma_{ii} + \sigma_{jj}) \tag{70}$$

$$\epsilon_{ij} = (\epsilon_{ii} \ \epsilon_{jj})^{1/2} \tag{71}$$

Although the arithmetic and geometric averages used above have been accepted thus far, other averaging techniques such as the one proposed by Magasanik based on weighed arithmetic average may be superior. However, these authors[57] have determined another parameter, namely α, to force fit the experimental data using Equations (70) and (71) for interaction parameter calculation. Thus any inaccuracy introduced in their combining rule is partially compensated for by using the force fit value of parameter α.

Leland and Mueller report an average deviation of 2.3 per cent for the density prediction of both vapor and liquid mixtures in coexistence by this method. They report that in only 8 out of 58 binary systems did the method of molal average of Kay yield a slightly better prediction than their empirical approach.

4. Other Multicomponent Density Prediction Methods

Sage and Lacey[78] suggested a method of using partial molal volumes for computing the density of hydrocarbon gas mixture. They approximate the complex multicomponent gaseous mixtures by a quarternary system of methane, ethane, propane, and butane. The residual partial specific volumes are presented for methane-ethane at 70°F-250°F, 0-3000 psig; methane-propane at 70°F-190°F, 0-3000 psig.

The specific volume of the complex system is then determined by the following formula:

$$V = \frac{10.732T}{M_a P} - \bar{V}_1 n1 - \bar{V}_2 n2 - \bar{V}_3 n3 - \bar{V}_4 n4 \qquad (72)$$

The first term of this equation represents the specific volume of the natural gas if it followed the perfect gas law, whereas the succeeding terms are the deviations of the partial specific volumes of each of the components from this idealized behavior. In this approach all components having greater molecular weight than propane are considered normal butane. All nonhydrocarbon gases are also considered hydrocarbons. The molal volume determined by this method yields a prediction with an average deviation of 1.4 per cent and maximum deviation of 4.9 per cent. The range of pressure is limited to 3000 psig and that of temperature is from 70°F to 190°F.[23]

Sage, Hicks, and Lacey[77] suggest a method of using partial molal volumes for computing the density of hydrocarbon liquids. The method is similar to the above-mentioned method for gaseous mixtures. The results agree within 3 per cent of the experimental values. However, the composition range is limited to about 10 per cent by weight of methane; consequently, this correlation does not cover the low-molecular-weight liquid similar to natural gasoline and high pressure gas condensates.

Standing and Katz[95] have presented a method for computing liquid densities assuming additive volumes for all densities less volatile than methane and ethane in the liquid at 60°F and one atmosphere pressure. This method is reported[42] to be reliable within about 1.5 per cent in predicting the densities of heavy crude oil saturated with natural gas.

Watson[103] reports a method of calculating the density of pure hydrocarbon liquids from molecular weight, critical temperature and pressure, and empirical method will only yield an approximate density and

recommends its use only in the absence of reliable density data. Watson's method was thoroughly covered in previous sections for pure compounds.

Hanson, Kuist, and Brown[26] extended the Standing and Katz[95] correlation to include a higher percentage of methane; but the only system they studied was under-saturated liquid. Furthermore, no hydrocarbons heavier than hexane were included in the system. In Natural Gasoline and the Volatile Hydrocarbon book sponsored by Natural Gasoline Association of America,[13] an extended form of Hanson, Kuist, and Brown[35] and Standing and Katz[92] correlations is presented. In this manuscript, for simplicity, this correlation is referred to as simply the N.G.A.A. method. When used in conjunction with phase behavior programs, this technique lead to some inconsistency near the critical region. This was later proved to be due to the inaccuracy of density prediction around the critical region.

Another technique for the determination of the density of liquid hydrocarbon mixtures has recently been presented by Alani.[1] In this technique van der Waals equation of state is used. The constants for the equation are given in terms of temperature for pure substances. A general equation for the constants of heptanes-plus is given in terms of molecular weight and specific gravity of the heptanes-plus fraction and the temperature. This general equation is obtained through regression analysis using a number of density-composition data with a limited range of specific gravity and molecular weight. For the mixture, the molal average of the constants is proposed to be used in the van der Waals equation. However, Alani does not recommend the use of his method for gas condensate systems.

In summary, there is no accurate technique presently available

to predict the density of multicomponent vapor and liquid in coexistence. The accuracy of the present techniques becomes even worse near the critical region where very accurate density prediction method is essential for the calculation of performance predictions of gas condensate and volatile oil reservoir depletion and many contemporary secondary recovery techniques.

The application of the modified theorem of corresponding states to the pure system has met with considerable success when proper mixing rules have been applied to obtain the pseudocritical properties. However none of the presently available third parameters, that are used in the modified theorem of corresponding states for pure substances, can be measured directly and accurately for such complex portions of hydrocarbon systems as heptanes-plus. Therefore, for accurate density prediction, a third parameter is needed that:

1) Can characterize the multicomponent mixture with regard to non-idealty.
2) Can be measured with high precision for complex mixtures such as heptanes-plus.
3) Varies between reference substances enough to allow for accurate interpolation of P-V-T properties.

To apply the modified theorem of corresponding states, a mixing rule is needed to calculate the pseudocritical properties. The only mixing rule available for the determination of the pseudocritical properties of the multicomponent systems in coexistent liquid-vapor region is that due to Leland and his co-workers.[57] Although the above mixing rule has been tested and proved to be successful for synthetic systems, it is based on the assumption that different combination rules may be applied

for the energy and distance parameters of unlike molecules in the potential function. This is somewhat contrary to the results found by Magasanik[64] who found an inter-relation between these two parameters and hence proposed an empirical weighted averaging rule.

Although an empirical weighting factor is not available for enough hydrocarbons to apply Magasanik's combination rule to Leland's mixing rule for pseudocritical properties, it is possible to test the influence of the application of similar combination rules in Leland's method as far as the final density prediction accuracy is concerned if only the region where the parameter α is kept constant is considered. Fortunately, the value of α is unity for most multicomponent liquid phases in coexistence with vapor which are encountered in gas condensates and volatile oils. This provides an opportunity to compare the pseudocritical mixing rule proposed by Leland to other mixing rules based on other averaging techniques for the distance and energy parameters of unlike molecules.

CHAPTER III

PROPOSED METHOD FOR THE DETERMINATION OF VOLUMETRIC BEHAVIOR OF HYDROCARBONS AND THEIR MIXTURES

A new third parameter is introduced for the modified theorem of corresponding states. Keeping all of the accuracy benefited by the other third parameters, it can also be measured directly, simply, and very accurately even for such complex liquid mixtures as heptanes-plus. Its value varies over a wide range for the reference substances allowing for very accurate interpolation of P-V-T properties.

A new mixing rule has also been introduced for the determination of pseudocritical properties which is shown to be superior to those presently available.

A. Proposed Third Parameter for the Theorem of Corresponding State

London dispersion forces were explained in the previous chapter, and the form was given in Equation (19). Now it is expressed that the London dispersion forces and light dispersion are intimately related. As a matter of fact, it is from this intimacy that the expression "London dispersion forces" was coined. As the light travels through a substance, the valance electrons of the molecules are disturbed so that the light is refracted. The degree of emersion and absorption of light depends on the instantaneous charge distribution of these electrons. However, this same instantaneous charge distribution is responsible for the induced dipole

moment expressed in London dispersion forces.

Thus, the light dispersion properties of a substance indicate the degree of its nonideality or its vulnerability to London dispersion forces.

In a previous chapter, the London dispersion forces were shown to have adequately explained the nonideality of the real systems. Therefore, any true third parameter yardstick for characterizing the nonideal behavior of the real systems should implicitly account for these forces. However, since it was shown that the light dispersion and London dispersion forces are related, then an implicit inclusion of light dispersion in a third parameter yardstick could suffice to characterize the nonideal behavior.

Refractive index appears to be a good third parameter which is influenced by the light dispersion and thus indicative of nonideal behavior. However, another third parameter is proposed which is dependent upon refractive index but was found to be superior to the refractive index.

The proposed parameter is the molecular or molar refraction $(R)_D$ which is closely related to the molar polarization of nonpolar substances expressed by Mossotti and Clausius[17] as follows:

$$\Pi = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = \frac{4}{3} \pi N \alpha \tag{73}$$

where Π = molar polarization
ρ = density
α = polarizability
ϵ = dielectric constant
M = molecular weight
N = Avagadro constant

The molecular polarizability α may be defined as the ease with which a molecule may be polarized, i.e., produce induced dipole m when an electric field F is applied on the molecule. In equation form this becomes:

$$m = \alpha F \tag{74}$$

The polarizability (deformability) may vary in a different direction unless the molecule is perfectly symmetrical, i.e., it represents a mean value.

For nonpolar molecules, the polarizability can be divided into two parts: Π_E and Π_A; the former is due to electronics and the latter to atomic or nucleus effects; thus: $\Pi = \Pi_E + \Pi_A$ where

$$\Pi = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = \frac{4}{3} \pi N\alpha \tag{75}$$

For polar molecules another term Π_o (orientation polarization) is added to Π so that[17]

$$\Pi = \Pi_E + \Pi_A + \Pi_o \tag{76}$$

where $\Pi_o = \frac{4}{3} \pi N(\frac{\mu^2}{3kT})$

The total polarization is a linear function of temperature so that

$$\Pi = a + \frac{b}{T} \tag{77}$$

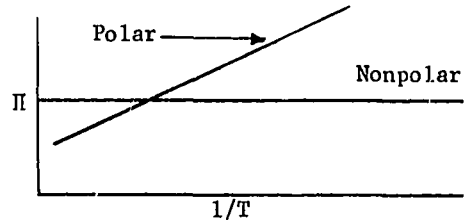
Comparison of Equations (75), (76), and (77) reveals that

$$a = \Pi_E + \Pi_A = \frac{4}{3} \pi N\alpha \tag{78}$$

$$b = \frac{4}{3} \pi N(\frac{\mu^2}{3k}) = \Pi_o T \tag{79}$$

Figure 10

Polarization-Temperature Curve for Polar and Nonpolar Substances



Accordingly, a plot of total polarization versus inverse temperature (see

Figure 10) should be a straight line: If the substance is nonpolar, then μ and hence b is zero; and the line will be parallel to 1/T axis. This provides one of the techniques for the determination of the dipole moment, i.e., from the slope b and the following equation:

$$\mu = \sqrt{9bk/4\pi N} \tag{80}$$

For nonpolar molecules Π is independent of temperature, and J. C. Maxwells' relation (1881) between dielectric constant and refractive index at infinite wave lengths n_∞ of $\epsilon = n_\infty^2$ holds true.

For nonpolar substances then

$$\Pi = \frac{n_\infty^2 - 1}{n_\infty^2 + 2} \frac{M}{\rho} = \frac{4}{3} N\pi\alpha \tag{81}$$

The value of n_∞ cannot be obtained by extrapolation to infinity, the wave length of refraction indices measured by visible light, for visible light can only disperse electrons while the positively charged nuclei remains unaffected. To actually measure Π it is therefore necessary to measure the refractive index by long wave length infrared rays because the low frequency vibrations are not able to displace the relatively heavy atomic nuclei.

Since Π_A is hard to measure and its value is rather small, it is generally approximated as five to ten per cent of Π_E measured by the D-line of sodium. When the electronic polarization Π_E is obtained from visible light rays, it is sometimes referred to as molecular refraction R. For sodium D-line the molecular refraction can be expressed as follows:

$$(R)_D = \frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho} = \Pi_E = \frac{4}{3} \pi N \alpha_E \tag{82}$$

Molecular refraction is an additive quantity,[28,40] so that for a

binary mixture of X_1, M_1, and X_2, M_2 mole fractions and molecular weights and overall density of ρ, the molecular refraction can be expressed as follows:

$$(R)_{D^{1,2}} = \frac{n^2 - 1}{n^2 + 2} \frac{M_1 X_1 + M_2 X_2}{\rho} \tag{83}$$

The molecular or molar refraction is a measure of the deformability of the electronic sheaths and hence merits dissection based on electron groups. A. L. von Sleiger[29,41](1921) suggested such a dissection as follows: Since the four valances in methane can be regarded as equivalent, the eight valance electrons may be assumed to be uniformly distributed between the four C-H bonds, so that the refraction equivalent of C-H bond is as follows:

$$R_{C-H} = \frac{1}{4} R_{CH_4} = \frac{1}{4} R_C + R_H \tag{84}$$

where R_H and R_C are the ordinary refraction equivalents of carbon and hydrogen as given in Table 3.[28]

TABLE 3

REFRACTION EQUIVALENTS OF VARIOUS GROUPS

Electron Group	C:H	C:C	C::C	C:::C	C:F:	C:Cl:
Refraction	1.705	1.209	4.15	6.025	1.6	6.57
Electron Group	E:I:	C:Br:	Si:cl:	S:F:	Se:F:	Te:F:
Refraction	14.51	9.47	7.04	1.95	2.23	2.47

As another example to evaluate refraction equivalent of C = C double bond, we can write $R_{C=C}$ as follows:

$$R_{C=C} = R_{C_2H_4} - 4R_{CH} = 2R_C + 4R_H - 4(\frac{1}{4} R_C + R_H) \quad (85)$$

or

$$R_{C=C} = R_C \quad (86)$$

similarly

$$R_{C=C} = \frac{3}{2} R_C \quad (87)$$

Molecular refraction also bears a linear relationship to the critical compressibility factor Z_c introduced by Meissner and Seferian[62] and used successfully as a third parameter by Lydersen-Greenkorn and Hougen[61] for pure substances. While the determination of Z_c for mixtures, especially those containing heptanes-plus, is very difficult if not impossible, the determination of $(R)_D$ can be made readily and directly with considerable accuracy.

For mixtures, the molecular refraction is simply the molal average of individual molecular refraction of various components including complex portions such as heptanes-plus. In the liquid phase the heptanes-plus molecular refraction is determined from molecular weight, density, and refractive index determinations. A rather complete list of molecular refraction for pure hydrocarbons and related compounds is given by Rossini.[82]

The molecular refraction can therefore indicate the degree of nonideality of a pure substance under study. That is, all nonpolar substances having the same molecular refraction should behave similarly when examined at the same reduced pressure and temperature. Thus, $(R)_D$ is proposed to be used as a third parameter in the theory of corresponding state to characterize the system with regards to nonideality.

Table 4 gives the value for molecular refraction and critical compressibility factor for several normal hydrocarbons which may be used as reference substances when a multicomponent hydrocarbon system is considered. Figure 11 exhibits a plot of $(R)_D$, the molecular refraction versus Z_c, the compressibility factor. A plot of critical constants versus $(R)_D$ is given in Figure 12 for a number of normal hydrocarbons which may be considered as heptanes-plus portion normally encountered in gas condensate and volatile oils.

For multicomponent systems the molal average of molecular refraction $(R)_D$ is proposed to be used as a third parameter in the modified theorem of corresponding states.

TABLE 4

MOLECULAR REFRACTION AND Z_c OF SOME H-C DATA

Compound	Molecular Refraction at 25°C	Z_c
nC_1	3.530	.290
nC_4	20.630	.274
nC_5	25.266	.269
nC_6	29.907	.264
nC_7	34.550	.260
nC_8	39.192	.256
nC_9	43.842	.251
nC_{10}	48.481	.247

Figure 11
CORRELATION OF Zc AND $(R)_D$

Normal Hydrocarbons

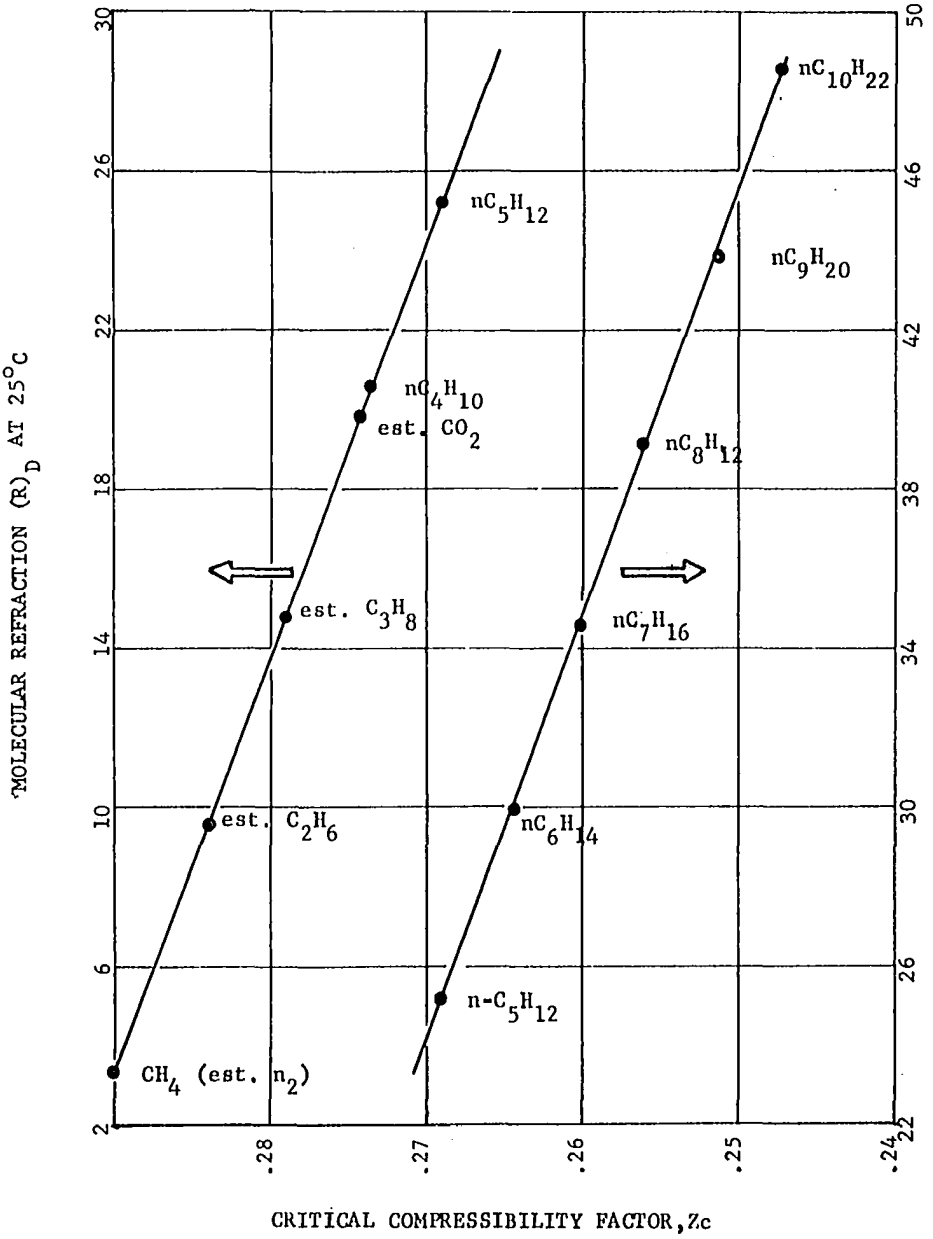
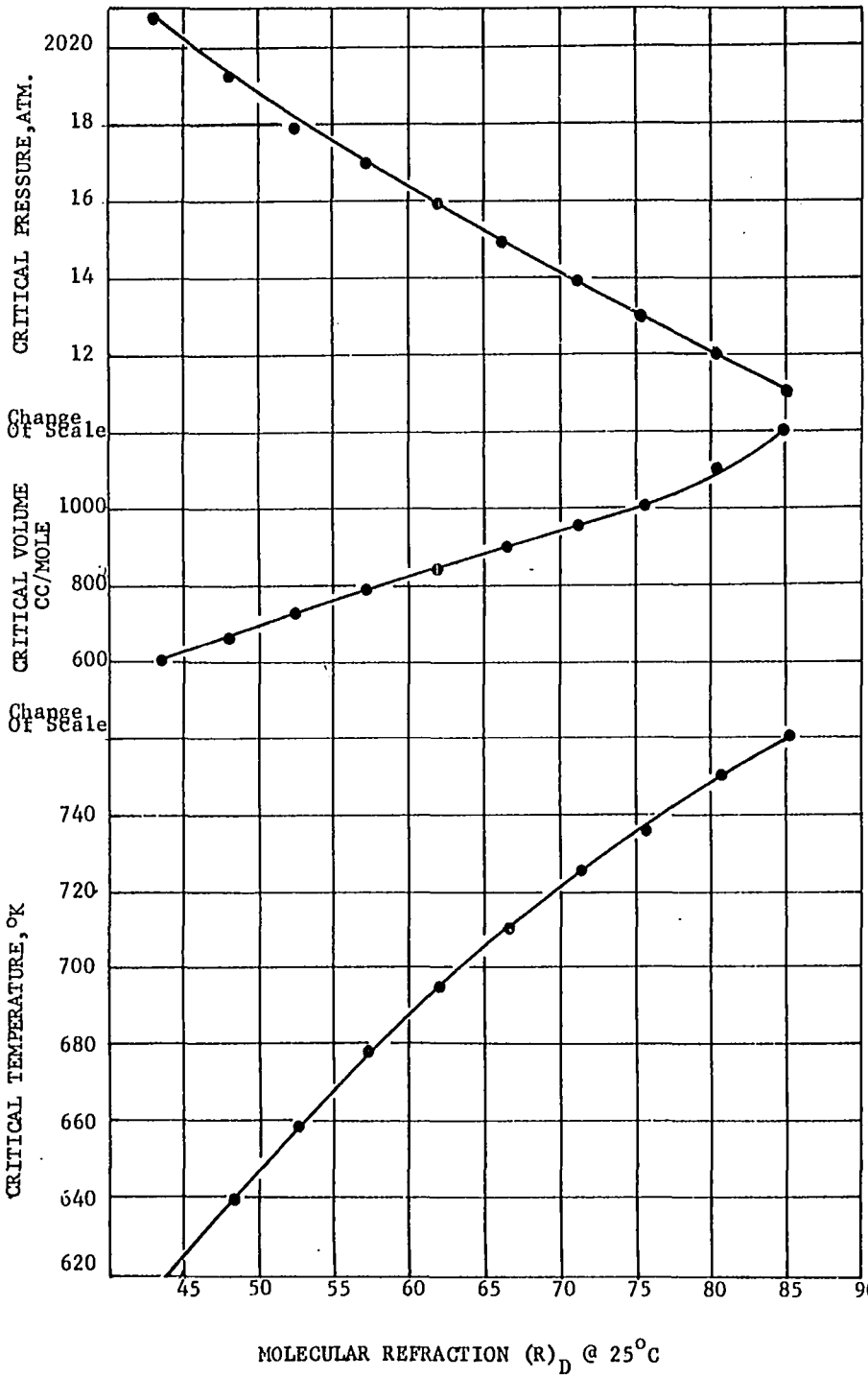


Figure 12
CORRELATION OF $(R)_D$ AND CRITICAL PROPERTIES OF NORMAL HYDROCARBONS



B. Proposed Mixing Rule for the Determination of Pseudocritical Properties

In arriving at their proposed mixing rule, Leland and Mueller used the following averaging technique for the interaction constants between unlike molecules:

$$(\epsilon\,\sigma^3)_{ij} = \sqrt{(\epsilon\,\sigma^3)_{ii}\,(\epsilon\,\sigma^3)_{jj}} \tag{88}$$

$$\sigma_{ij} = \frac{1}{2}\,(\sigma_{ii} + \sigma_{jj}) \tag{89}$$

$$\sigma_{ij}^{\,3} = \left[\frac{1}{2}\,(\sigma_{ii}^{\,3})^{1/3} + \frac{1}{2}\,(\sigma_{jj}^{\,3})^{1/3}\right]^3 \tag{90}$$

Magasanik[64] reports that the distance parameter σ is related to the energy parameter ϵ. Furthermore, he proposes an averaging technique for unlike molecules for either one of the parameters σ or ϵ. In his technique he simply takes a weighted average of the parameter of like molecules whereby the weighting parameter is determined empirically from binary experimental data. He has reported this parameter for a few hydrocarbon and nonhydrocarbons. Although Magasanik's technique cannot be applied presently to all multicomponent systems because of the lack of the weighting parameter and the functional relationship between σ and ϵ, it does provide a clue that whatever mixing rule is used for one of the parameters must also be used for the other because of the apparent relationship between the parameters.

With this idea in mind, an attempt was made to test the effect of a different averaging technique on the mixing rule proposed by Leland and Mueller, by employing the same type of averaging technique for both energy and distance parameters. Leland and Mueller had used an arithmetic average for a part of the distance parameter as shown in Equation (89) and

geometric average for the energy parameter ϵ and another part of the distance parameter σ^3 as shown in Equation (88). To develop a new averaging technique, an arithmetic average was ruled out because it cannot be applied to the energy parameter ϵ.[41] However, two additional mixing rules were generated by using the geometric mean for both parameters in the first case and the harmonic mean for both parameters in the second case to average the parameters for unlike molecules. Thus the following mixing rules were developed based on Leland and Mueller's approach, but with different averaging techniques.

1. Geometric mean used for parameters as follows:

$$\sigma_{ij} = \sqrt{\sigma_{ii}\,\sigma_{jj}} \tag{91}$$

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\,\epsilon_{jj}} \tag{92}$$

$$T_c' = \left[\frac{\sum_{i=1}^{n}\sum_{j=1}^{n} X_i X_j \left(\frac{Z_c T_c}{P_c}\right)_i^{\alpha+1/2} \left(\frac{Z_c T_c}{P_c}\right)_j^{\alpha+1/2}}{\sum_{i=1}^{n}\sum_{j=1}^{n} X_i X_j \left(\frac{Z_c T_c}{P_c}\right)_i^{1/2} \left(\frac{Z_c T_c}{P_c}\right)_j^{1/2}} \right]^{1/\alpha} \tag{93}$$

$$P_c' = \frac{T_c' \sum_{j=1}^{n} X_j (Z_c)_j}{\sum_{i=1}^{n}\sum_{j=1}^{n} X_i X_j \left(\frac{Z_c T_c}{P_c}\right)_i^{1/2} \left(\frac{Z_c T_c}{P_c}\right)_j^{1/2}} \tag{94}$$

2. Harmonic mean used for parameters as follows:

$$\sigma_{ij} = \frac{2\,\sigma_{ii}\,\sigma_{jj}}{\sigma_{ii}\,\sigma_{jj}}, \qquad V_{cij} = \frac{8\,V_{ci}\,V_{cj}}{(V_{ci}^{1/3} + V_{cj}^{1/3})^3} \tag{95}$$

$$\epsilon_{ij} = \frac{2\epsilon_{ii}\,\epsilon_{jj}}{\epsilon_{ii} + \epsilon_{jj}} \tag{96}$$

$$T_c' = \left[\frac{\sum_{i=1}^{n}\sum_{j=1}^{n} X_i X_j \left[\frac{8\left(\frac{Z_c T_c}{P_c}\right)_i \left(\frac{Z_c T_c}{P_c}\right)_j}{\left[\left(\frac{Z_c T_c}{P_c}\right)_i^{1/3} + \left(\frac{Z_c T_c}{P_c}\right)_j^{1/3}\right]^3} \frac{2(T_c)_i (T_c)_j}{(T_c)_i + (T_c)_j} \right]}{\sum_{i=1}^{n}\sum_{j=1}^{n} X_i X_j \frac{8\left(\frac{Z_c T_c}{P_c}\right)_i \left(\frac{Z_c T_c}{P_c}\right)_j}{\left[\left(\frac{Z_c T_c}{P_c}\right)_i^{1/3} + \left(\frac{Z_c T_c}{P_c}\right)_j^{1/3}\right]^3}} \right]^{1/\alpha} \tag{97}$$

$$P_c' = \frac{T_c' \sum_{i=1}^{n} X_i (Z_c)_i}{\sum_{i=1}^{n}\sum_{j=1}^{n} X_i X_j \frac{8\left(\frac{Z_c T_c}{P_c}\right)_i \left(\frac{Z_c T_c}{P_c}\right)_j}{\left[\left(\frac{Z_c T_c}{P_c}\right)_i^{1/3} + \left(\frac{Z_c T_c}{P_c}\right)_j^{1/3}\right]^3}} \tag{98}$$

It must be realized that inaccuracy caused by the mixing rule may be improved by the use of the empirical parameter α which Leland and Mueller have presented. It follows, incidentally, that the value of parameter α shown in Equations (93), (94), (95), (96) may necessarily be different from what was presented by Leland and Mueller.

In order to show the effect of various averaging techniques upon the prediction of pseudocritical properties, those regions for which α is constant can only be looked upon because in these regions the pseucocriticals are not dependent upon α and no compensation of error is

encountered. Such regions are found in saturated multicomponent hydrocarbon liquids for which the value of α is unity.

CHAPTER IV

EXPERIMENTAL INVESTIGATION

A. Fluids Used

Oil and gas sample from high pressure separators of several volatile oil and gas condensate reservoirs were recombined in the laboratory to synthesize seven hydrocarbon systems. Heavy crude oil was added to some of the systems to obtain a wider range of the properties of heptanes-plus. The range of the properties of the heptanes-plus of the systems studied are given below:

Heptane-plus Properties	Range
Molecular weight	134-194
Specific gravity, 60/60	.7825-.8196
Refractive index at 25°C.	1.4400-1.4468

B. Experimental Equipment

In the following sections the integral parts of the equipment used in this study will be discussed separately.

1. Multipurpose Free-Piston P-V-T and Phase Equilibrium Test Cell

The P-V-T cell designed for this work was a visual, variable volume cylinderical vessel which was used for two purposes. First, it provided a container for mixing the original gas and oil in which the

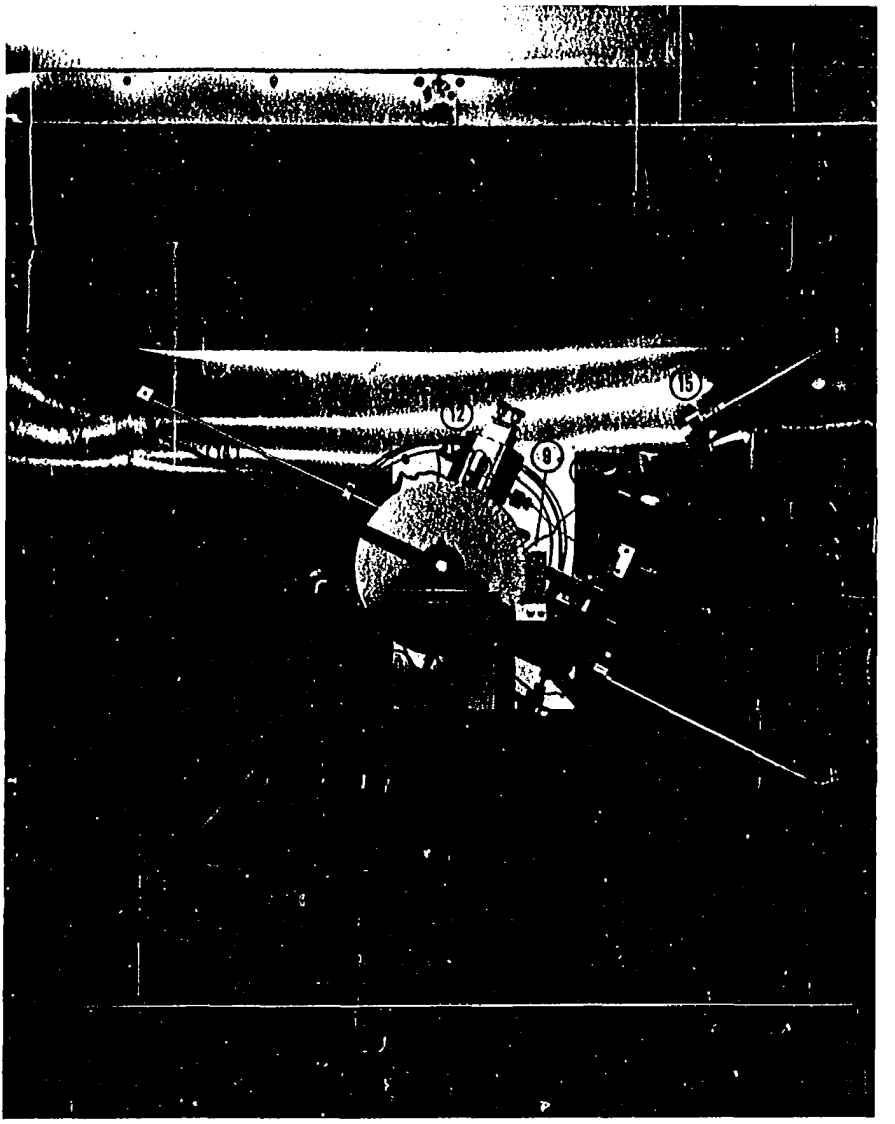
mixture was rocked to attain equilibrium before taking vapor and liquid samples. Second, it provided data for the volumetric liquid fraction versus pressure for characterizing the phase behavior of the system under study. The use of the mercury was completely avoided in this cell by providing a hydraulically actuated sliding piston inside the vessel. The movement of the piston was indicated by a sliding scale which was attached to the piston by a U-shaped polished rod. A photograph of the cell as placed inside the high-low temperature bath is given in Figure 13. Of particular interest in this figure are the bull's-eye windows (8), scale and vernier (11) and the protractor and angular vernier (9 and 10), and vapor and liquid valves (6 and 7).

The total volume of the cell at any particular piston position was determined by adding the dead volume of the cell to the product of the piston travel and the piston area. The liquid volume at any given piston position was determined from the calibration chart given in Figure 14 which is based on the piston position determined by the scale and vernier (11) and the angle of rotation of the cell required to bring the bottom of the vapor-liquid maniscus inside the cell to coincide with the center of the bull's-eye windows as determined by the protractor and vernier (9 and 10). The volumetric liquid fraction was then determined simply from the ratio of the liquid volume to the total volume.

The working pressure of the cell was designed for 20,000 psi at temperatures $-40^{o}F$ to $350^{o}F$.

To avoid any error in volume readings due to expansion and contraction of the scale, the scale was fabricated from a Nickel alloy called Invar which has a very low coefficient of thermal expansion of 8×10^{-7} cm/cm, ^{o}C.

FIGURE 13
INTERIOR OF HI-LO TEMP. BATH
AND GENERAL PURPOSE CELL



1. Alloy Steel Frame
2. External Valve Operator
3. Liquid Pycnometer
4. Vapor Pycnometer
5. 3-Way Autoclave Valve
6. Cell Vapor Valve
7. Cell Liquid Valve
8. Bullseye Window
9. Protractor Vernier
10. Protractor
11. Scale and Vernier
12. Differential Pressure Indicator
13. General Purpose Cell
14. Piston Rod
15. External Valve Operator
16. Pencil Thermometer
17. Pillow Block With Bearing
18. Air Exit
19. Air Inlet

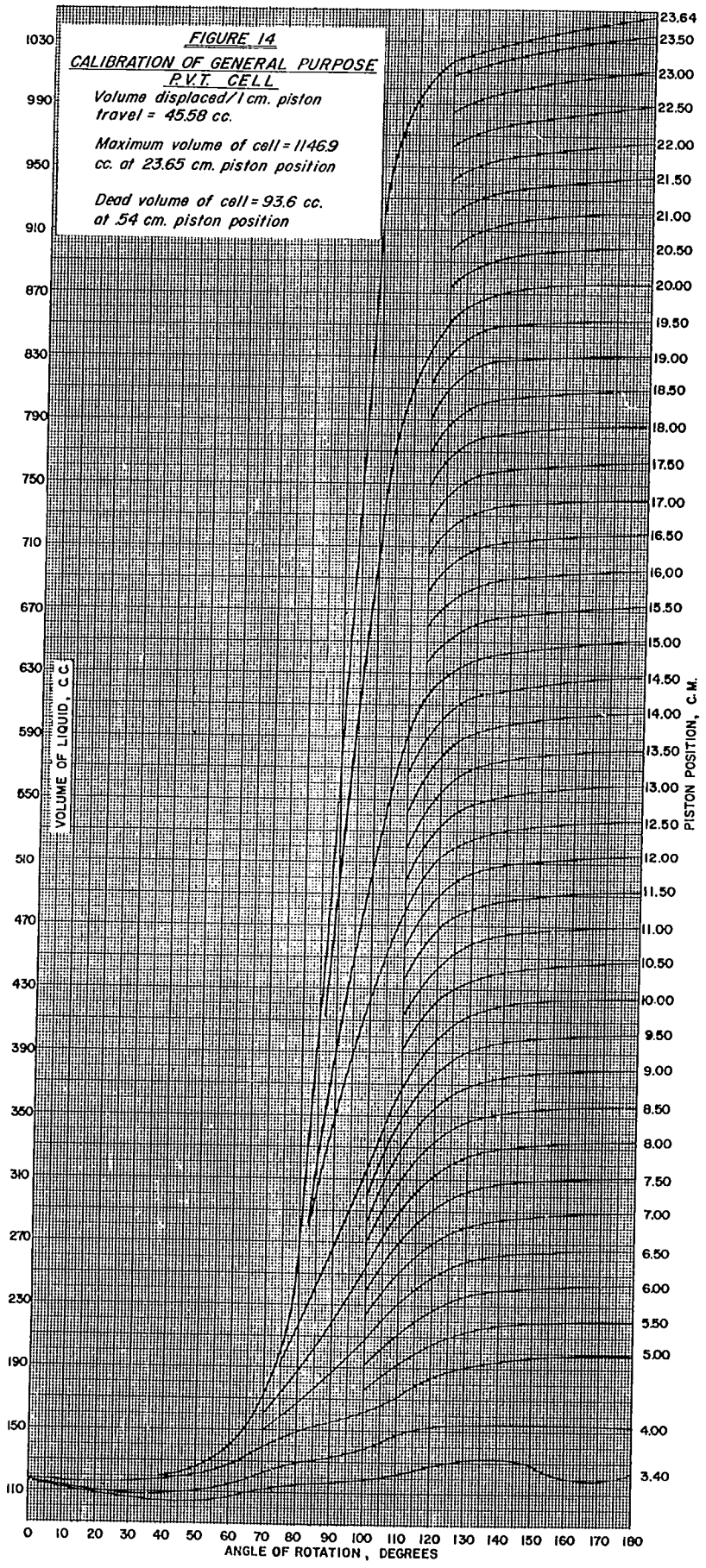


FIGURE 14
CALIBRATION OF GENERAL PURPOSE P.V.T. CELL
Volume displaced/1 cm. piston travel = 45.58 cc.
Maximum volume of cell = 1146.9 cc. at 23.65 cm. piston position
Dead volume of cell = 93.6 cc. at .54 cm. piston position
VOLUME OF LIQUID, C.C.
1030
990
950
910
870
830
790
750
710
670
630
590
550
510
470
430
390
350
310
270
230
190
150
110
PISTON POSITION, C.M.
23.64
23.50
23.00
22.50
22.00
21.50
21.00
20.50
20.00
19.50
19.00
18.50
18.00
17.50
17.00
16.50
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12.50
12.00
11.50
11.00
10.50
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.00
3.40
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180
ANGLE OF ROTATION, DEGREES

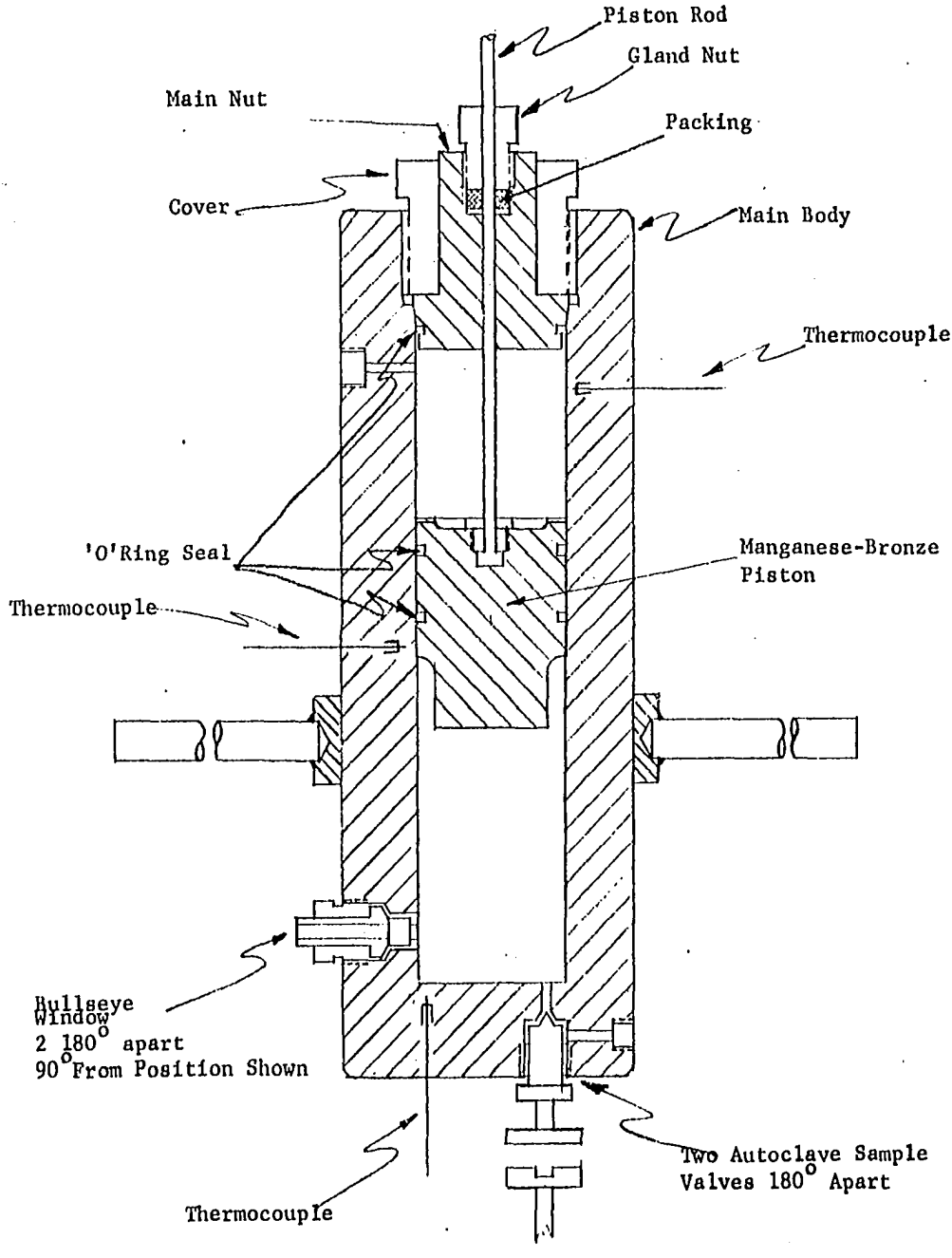


FIGURE 15

GENERAL PURPOSE CELL

The chemical composition of the special alloy used in the construction of this cell is given in Table B-1. A cutaway drawing of this cell is given in Figure 15.

2. High-Low Temperature Bath

a. General features. The unit is a Harris Manufacturing Company precision environmental test machine, 32 cubic feet capacity, 48" long by 23" wide by 48" high inside dimensions (Figures 13 and 16). There are six inches of polyurethane insulating foam around all sides of the chamber.

The cabinet is constructed of 14 gauge cold rolled steel. The interior is constructed of 16 gauge type 304 stainless steel, heliarc welded, and liquid tight. There is plenum chamber which houses two refrigerated coils, four air circulating blowers each operated by a 1/3 horsepower motor mounted on the top of the cabinet with extended shafts providing ball bearings external to the test chamber. The plenum chamber surrounds the test chamber on two sides with the blowers, heaters, and refrigerated coils located at the top; the air flow to and from the test chamber is regulated on each side.

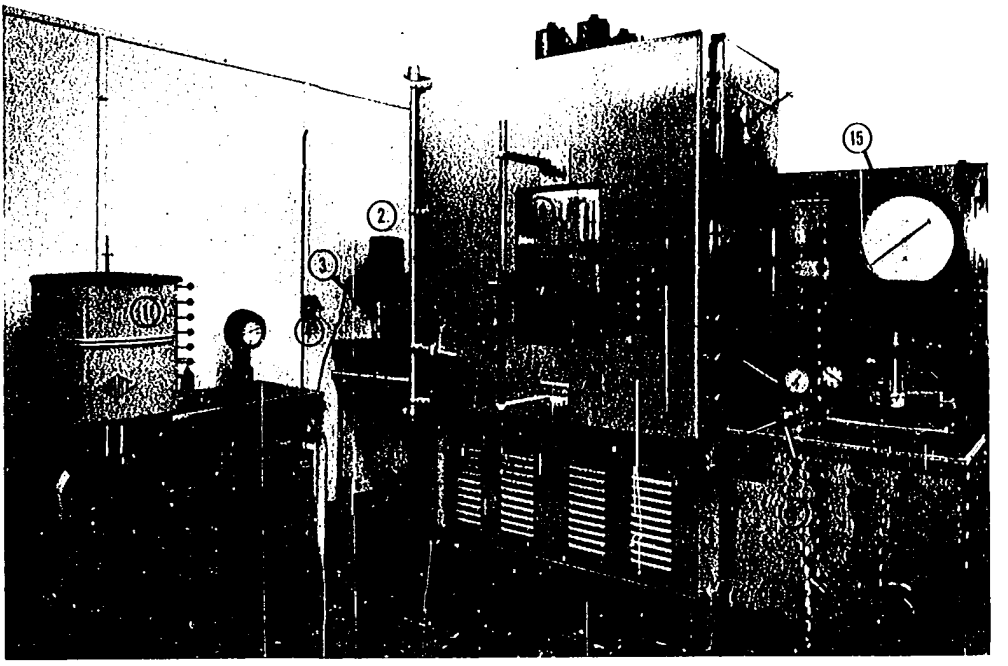
b. Refrigeration. The refrigeration system is of cascade type having a 2 horsepower and a 3 horsepower 208-200/3/60 water-cooled accessible hermatic motor compressor using Freon 13 and Freon 22 as refrigerants.

c. Heat. Four chrome steel sheathed heaters of one KW each are provided for controlling air temperature above room temperature with a minimum of overheat.

d. Oscillating mechanism. An A frame within the chamber is constructed of structural steel channel and has a hot dip galvanized finish.

Figure 16

BIRD'S-EYE VIEW OF ENTIRE P-V-T EQUIPMENT



1. Hart Pressure Balance
2. Galvanometer
3. Ice Bath
4. Pycnometer Box
5. Potentiometer
6. AMINCO Intensifier Pump
7. Air Regulator for Sprague Pump
8. Switch for Vacuum Pump
9. 2-Way Autoclave Valves
10. Hydraulic Pump for Ruska DWT
11. Ruska Dead Weight Tester
12. Vacuum Gauge
13. High Pressure Gauge
14. DAT L-N Temperature Controller
15. Heise Gauge
16. Switch for High Low Temp. Bath
17. Manometer
18. Safety Glass Window
19. Cathetometer
20. Door Latch
21. Rocking Manual Control
22. Weight Box for Ruska DWT
23. External Handle for Valve Operator

Shaft couplings connect the P-V-T cell clamping ring to a shaft which is extended through the rear wall of the cabinet. A gear on the shaft is driven by a second gear which will oscillate the P-V-T cell 180 degrees. The second gear has an extended arm attached to the shaft of a one-horsepower, 220-volts, 3-phase, 60-cycle totally enclosed reduction gear motor. The shaft rotates the P-V-T cell at 9 rpm. An entrance hole is placed under the lower right-hand corner of the cabinet door. A handle is inserted through the hole which turns the shaft and a sprocket placed in a suitable bearing through a hydraulic system. This sprocket is connected by a chain drive to a sprocket on the main shaft. Thus, the operator is able to view the cell through the window while rotating it to desired angle for viewing the liquid level or taking samples. The manual control does not interfere with the automatic control and can be applied whenever desired.

e. Performance. The machine is adjustable from -100°F to 350°F., controlled with a controller listed below. The temperature within the chamber is within 1°F at all times. This includes the temperature variation within the chamber and variations due to cycling of the temperature control.

f. Window. A multipane inspection window is located in the door for viewing the cell through the normal 180 degree oscillating arc. The window is constructed of a pane of one-inch thick tempered glass and six panes of 1/4-inch thick tempered glass with 1/2-inch air spaces between panes. A 100-watt vapor-proof light is mounted on the door above the window for interior illumination.

g. Temperature indicating recorder controller. A duration-adjusting type control was mounted integrally with indicating and

recording instrument to provide proportional pulsing type control with automatic reset and impulse rate control.

3. High Pressure Pycnometers

Figure 17 shows the essential parts of the high pressure spherical pycnometers which provide the following features:

1) Maximum volume to weight ratio
2) Pressure tested to 18,500 psi at room temperature
3) Possess a positive shut-off valve
4) The total weight is under 1000 gm when filled with any liquid so that a highly sensitive Metler grammatic balance which has a limit of 1000 gm can be used for weight measurements.
5) Highly polished exterior to eliminate the clinging of oil or any other foreign material on the outside while weighing
6) Fabricated from corrosion-resistant stainless steel.

In all, four pycnometers were fabricated, two for liquid and two for gas density measurements. All pycnometers were x-rayed and pressure tested before actual use. The x-ray revealed that pycnometer number one did not have adequate weld penetration. This was revealed after the experimental coefficient of volume expansion differed from the theoretical value more than can be attributed to the chance error and was confirmed by x-ray photograph. Table 5 gives a summary of the statistics pertaining to these pycnometers.

Figure 17
HIGH PRESSURE PYCNOMETER

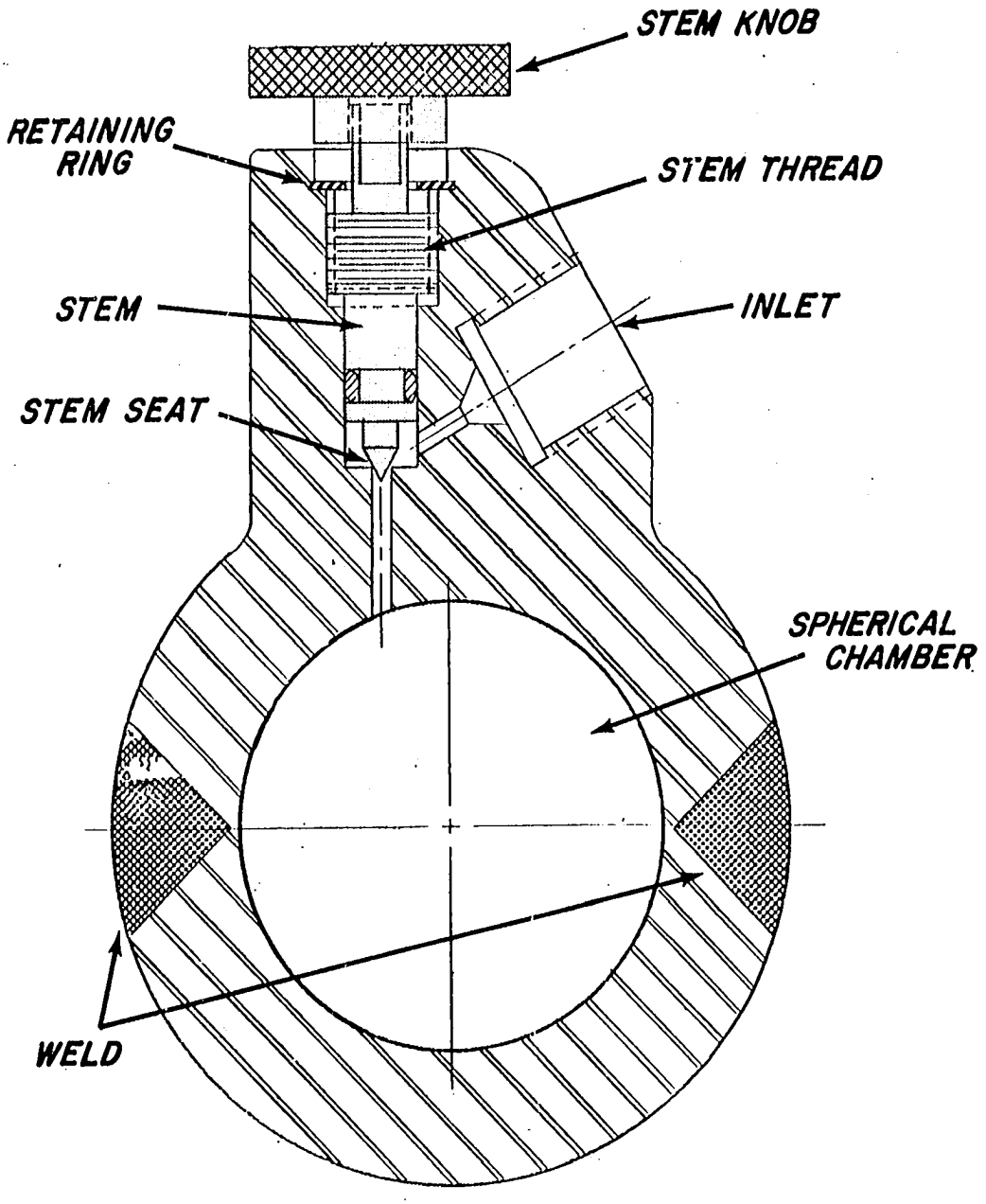


TABLE 5

HIGH PRESSURE PYCNOMETER STATISTICS

Pycnometer Number	Material	Volume at Atmospheric Pressure - cc	Weight gm
1	304 S.S.	5.5	178
2	304 S.S.	21.4	691
3	304 S.S.	5.3	183
4	304 S.S.	21.3	681

4. Temperature Measurements

The cell temperature was measured by three copper-constantan thermocouples which were hooked to the potentiometer-galvanometer circuit as shown in Figure 18.

The constantan wire of all three copper-constantan thermocouples on the P-V-T cell inside the high-low temperature air bath were connected to the constantan wire of the cold junction inside a copper block and immersed in ice water. The copper wires of all four junctions are connected to a selector switch as shown in Figure 18. The selector switch will selectively connect one of the P-V-T cell thermocouples at a time to the cold junction and to the potentiometer-galvanometer circuit. Thus, the additional voltage produced by the silver-copper junctions at the switch are bucked upon entrance and exit because it may safely be assumed that entrance and exit connectors on the switch are at the same temperature. The calibration curves for these thermocouples were supplied by the manufacturer and verified against standardized ASTM extreme precision thermometers.

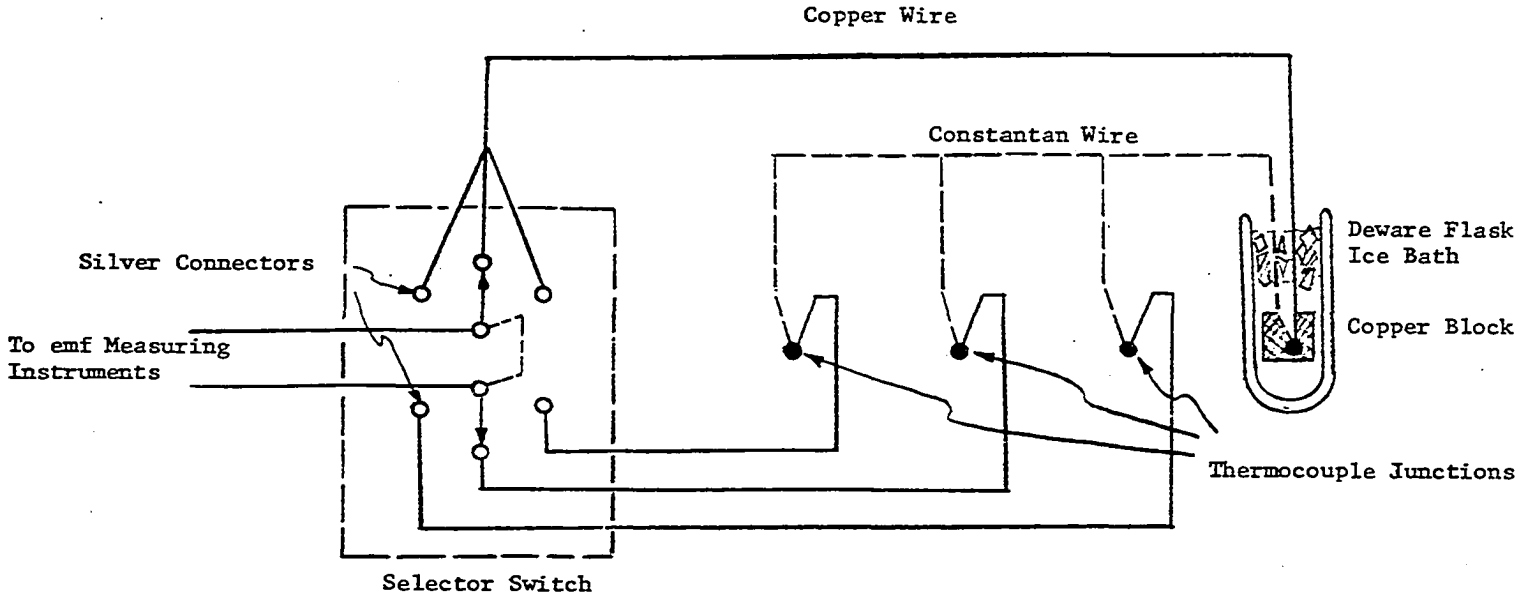


Figure 18
WIRING DIAGRAM FOR TEMPERATURE MEASUREMENTS

5. Pressure Measurement

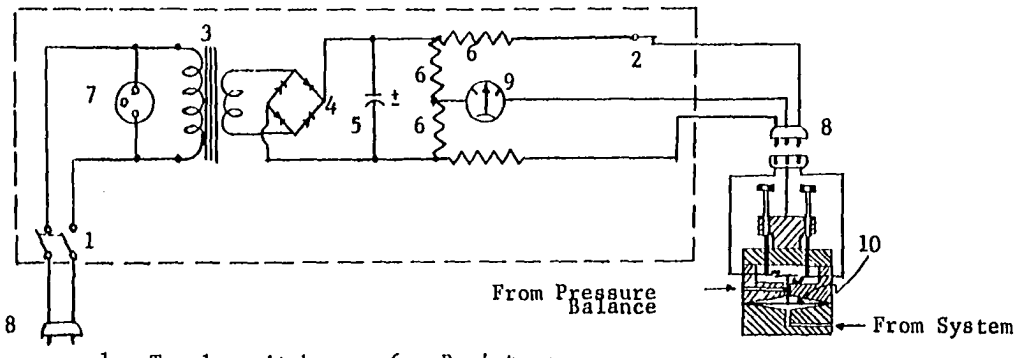
A combination of Hart pressure balance and Ruska dead weight tester was used for standardization of the pressure gauges and direct pressure measurements. A sensitivity of 1:2000 was certified for the Hart pressure balance and Ruska dead weight tester against Netherland and U. S. Bureau of Standards reference weights, respectively. The Hart pressure balance is model 1959.0 with a special pan for the addition of small weights to get pressure increments of as small as one psi. Figure 16, Part 1 is a photograph of this pressure balance. Figure 16 illustrates the position of the Hart pressure balance and Ruska dead weight gauge in a bird's-eye view of the entire P-V-T equipment.

The Ruska dead weight tester has a range of 6-2417 psi. A fluid reservoir, hand pump, and reference dial gauge are also provided.

A Ruska diaphragm differential pressure indicator (D.P. cell) was used to separate the test system from the hydraulic system of pressure balance.

The Ruska D.P. cell is a precision instrument for detecting small differential pressures in high pressure systems. The instrument consists of a diaphragm differential cell and an indicating-control unit.

The diaphragm differential cell consists of two high pressure chambers separated by a thin metal diaphragm (Figure 19). The diaphragm-stem assembly constitutes the actuation element of an internally adjustable, single-pole, double-throw switch. The two contact points are adjustable to facilitate selection of the desired null range by means of the independent micrometer spindles. All fluid contact surfaces are machined from stainless steel to minimize possible corrosion. The reference



1. Toggle switch
2. Momentary switch
3. Transformer
4. Rectifier
5. Capacitor
6. Resistors
7. Pilot light
8. Connectors
9. Microammeter
10. Diaphragm

FIGURE 19

Wiring Diagram for Diaphragm Differential Pressure Indicator

pressure from the dead weight gauge standard is applied to the upper pressure chamber; the pressure which is to be compared to the standard is applied to the lower chamber. The thin diaphragm is unbalanced and flexed by the presence of a differential pressure between the two chambers. The unbalanced condition is detected by the contacts.

Indication of the make or break contact arrangement is provided via the indicator unit as shown in Figure 19.

6. Chromatographic Analysis

A multistage chromatograph which was recently built and tested at Tulsa Research Center of Sinclair Research, Inc., was used in this study. This chromatograph essentially comprises three constant temperature air baths where the chromatographic columns are kept, selector valve for introduction of gaseous sample from sample loops, and a heated chamber provided with a rubber septum for introducing of microquantities of low pressure liquid samples.

For the study of multicomponent systems, generally, three and sometimes four columns were used several times for each sample and statistical average was obtained for each column. The column materials used were: 1) molecular Seive 5-A for the separation of O_2, N_2, and C_1; 2) Silicone oil 200/500 for the separation of O_2, N_2, and C_1 lump from the rest; 3) Silica gel column for the separation of CO_2; 4) Silicone oil 550 for the separation of heavier hydrocarbons.

7. Refractometer Abbe-Type

An American Optical Spencer refractometer was used for the determination of refractive index. The accuracy of this instrument is reported to be $\pm$ 0.0002 by the manufacturer.

C. Calibration of Equipment

1. Multipurpose P-V-T Cell

a. Total volume. This cell was calibrated by two independent techniques. The arrangements of equipment used in both cases are given in Figure 20.

In the first technique an expansion cell having approximately the same volume as the P-V-T cell was calibrated by slow injection of helium from a positive displacement transfer cylinder at almost isobaric, isothermal conditions. The mean volume of the expansion vessel was found to be 1423.9 cc. Then the expansion cell was charged with helium at pressure P_1, then expanded slowly into the lines excluding the P-V-T cell to pressure P_2, and finally expanded into the P-V-T cell to record the final pressure P_3. The pressure readings were made with a precision gauge. The order of magnitude of pressures were for instance 140.6" Hg, 136.8" Hg, 77.2" Hg for P_1, P_2, and P_3, respectively. Since the amount of helium, temperature, and Z factor were assumed constant, then the pressure volume product of each stage was constant, that is:

$$P_1 V_1 = P_2 V_2 = P_3 V_3 \tag{99}$$

Knowing V_1 from the calibration of the expansion cell, the total volume of the cell was calculated to be 1138.5 $\pm$ 18 cc at 95 per cent precision limit (based on student's t distribution).

In the second technique a light synthetic paraffin oil was used to calibrate the cell. The oil was injected by a positive displacement pump. The piston area was calculated each time from the volume of the oil injected and the piston travel. After numerous trials it was found

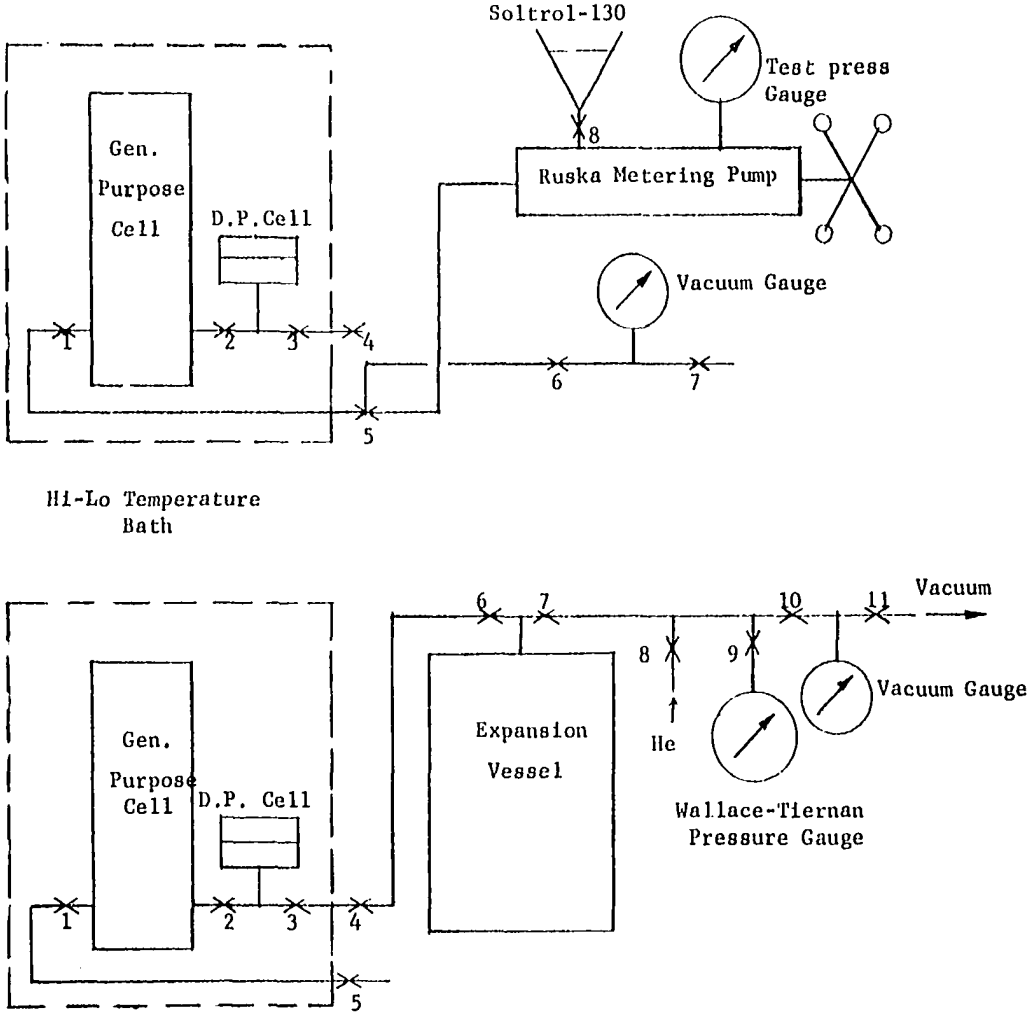


FIGURE 20

CALIBRATION OF GENERAL PURPOSE CELL

that the sample mean of the area of the piston was approaching the theoretical mean calculated from the diameter of the piston. The dead volume of the cell, when the piston was pushed all the way in, was found to be 93.5 cc. Thus an accurate estimate of the total volume was made by adding the dead volume to the product of total piston travel, 23.11 cm, and the piston area 45.58 cm^2, as follows:

Total volume = 93.15 + 45.58 x 23.11 = 1146.9 cc

b. Liquid volume. The liquid volume versus angle of rotation of the cell required to bring the meniscus up to the bull's-eye window was determined for seven piston settings (3, 4, 3.9, 5, 10, 15, 20, 23.64 cm), and the results were plotted in Figure 14. The intermediate curves were fitted for other values of piston setting to match the experimental curves.

2. High Pressure Pycnometers

The high pressure pycnometers were X-rayed after fabrication. If the welding was satisfactory, the interior of the pycnometer was then blown with high pressure nitrogen through a hypodermic tube for several days to remove any loose welding flux. Thus the constancy of the volume of the pycnometers was assured and confirmed by periodic checks.

Volume calibrations and the experimental determination of the coefficient of volume expansion were carried out by saturating the evacuated pycnometer with distilled water under pressure. From the increase in weight, due to water weight, and the specific volume of distilled water, the volume of the pycnometer at various pressures was determined. The sample standard deviation of the calibrated volume was less than .05 per cent in all cases.

To determine the coefficient of thermal expansion, the volume of the pycnometers was determined at 100°F and 221°F, using normal decane as the calibrating fluid. Then, using the following two equations, the thermal coefficient of volume expansion was calculated:

$$V_{T1} = V_0 (1 + \alpha_v T1) \quad (100)$$

$$V_{T2} = V_0 (1 + \alpha_v T2) \quad (101)$$

where T1 = 100°F, T2 = 221°F, and V is the pycnometer volume. Table 6 gives the experimental values for pycnometers 2 and 3. The other pycnometers have the same values as these since they are made of the same material and have approximately the same shape and volume.

TABLE 6

COEFFICIENT OF THERMAL VOLUME EXPANSION
OF HIGH PRESSURE PYCNOMETERS

Pycnometer No.	Volume, cc			Average	Pressure psia	Temperature °F	Coefficient of Volume Expansion α_v
	Run 1	Run 2	Run 3				
2	21.274	21.278		21.2825	4000	100	.000036
2	21.374	21.378		21.376	4000	221	
3	5.298	5.271	5.286	5.285	4000	100	.000056
3	5.299	5.297		5.298	4000	221	

The experimental values of the volume coefficient of thermal expansion was checked against the theoretical value which can be calculated

from the linear coefficient of thermal expansion as follows:

$$V = A\, l^3 \tag{102}$$

$$\frac{dV}{dT} = 3\, A\, l^2 \frac{dl}{dT} = 3\, A\, l^2\, (l_0 \alpha_L) \tag{103}$$

$$\alpha_V = \frac{1}{V_0} \frac{dV}{dT} = \frac{1}{V_0} (3\, A\, l^2)\, (l_0 \alpha_L) = 3\alpha_L \left(\frac{l_T}{l_0}\right)^2 \tag{104}$$

if it is assumed that $\left(\frac{l_T}{l_0}\right) = 1$, then

$$\alpha_V = 3\alpha_L \tag{105}$$

for the pycnometer material $\alpha_L = 9.5 \times 10^{-6}$ cm/cm, ^{o}F,

therefore

$$\alpha_V = 28.5 \times 10^{-6} \tag{106}$$

The average experimental value of 0.000046 cc/cc^{o}F compares to the theoretical value of 0.000028 cc/cc^{o}F in which an assumption was made that $\left(\frac{l_T}{l_0}\right)^2 = 1$ where l_T and l_0 are lengths at T and base temperatures. An average between the theoretical and experimental value, 0.000037, was used in the calculations. Thus considering the thermal and pressure expansions, the volume of the pycnometers was found to be as follows:

TABLE 7

EXPANSION OF HIGH PRESSURE PYCNOMETERS

Pycnometer No.	Volume at 75°F and 0 psig	Expansion	
		cc/cc °F	cc/cc/1000 psi
1	5.522	Negligible	Negligible
2	21.352	3.7×10^{-5}	.0045
3	5.287	Negligible	Negligible
4	21.258	3.7×10^{-5}	.0045

D. Experimental Procedure

The experimental procedure for the calibration of various parts of the P-V-T equipment and chromatographic analysis is given elsewhere. Here the procedure for actual sample taking is outlined.

1) The P-V-T cell is charged with liquid and gas to arrive at the desired GOR as shown in Figure 21.

2) The vapor and liquid pycnometers are taken apart and cleaned with Chlorethene, air, pentane, air in that order, then evacuated for 30 minutes.

3) The evacuated dry weight of both pycnometers is determined by Metler grammatic balance. The balance is zero'd every time and checked for zero drift after the weighing is completed. In case of zero drift the weighing is repeated.

4) The pycnometers are mounted on the general purpose cell as shown in Figure 13, and the line leading from the pycnometer to the

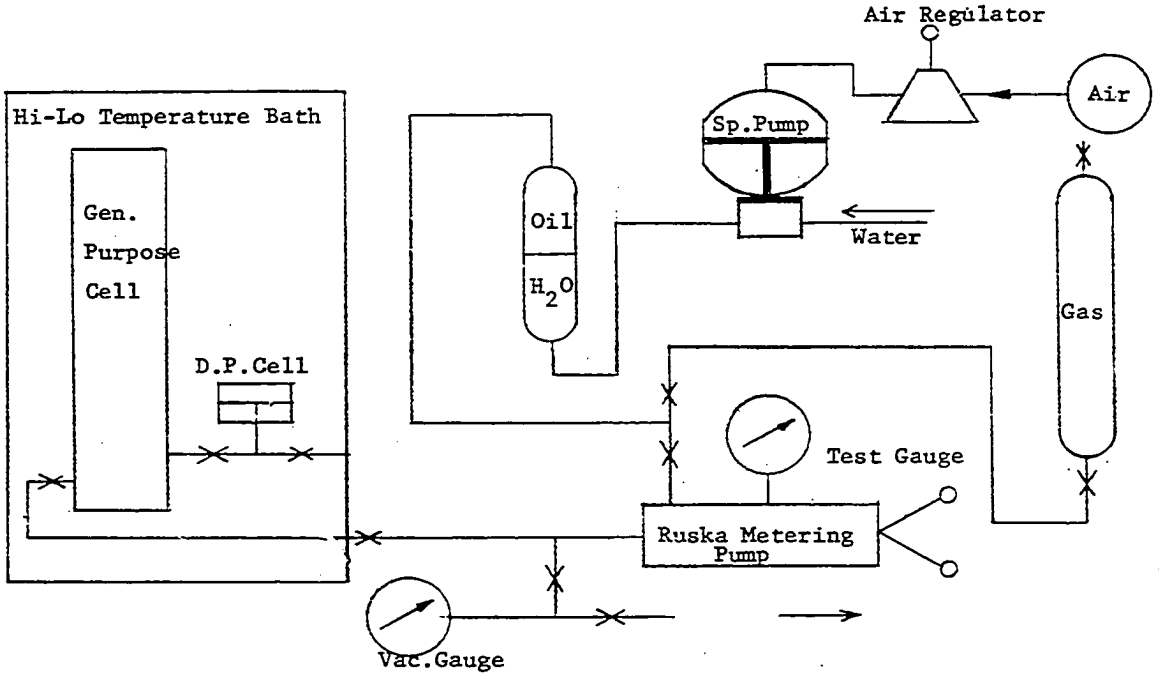


FIGURE 21

APPARATUS FOR CHARGING THE PVT CELL

cell proper is evacuated for 30 minutes. Then the vacuum valve is shut off, and the pycnometer valves are opened.

5) The bath is brought up to the desired temperature and kept there for at least four hours. This amount of time is required for the bath to bring the cell to thermal equilibrium.

6) The cell is brought up to the desired pressure by injection of hydraulic oil by a Sprague pump (see Figure 22) while the cell is rocked by the automatic rocking device 180°, about 10 cycles per minute. Rocking is continued for at least 10 minutes until the pressure of the system has reached an equilibrium point. Figure 22 gives a flow diagram of the entire P-V-T equipment.

7) The manual rocking device is used to position the general purpose cell such that the bottom of the vapor-liquid meniscus inside the cell coincides with the center of the bull's-eye windows. See Figure 16, part 21.

8) The position of the piston is read by the Vernier and the scale which moves with the piston.

9) From the piston position, the angle of rotation, and Figure 14, the liquid volume in the cell is determined. The total volume is determined as described previously.

10) Steps 6-9 are repeated for various pressures to determine the volumetric liquid fraction versus pressure to characterize the system under study.

11) The cell is brought to the pressure at which vapor and liquid samples are desired.

12) The general purpose cell is positioned such that the external

valve operator fits the liquid sample valve. See Figures 13 and 16.

13) The liquid sample valve is opened while the system pressure is kept constant by the injection of the same amount of hydraulic oil by the Ruska metering pump into the hydraulic side of the piston in the general purpose cell. After 5 minutes, the liquid sample valve is closed after the pressure is determined by a Heise pressure gauge and pressure balance while the D. P. cell is kept in null position by injection or withdrawal of oil in the DWT system by an AminCo pump, as shown in Figure 22.

14) The above process is repeated for vapor sample, except that now the upper valve operator is used to open the gas sample valve.

15) The bath door is opened, the pycnometer valves are closed immediately by removable valve knobs, and the pycnometers are dismantled from the general purpose cell.

16) The pycnometers are cleaned with a hypodermic syringe containing normal pentane. Pentane is forced into the space between valve stem, "O" ring and valve seat to clean out all remaining oil adhered to the valve stem.

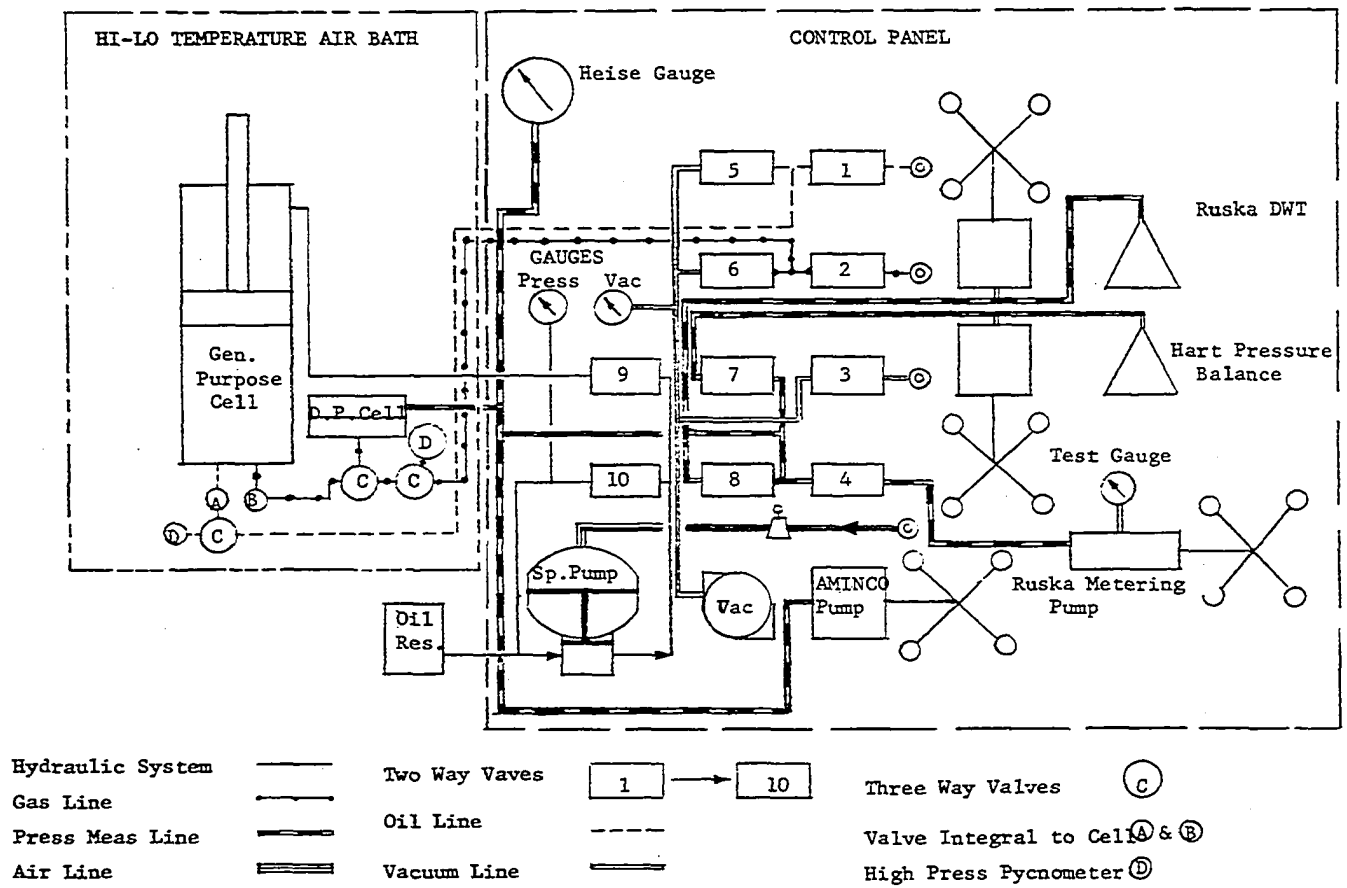
17) The pycnometers are weighed by a Metler grammatic balance. The zero drift is again checked as before, and as many weighings are repeated as necessary.

18) From the calibrated volume of the pycnometer and the hydrocarbon weight, the density of coexisting liquid and vapor are determined separately.

19) The vapor sample is heated to $40^{\circ}F$ above the dew point temperature and directly analyzed on the chromatograph.

FIGURE 22

FLUID-FLOW FLOW DIAGRAM OF PVT EQUIPMENT



20) The high pressure liquid sample is flashed into a small glass separator which is under atmospheric pressure and is provided with a burette for measuring oil. The separator is connected to a gas sampling bomb which in turn is connected to a gas meter described elsewhere.[89] The gas meter is of the water displacement type whereby the gas volume is measured by the displacement of water which is presaturated with air. From the weight and density of the displaced water, the gas volume can be measured; then from the knowledge of barometric pressure and the temperature, the moles of gas is calculated. To get the moles of low pressure liquid, the density of liquid is directly measured by a glass pycnometer; the volume is also read directly from the burette on the separator.

The separator is placed in a constant temperature room. The flashing is carried out with a 1/8-inch stainless steel tubing which connects che high pressure pycnometer to the separator through a rubber stopper. The end of this tubing is flattened and bent so that the liquid emerges in a very fine mist and strikes the wall of the separator before draining to the burette. In this manner only true equilibrium liquid will stay as liquid.

The low pressure liquid sample is then analyzed by the chromatograph.

21) The low pressure gas which was trapped in a gas sample bomb is analyzed by the chromatograph.

22) The low pressure liquid and vapor are mathematically recombined to obtain the composition of high pressure liquid.

23) For samples of group A, enough liquid or vapor was withdrawn from the P-V-T cell after sampling to make the overall liquid to vapor rate the same as before sampling at the same pressure. In this manner the overall composition of the system was kept constant from sample to sample.

24) In later experiments (groups B-G) only three samples were taken from each system; one sample from above saturation pressure, two coexistent liquid and vapor samples from below saturation pressure at constant pressure.

Since, even after very careful procedure and controlled conditions, the atmospheric experimental "K" values obtained from chromatographic analysis of liquid and vapor did not always agree with literature for components of low concentration in either liquid or gaseous phases, the literature "K" values, or vapor-liquid equilibrium constant, were used to adjust the composition. Thus, for those components that were predominately in vapor, that is their "K" values were greater than unity, the vapor composition was assumed correct; and the corresponding liquid composition was calculated from the relation $X = Y/K$. In general these components were butanes and lighter components. For pentanes and heavier components which exist predominately in liquid form at atmospheric conditions, the liquid composition was assumed correct and the vapor composition was calculated from the relation $Y = K \cdot X$. The original and calculated portion of the composition of various components in liquid and vapor were combined and normalized: This process was repeated twice. In the second try, generally, the experimental and literature "K" values agreed quite well.

CHAPTER V

RESULTS AND DISCUSSIONS

Since the proposed third parameter exhibited a linear relationship to the critical compressibility factor and the latter was proved by Lydersen and his co-workers to be an excellent third parameter for pure systems, it followed that the proposed parameter must be as good as Z_c and, therefore, sufficiently good for pure hydrocarbon systems. However, before applying the proposed third parameter to multicomponent experimental data, it was tested on 84 experimental data on three synthetic systems for which experimental data were already available in the literature.

A. Synthetic Systems

Using the proposed molal average molecular refraction $(R)_D$ and the mixing rule proposed by Leland for pseudocritical properties, the molal volume was calculated for 19 data points of nC_4-nC_{10} system and 14 data points of C_1-nC_5 system at saturation pressure. The results and percentage deviations are presented in Tables D-1 and D-2. The average percentage deviation was found to be 2.65 for nC_4-nC_{10} system and 3.34 for C_1-nC_5 system. The same techniques were applied on 51 data points of the C_1-nC_4-nC_{10} system at saturation pressure. The results are presented in Tables D-3, D-4, and D-5. The average percentage deviation

was found to be 2.22 for these data. The modified prediction method of Standing and Katz presented in NGAA publication by Brown[13] and co-workers was also applied to the bubble point liquid portion of the above data points and the results are presented in Table D-7. The average percentage deviation by the NGAA method was found to be 13.1.

B. Multicomponent Systems

Seven groups of natural multicomponent hydrocarbon systems were prepared covering a wide range of heptanes-plus properties. These systems were studied at their respective reservoir temperatures. The GOR were chosen such that either a gas condensate or a highly volatile oil system was synthesized. Figures 23, 24, and 25 present the volumetric behavior of these systems with regard to the percentage liquid volume as a function of pressure. The gas condensate systems exhibit an upper and a lower dew point while the highly volatile oil systems exhibit a dew point and a bubble point. A total of 45 samples of vapor and liquid in coexistence and undersaturated liquid were studied. The heptanes-plus properties of all samples of group A were assumed to be constant while only the pressure and temperature were changed together with the GOR to obtain various samples. This procedure was changed in all other groups where only one vapor sample and two liquid samples were taken from each batch for which the properties of heptanes-plus were determined.

A summary of experimental data is given in Tables C-1 and C-2. The compositions of the coexistent vapor and liquid samples studied are given in Tables C-3 through C-8.

For comparison, three methods were used to predict the liquid densities: 1) a corresponding state theorem using the proposed molal

Figure 23
PHASE BEHAVIOR OF GROUP A PART I
MULTICOMPONENT SYSTEM

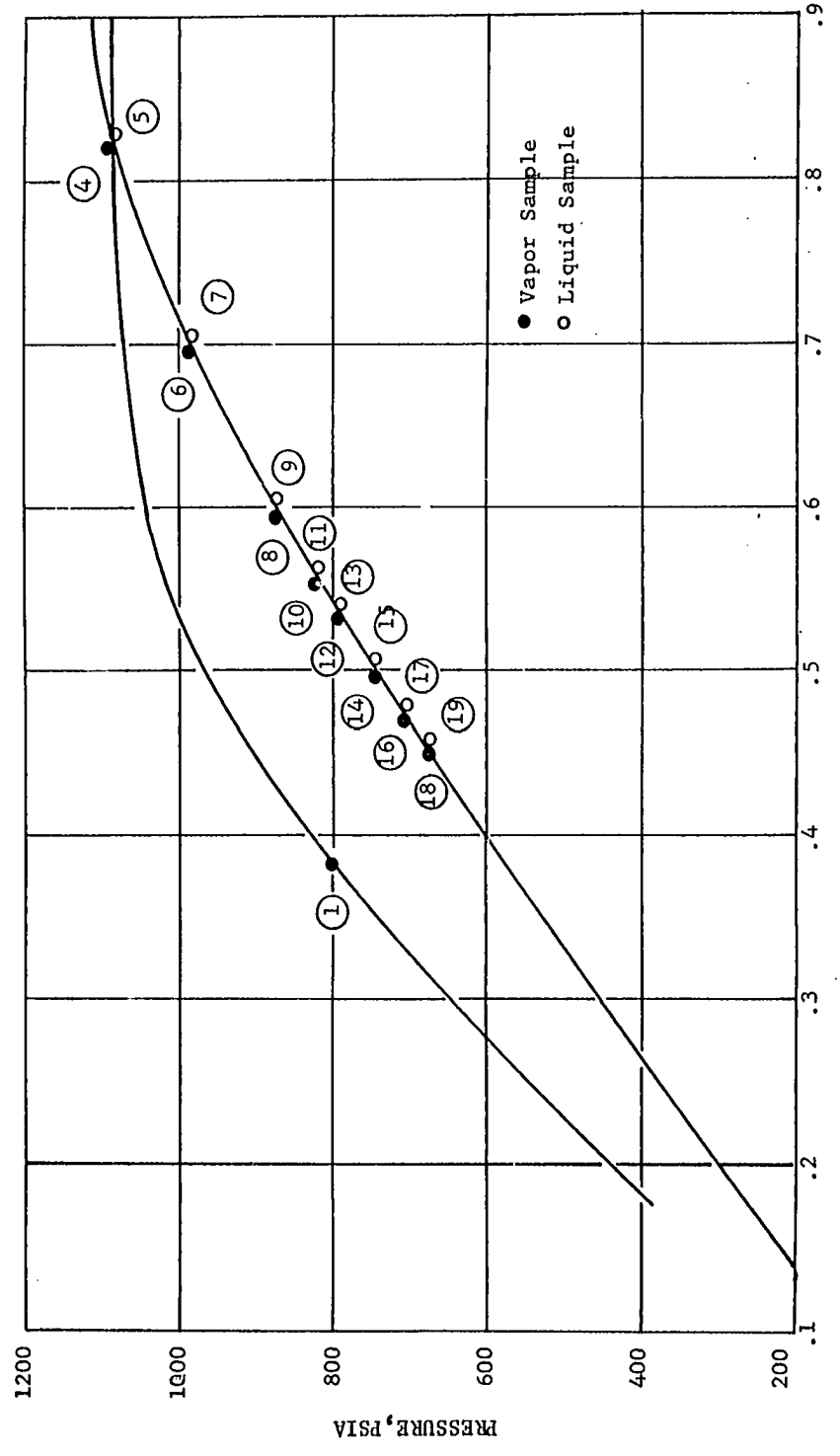
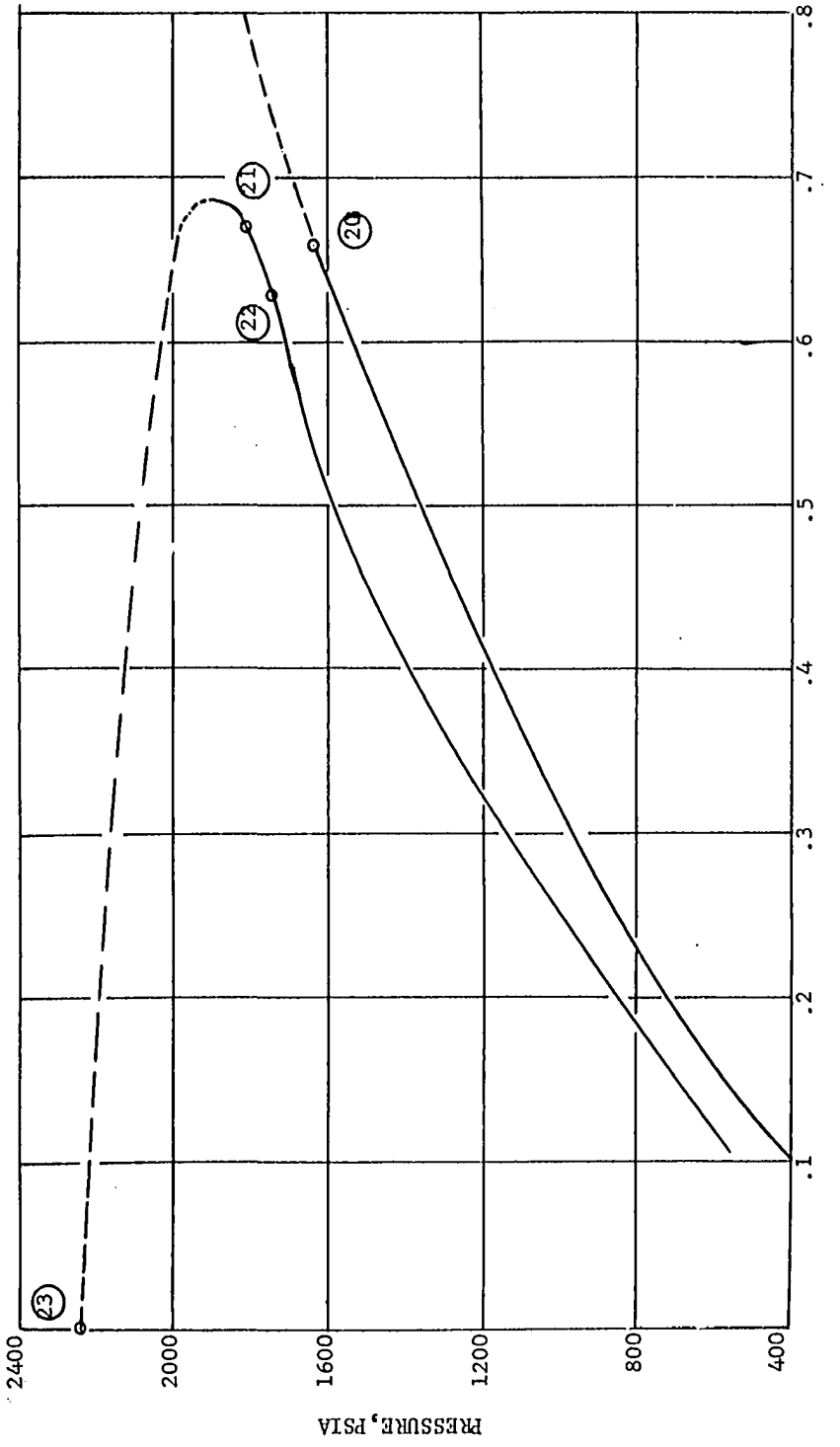


Figure 24
PHASE BEHAVIOR OF GROUP A PART II
MULTICOMPONENT SYSTEM



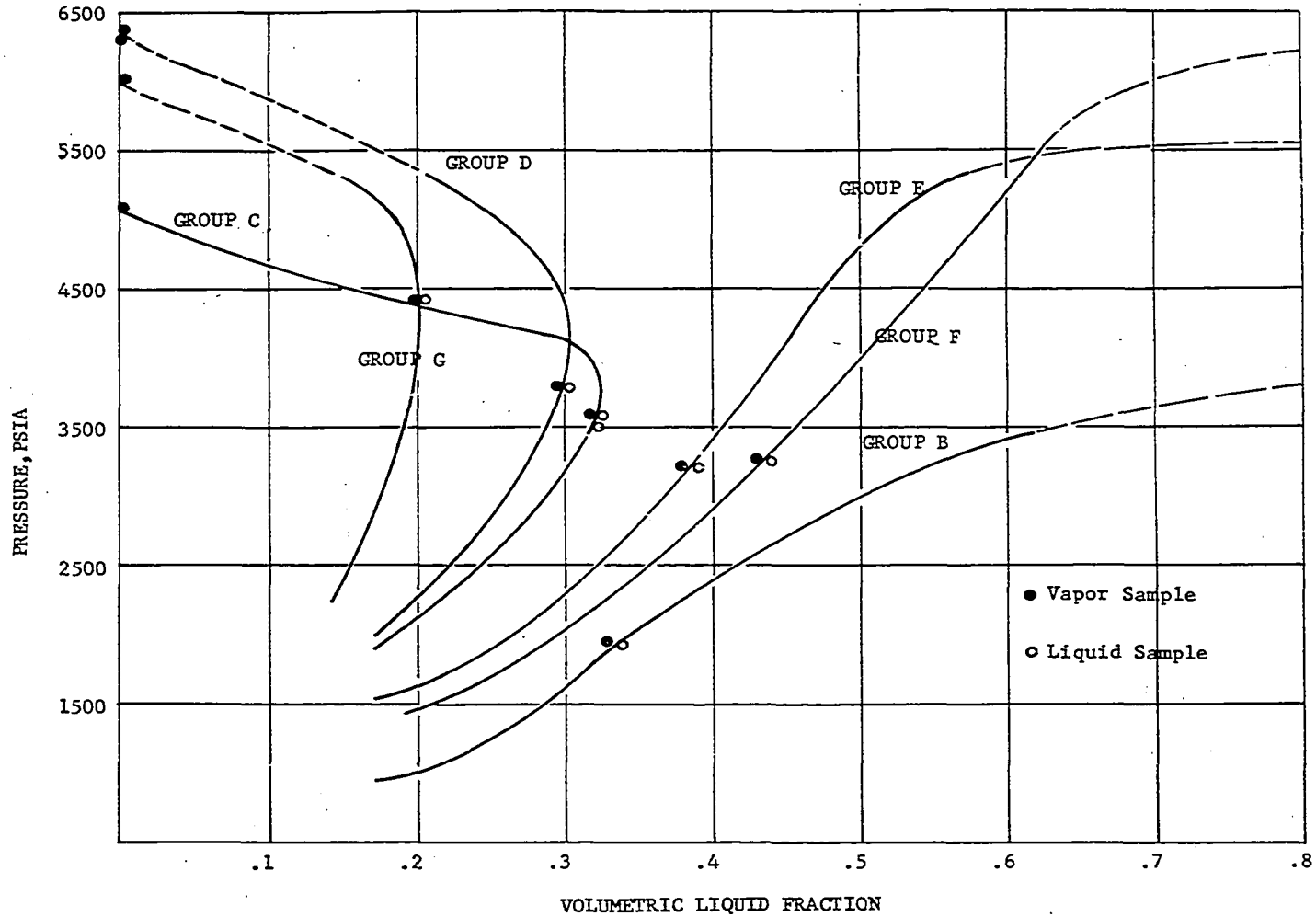


Figure 25
PHASE BEHAVIOR OF GROUP B-G
MULTICOMPONENT SYSTEM

average molecular refraction as a third parameter and the statistical mechanics oriented mixing rule proposed by Leland for pseudocritical properties; 2) Alani's method which is based on a modified van der Waals equation of state with an empirical temperature dependent equation for the heptanes-plus constants; 3) NGAA modified method previously discussed.

The results of the calculations are summarized in Tables D-7 and D-8 and illustrated in Figure 26. In this figure only the first two liquid samples of group A which were taken right after the determination of heptanes-plus properties were considered. Figure 26 actually compares the average percentage absolute deviation of both saturated and unsaturated liquids. The comparison of the density prediction of saturated liquid alone is illustrated in Figure 27. In this figure the actual density values of various groups as predicted by these methods are presented. In this figure it is shown that very good accuracy is obtained by the proposed method for saturated liquid density predictions. Only sample C shows a little higher than average deviation. This is perhaps due to adverse combination of the experimental error.

The overall average percentage deviation for all groups, consisting of 26 liquid samples, was found to be 5.08 for the proposed method, 12.91 for Alani's method, and 8.4 for the method of NGAA. Excluding the samples of group A, for which the heptanes-plus properties were uncertain, the average percentage deviation was 3.78 for the proposed method, 12.98 for Alani's method, and 7.88 for the method of NGAA. This shows that the latter two methods are rather insensitive to the heptanes-plus properties while the proposed method yields accurate predictions when the heptanes-plus properties are characterized.

Figure 26

COMPARISON OF DENSITY PREDICTION METHODS
SATURATED AND UNSATURATED LIQUIDS

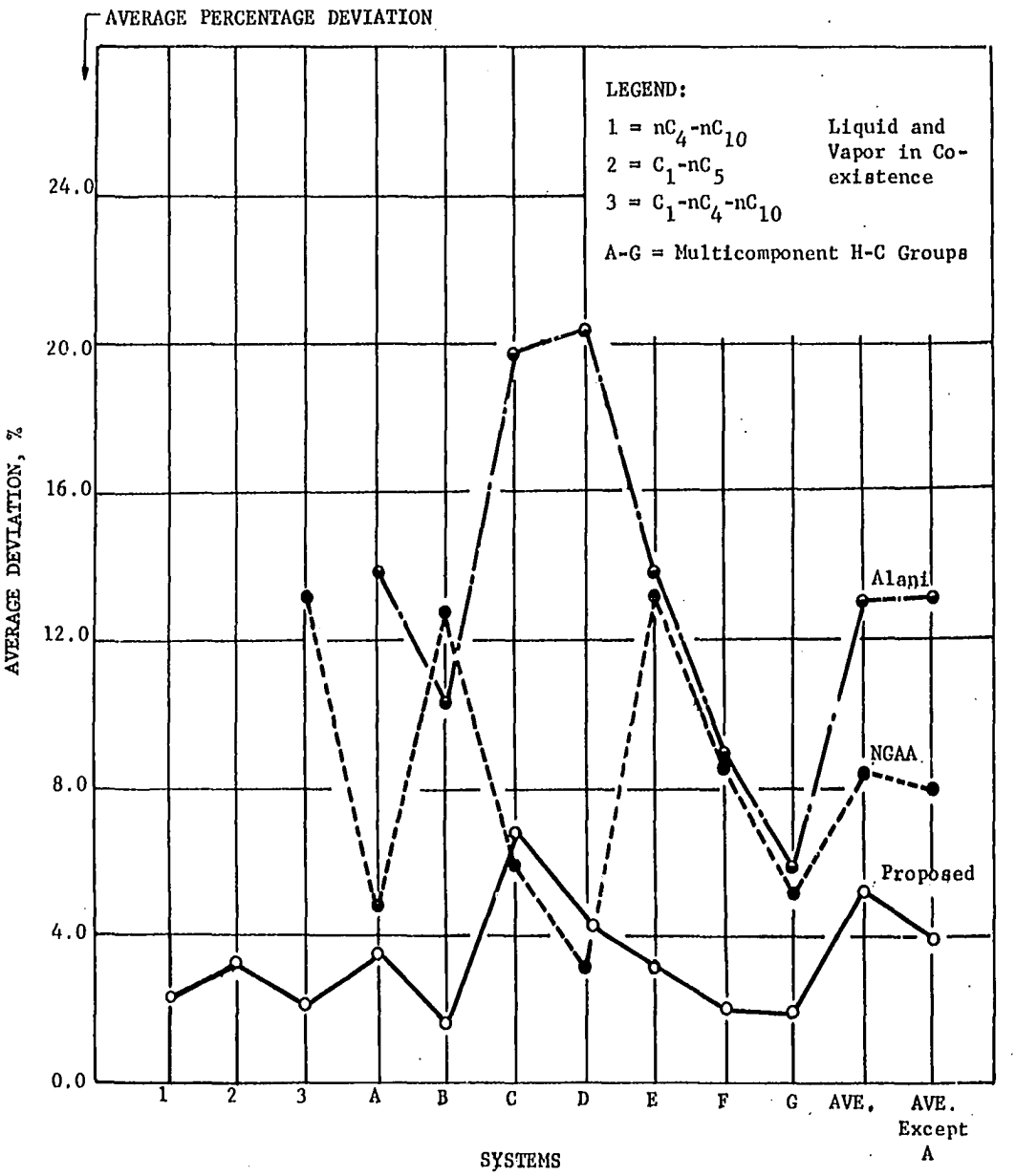
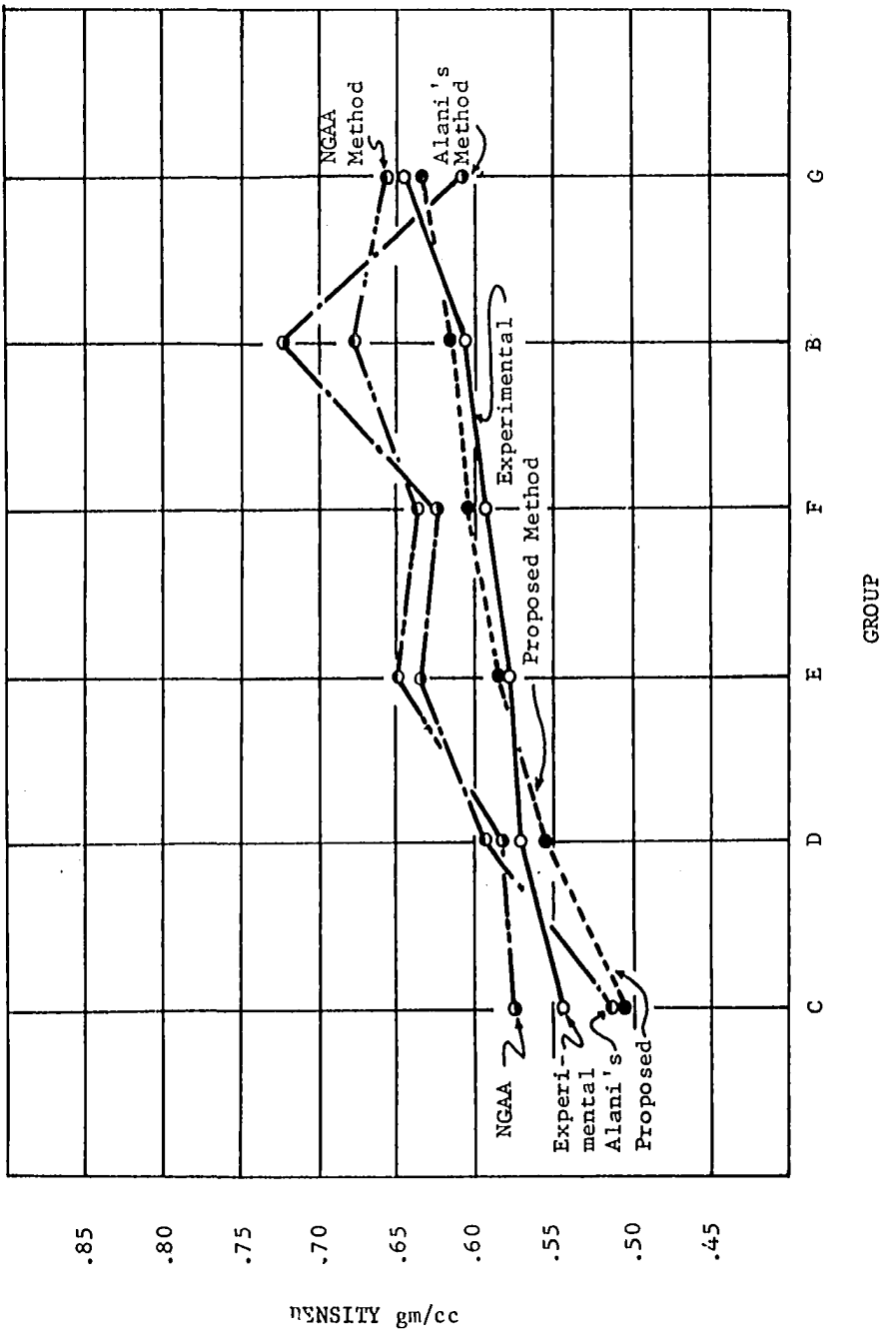


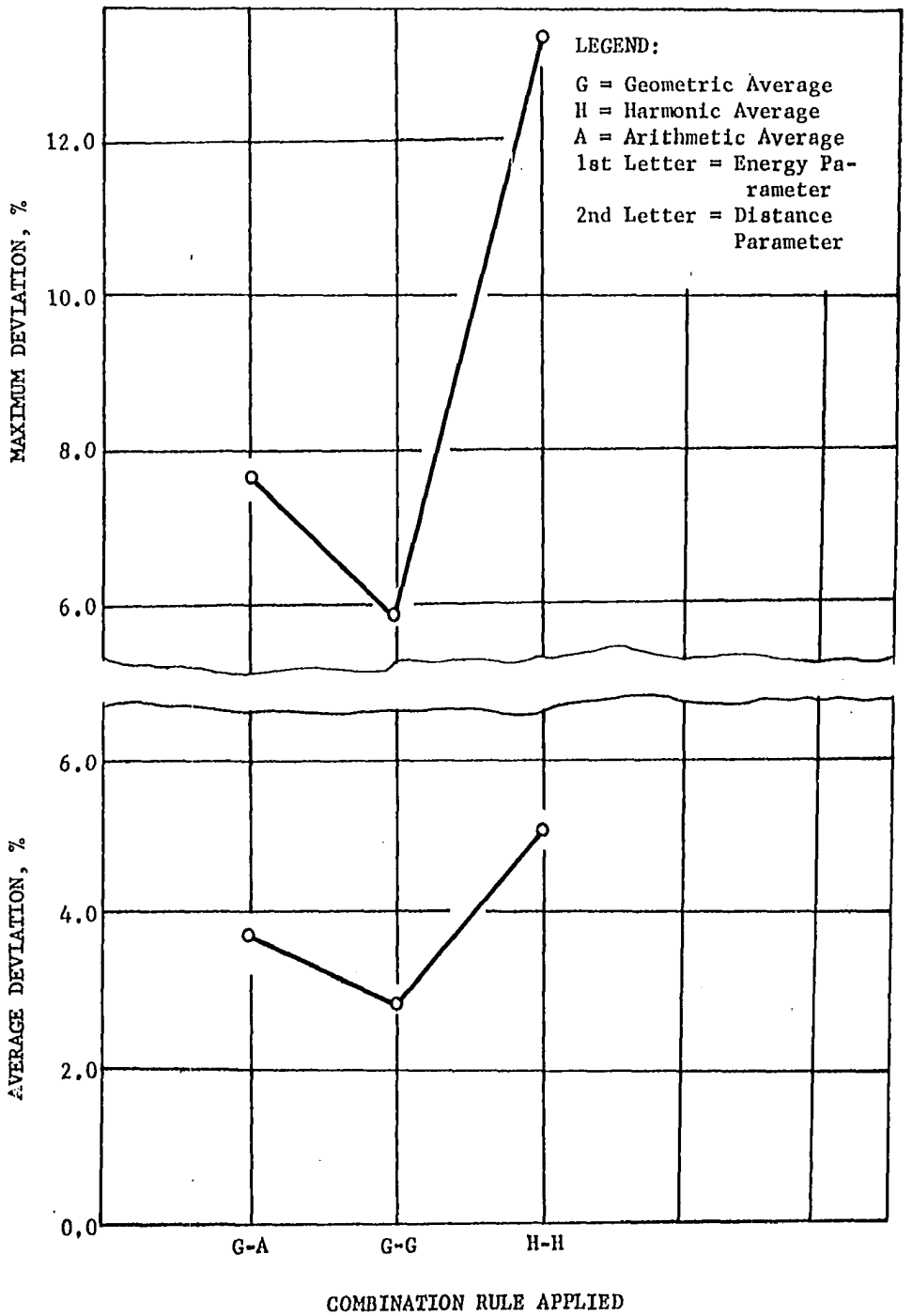
Figure 27
COMPARISON OF DENSITY PREDICTION METHODS
SATURATED LIQUIDS



The validity of the combination rule used in Leland's mixing rule for pseudocritical properties was checked by changing the mixing rule of Leland by using a different combination rule as follows: 1) based on geometric average of both energy and distance parameters, Equations (93) and (94); 2) based on harmonic average of both energy and distance parameters, Equations (97) and (98). These mixing rules together with the average molecular refraction were used to predict the densities of eleven multicomponent liquid and one sample each of C_1-nC_5, nC_4-nC_{10}, and C_1-C_4-C_{10} systems for which the value of alpha was invariant (equal to unity). The results of the comparison are given in Tables D-9 and D-10 and illustrated in Figure 28. The average percentage deviation was found to be 4.08 for the method of Leland (method 1), 3.10 for method 2 (geometric-geometric), and 5.49 for method 3 (harmonic-harmonic).

For the vapor samples in coexistence with the liquid, the heptanes-plus properties were, of course, quite different than the liquid heptanes-plus properties. It is believed that if the heptanes-plus molecular refraction and composition are known, the proposed technique will predict the compressibility factor as it did for the C_1-nC_4-C_{10} system. However, in the absence of such information, Kay's molal average critical was applied to the data assuming that the properties of heptanes-plus in the vapor are the same as for the liquid. The predicted results based on this assumption are presented in Table D-11. The average percentage deviation was found to be 16.5. However, when the vapor of group A alone, which characteristically had lower amounts of heptanes-plus, were considered, the average percentage deviation reduced to 5.6.

Figure 28
COMPARISON OF COMBINATION RULES



C. Procedure for the Application of the Proposed Method

A sample calculation is given in Appendix E for a methane-pentane system. In general the required data consists of the pressure, temperature, and composition. If complex portions such as heptanes-plus are also included, then enough information should be given to calculate the molecular refraction of the heptanes-plus. This information consists of density, molecular weight, and refractive index. The calculation is carried out in the following sequence.

1) Determine F, Equation (69)

2) Calculate the value of α, Equation (69)

3) Calculate P_c' and T_c'

   a) Vapor sample: use Equations (67) and (68)

   b) Saturated liquid sample: set $\alpha = 1$ and use Equations (93) and (94)

4) Calculate $P_r = \frac{P}{P_c'}$, $T_r = \frac{T}{T_c'}$

5) Determine molar average molecular refraction for the mixture:

$$(R)_{mix} = \sum_{i=1}^{n} X_i R_i$$

6) Choose a normal pure hydrocarbon which has a molecular refraction equivalent to the value of $(R)_{mix}$. Or choose two pure hydrocarbons whose molecular refraction covers the range of $(R)_{mix}$.

7) Calculate the equivalent pressure and temperature for the reference substance $P^o = P_c \cdot P_r$, $T^o = T_c \cdot T_r$

8) Look up the compressibility factor or the density for the reference substance at P^o and T^o. This is equivalent to the compressibility factor or density of the mixture at P and T.

D. Accuracy of the Experimental Method

The temperature measurements could be made to within .1°F or ± .05°F or approximately 1:5000, but the temperature variation within the bath is not believed to be that close. An accuracy of 1:2000 is believed to be a more reasonable figure for temperature measurements. For pressure measurements again the lower limit of accuracy of 1:2000 is believed to be applicable to the experimental data. The density measurements had a lower limit of accuracy of .05 per cent or again 1:2000. To determine the precision and reproducibility of the chromatographic analysis, a mixture of n hexane and normal heptane was prepared and analyzed fourteen times by the chromatograph. In the first six runs hexane and heptane were both run through the chromatograph in the forward direction. In the next six runs the hexane was run in the forward direction while the heptane was immediately backflushed as soon as the hexane peak had passed. In the next two runs the interval between the end of hexane and the backflush was varied.

The standard deviation of the chromatograph was found to be one per cent. However, the forward calibration was different than the backflush calibration, backflush calibration being (.436 -.426)/.436 = 2.35 per cent lower than forward calibration for the case of immediate backflush. As the backflush time was changed, the calibration factor was also changed, but not significantly, perhaps because the backflush delay could not be any longer.

Based on this observation, it was decided that to attain better accuracy a different response factor should be used for the reverse than for the forward flow. Accordingly for the heptanes-plus, which was

determined by backflush technique, an experimental response factor was determined from a synthetic mixture of normal hexane and heptanes-plus. The precision of the response factor for the backflushed heptanes-plus was dependent upon several factors. These factors were: 1) The efficiency of the heptanes-plus separation from the oil; 2) the accuracy of measurement of hexane and heptane-plus for mixing; 3) the degree of evaporation of hexane from the mixing before actual calibration, which was normally a very short time.

Thus, at best the degree of accuracy of chromatographic analysis is speculative. It is believed that when all factors are considered, an overall error of 3 per cent for heptanes-plus and 1 per cent for the rest of the individual composition numbers is inherent in the results.

CHAPTER VI

CONCLUSIONS

A better understanding of the fundamental causes of the nonideal behavior of pure hydrocarbons and their mixtures has been achieved.

A new equation of state has been proposed for coexisting vapor and liquid phases of pure hydrocarbons and their mixtures. This equation is based on the modified theorem of corresponding states and utilizes a new third parameter to account for the nonideality of the system. The proposed third parameter is the molecular refraction determined by the sodium-D line which is superior to the existing parameters because: 1) it can be measured directly and more accurately for pure as well as complex mixtures of hydrocarbons; 2) it is a direct measure of London dispersion forces; 3) its value ranges over a wide range: from 3.350 for methane to 48.481 for decane, allowing for very accurate interpolation of properties between reference substances.

This parameter bears a linear relationship to the critical compressibility factor Z_c successfully used as a third parameter in the modified theorem of corresponding states for pure compounds.

Since the molecular refraction is an additive quantity, the molal average molecular refraction has been proposed as a third parameter for mixtures. In mixtures containing heptanes-plus, the molecular refraction of the heptanes-plus portion can be measured by standard laboratory

hardware and added to the rest of the system on a molal basis.

The relative ease and accuracy with which this technique can be applied to natural hydrocarbon mixtures such as gas condensates and volatile oils is in direct contrast to the use of other third parameters for mixtures where the measurement of the third parameter for heptane-plus (critical compressibility factor, Pitzer's acentric factor, etc.) is a very difficult, if not an impossible, task.

An entirely new equipment capable of highly accurate P-V-T composition measurements was designed and built for this study comprising a high-low temperature bath (range -40^{o}F to 350^{o}F), P-V-T variable volume, visual cell (1100 cc capacity, 20,000 psi working pressure) and stainless spherical pycnometers (5 cc for liquid, 22 cc for vapor) and other auxiliary equipment together with a multicolumn thermal conductivity chromatograph for the determination of the composition of the multicomponent systems.

The results shown herein indicate that the use of molecular refraction as a third parameter is inherently simpler and yields more precise results than other available third parameters. With the development of additional understanding of combination rules, this approach furnishes an opportunity for an extremely precise prediction of fluid densities.

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APPENDIX A

NOMENCLATURE

NOMENCLATURE

a	=	Constant of Equation of State
A	=	Area
B	=	Second virial coefficient
C	=	Third virial coefficient
E	=	Total energy
$\dot{e}$	=	Electron charge
f	=	Partition function for one molecule
h	=	Planck's constant
k	=	Boltzman's constant
KE	=	Kinetic energy
M	=	Molecular weight
m	=	Mass of one molecule
N	=	Avogadro's number
n	=	Moles of a substance
p	=	Momentum
P	=	Pressure
PE	=	Potential energy
q	=	Charge
R	=	Universal gas constant
r	=	Distance between molecules
T	=	Absolute temperature

t = Degrees centigrade

U = Interaction potential

u = Internal energy

V = Volume

$\underline{V}$ = Molal volume

$\overline{\underline{V}}$ = Residual partial molal volume

X, Y = Mole fraction

Z = Compressibility factor

x,y,z = Spacial coordinates

Greek Letters

α = Polarizability

μ = Dipole moment

Φ = Potential energy

θ = Quadrupole moment

Ω = Octapole moment

σ = Distance parameter of potential function

ϵ = Energy parameter of potential function

ω = Acentric factor

Π = Total polarization

ρ = Density

Subscripts

A = Atomic

b = boiling point

c = Critical

E = Electronic

i,j,k = Components i,j,k

l = Liquid

o = Orientation

r = Reduced

' = Pseudo

V = Vapor

APPENDIX B

CHEMICAL COMPOSITION OF ALLOYS

TABLE B1

CHEMICAL COMPOSITION OF ALLOY USED IN THE P-V-T CELL CERTIFIED BY THE MANUFACTURER

Component	Percentage		
	17-7PH	Unloy 19-9DL	Mn Bronze No. 937
C	.07 max	.32	-
Mn	1.00 max	1.15	.25
P	.04 max	.024	-
S	.03 max	.01	-
S_i	1.00 max	.55	-
C_r	17.50 max	18.00	-
N_i	5.00 max	9.00	-
Col	.45 max	.40	-
T_i	-	.25	-
F_e	Balance	Balance	1.00
C_u	-	-	58.5
Z_n	-	-	39.25
T_{in}	-	-	1.0

APPENDIX C

SURVEY OF EXPERIMENTAL RESULTS

TABLE C1

SUMMARY OF VAPOR AND LIQUID EXPERIMENTAL DENSITIES

Source of Samples: Willshire Field, Group A
Heptanes-plus Properties:
Sp.Gr. = .7825, M.Wt. = 171, R.I. = 1.4402

Sample	Pressure psia	Temperature ^{o}F	Density g/cc	Phase
1	817	100.4	.05426	Saturated Vapor
2	4015	195.0	.6165	Unsaturated Liquid
3	4025	195.9	.6233	Unsaturated Liquid
4	1095	194.7	.5041	Saturated Liquid
5	1095	194.7	.0800	Saturated Vapor
6	995	197.5	.5432	Saturated Liquid
7	995	197.5	.0700	Saturated Vapor
8	865	196.0	.0652	Saturated Vapor
9	865	196.0	.5265	Saturated Liquid
10	830	196.7	.4995	Saturated Liquid
11	830	196.7	.0617	Saturated Vapor
12	805	197.3	.5005	Saturated Liquid
13	805	197.3	.0575	Saturated Vapor
14	745	198.0	.5128	Saturated Liquid
15	745	198.0	.0522	Saturated Vapor
16	705	197.7	.5085	Saturated Liquid
17	705	197.7	.0526	Saturated Vapor
18	685	198.2	.5440	Saturated Liquid
19	685	198.2	.0455	Saturated Vapor
20	1655	308.0	.4650	Unsaturated Liquid
21	1840	328.0	.4770	Unsaturated Liquid
22	1745	329.0	.4400	Unsaturated Liquid
23	2245	321.2	.4251	Unsaturated Liquid

TABLE C2
SUMMARY OF VAPOR AND LIQUID EXPERIMENTAL DENSITIES
GROUPS B-G

Sample -Group		Pressure psia	Temperature °F	Density g/cc	Heptanes-plus			Phase	Source
					Sp. Gr.	M. Wt.	R. I.		
1	B	4825	197.6	.5724	.805	169	1.4468	UL	Devonian, Texas
2	B	1965	199.9	.6073	.805	169	1.4468	SL	Devonian, Texas
3	B	1965	199.9	.1106	.805	169	1.4468	SV	Devonian, Texas
4*	C	4987	200.9	.4061	.7968	134	1.4409	UL	Lea Unit, N.M.
5*	C	3637	201.1	.5596	.7968	134	1.4409	SL	Lea Unit, N.M.
6	C	3637	201.6	.2580	.7968	134	1.4409	SV	Lea Unit, N.M.
7	C	5058	201.1	.4040	.7968	134	1.4409	UL	Lea Unit, N.M.
8	C	3621	200.0	.5438	.7968	134	1.4409	SL	Lea Unit, N.M.
9*	C	6050	201.1	.4150	.7968	134	1.4409	UL	Lea Unit, N.M.
10	D	6295	201.1	.4293	.7943	174	1.4400	UL	McElroy Ranch, Texas
11	D	3860	200.6	.5726	.7943	174	1.4400	SL	McElroy Ranch, Texas
12	D	3885	201.0	.2475	.7943	174	1.4400	SV	McElroy Ranch, Texas
13	D	6195	201.4	.3941	.7943	174	1.4400	UL	McElroy Ranch, Texas
14	E	6180	202.8	.4726	.7972	178	1.4435	UL	Ellenberger, Texas
15	E	3296	201.9	.5774	.7972	178	1.4435	SL	Ellenberger, Texas
16	E	3296	202.0	.1994	.7972	178	1.4435	SV	Ellenberger, Texas
17	F	6352	202.0	.5100	.8196	194	1.4500	UL	Cond.& Bl.Oil Blend
18	F	3264	200.2	.5945	.8196	194	1.4500	SL	Cond. & Bl.Oil Blend
19	F	3264	200.2	.1886	.8196	194	1.4500	SV	Cond. & Bl. Oil Blend
20	G	6359	201.0	.6463	.8090	184	1.4462	UL	2 Cond. & 1 Bl. Oil Blend
21	G	4445	203.3	.6047	.8090	184	1.4462	SL	2 Cond. & 1 Bl. Oil Blend
22	G	4445	203.1	.2659	.8090	184	1.4462	SV	2 Cond. & 1 Bl. Oil Blend

UL = Unsaturated Liquid SL = Saturated Liquid
SV = Saturated Vapor * Composition was not determined

TABLE C3

MULTICOMPONENT VAPOR AND LIQUID IN COEXISTENCE
EXPERIMENTAL DATA

Group	A	A	A	A	A	A	A
Sample	1	2	3	4	5	6	7
Phase	SV	UL	UL	SL	SV	SL	SV
Density, g/cc	.05426	.6165	.6233	.5041	.0800	.5432	.0700
Pressure, Psia	817	4015	4025	1095	1095	995	995
Temperature, ^{o}F	100.4	195	195.9	194.7	194.7	197.5	197.5
Composition							
N_2	.0098	.0003	.0086	.0003	.0060	.0035	.0052
CO_2	0	.0040	.0032	.0020	.0071	.0028	.0072
C_1	.7644	.2549	.3362	.1993	.6520	.2025	.6264
C_2	.1485	.1430	.0898	.0748	.1754	.0918	.1826
C_3	.0524	.1044	.0987	.0829	.0879	.0982	.0929
iC_4	.0047	.0155	.0204	.0177	.0097	.0196	.0107
nC_4	.0126	.0535	.0707	.0601	.0283	.0685	.0306
iC_5	.0019	.0260	.0282	.0406	.0053	.0379	.0057
nC_5	.0031	.0511	.0554	.0851	.0095	.0793	.0104
C_6	.0014	.0574	.0512	.0912	.0069	.0786	.0084
C_7+	.0011	.2899	.2376	.3459	.0119	.3174	.0199

UL = Unsaturated Liquid
SL = Saturated Liquid
SV = Saturated Vapor

- continued -

TABLE C4

MULTICOMPONENT VAPOR AND LIQUID IN COEXISTENCE
EXPERIMENTAL DATA

Group	A	A	A	A	A	A	A
Sample	8	9	10	11	12	13	14
Phase	SV	SL	SV	SL	SV	SL	SV
Density, g/cc	.06515	.4995	.06165	.5005	.05747	.5128	.05217
Pressure, psia	865	830	830	805	805	745	745
Temperature, ^{o}F	196	196.7	196.7	197.3	197.3	198	198
Composition							
N_2	.0042	.0001	.0037	.0012	.00395	.0002	.0038
CO_2	.0065	.0029	.0072	.0024	.00675	.0022	.00675
C_1	.6140	.1308	.6149	.1211	.6197	.1131	.5895
C_2	.1885	.1263	.17755	.1256	.19125	.1203	.1995
C_3	.1021	.1356	.09985	.1338	.0991	.1316	.1071
iC_4	.0113	.0248	.01085	.0236	.01075	.0240	.0126
nC_4	.0331	.0834	.03235	.0752	.03185	.0797	.0349
iC_5	.0062	.0330	.0062	.0346	.00585	.0310	.0067
nC_5	.0117	.0359	.0119	.0706	.0107	.0689	.01155
C_6	.0080	.0814	.0097	.0661	.0073	.0782	.0080
C_7+	.0144	.3459	.02585	.3459	.01275	.3507	.0196

UL = Unsaturated Liquid
SL = Saturated Liquid
SV = Saturated Vapor

-continued-

TABLE C5

MULTICOMPONENT VAPOR AND LIQUID IN COEXISTENCE
EXPERIMENTAL DATA

Group	A	A	A	A	A	A	A
Sample	15	16	17	18	19	20	21
Phase	SL	SV	SL	SV	SL	SL	SL
Density, g/cc	.5085	.05259	.5440	.0455	.4650	.4770	.4400
Pressure, psia	705	705	685	685	1655	1840	1745
Temperature, ^{o}F	197.7	197.7	198.2	198.2	308.0	328.0	329.0
Composition							
N_2	.0009	.0036	.0001	.0046	.0021	.0016	.0001
CO_2	.0021	.0068	.0017	.0068	.0032	.0052	.0035
C_1	.1018	.5940	.0881	.5942	.2488	.2826	.2321
C_2	.1129	.1948	.1005	.2022	.1374	.1118	.1368
C_3	.1330	.1082	.1174	.1104	.1187	.1091	.1193
iC_4	.0246	.0139	.0208	.0127	.0180	.0178	.0191
nC_4	.0793	.0379	.0739	.0360	.0654	.0614	.0579
iC_5	.0327	.0066	.0334	.0058	.0294	.0280	.0372
nC_5	.0696	.0126	.0719	.0120	.0582	.0669	.0761
C_6	.0793	.0069	.0843	.0074	.0610	.0680	.0681
C_7+	.3638	.0146	.4078	.0079	.2579	.2476	.2497

UL = Unsaturated Liquid
SL = Saturated Liquid
SV = Saturated Vapor

- continued -

TABLE C6

MULTICOMPONENT VAPOR AND LIQUID IN COEXISTENCE
EXPERIMENTAL DATA

Group	A	B	B	B	C	C	C
Sample	22	1	2	3	1	2	3
Phase	SL	UL	SL	SV	SV	UL	SL
Density, g/cc	.4250	.5724	.6073	.1106	.2580	.4040	.5438
Pressure, psia	2245	4825	1965	1965	3637	5058	3621
Temperature, ^{o}F	321.2	197.6	199.9	199.9	201.6	201.1	200
Composition							
O_2	0	0	0	.0001	0	0	0
N_2	.0003	.0023	0	.0076	.0059	0	C
CO_2	.0045	.0041	.0047	.0069	.0064	.0079	.0062
C_1	.3851	.5819	.3258	.8110	.6156	.7099	.5097
C_2	.1398	.0810	.0948	.1078	.1074	.1227	.1224
C_3	.0907	.0248	.0386	.0268	.0375	.0381	.0463
iC_4	.0129	.0024	.0039	.0022	.0033	.0037	.0046
nC_4	.0430	.0059	.0116	.0053	.0089	.0059	.0098
iC_5	.0295	.0058	.0072	.0017	.0038	.0032	.0060
nC_5	.0594	.0133	.0168	.0033	.0060	.0059	.0099
C_6	.0536	.0207	.0305	.0048	.0116	.0084	.0165
C_7+	.1812	.2578	.4660	.0225	.1937	.0943	.2687

UL = Unsaturated Liquid
SL = Saturated Liquid
SV = Saturated Vapor

- continued -

TABLE C7

MULTICOMPONENT VAPOR AND LIQUID IN COEXISTENCE
EXPERIMENTAL DATA

Group	D	D	D	E	E	E
Sample	1	2	3	1	2	3
Phase	UL	SL	SV	UL	SL	SV
Density, g/cc	.4293	.5726	.2475	.4726	.5774	.1994
Pressure, psia	6295	3860	3885	6180	3296	3296
Temperature, ^{o}F	201.1	200.6	201.0	202.8	201.9	202.0
Composition						
O_2	0	0	.0003	0	0	0
N_2	0	0	.0082	.0062	.0032	.0056
CO_2	.0055	.0071	.0077	.0074	.0050	.0067
C_1	.6788	.4988	.7364	.7121	.5252	.6566
C_2	.1419	.1299	.1215	.0975	.0818	.1043
C_3	.0514	.0524	.0398	.0203	.0192	.0281
iC_4	.0057	.0041	.0040	.0008	.0009	.0035
nC_4	.0100	.0093	.0122	.0015	.0022	.0102
iC_5	.0042	.0079	.0030	.0036	.0052	.0025
nC_5	.0101	.0192	.0068	.0119	.0153	.0089
C_6	.0083	.0211	.0069	.0133	.0215	.0106
C_7+	.0804	.2501	.0532	.1254	.3205	.1631

UL = Unsaturated Liquid
SL = Saturated Liquid
SV = Saturated Vapor

- continued -

TABLE C8

MULTICOMPONENT VAPOR AND LIQUID IN COEXISTENCE
EXPERIMENTAL DATA

Group	F	F	F	G	G	G
Sample	1	2	3	1	2	3
Phase	UL	SL	SV	UL	SL	SV
Density, g/cc	.5100	.5945	.1886	.6463	.6047	.2659
Pressure, psia	6352	3264	3264	6359	4445	4445
Temperature, ^{o}F	202.0	200.2	200.2	201.0	203.3	203.1
Composition						
O_2	0	0	0	0	0	0
N_2	.0059	.0036	.0099	.0075	.0113	.0084
CO_2	.0073	.0054	.0042	.0067	.0071	.0043
C_1	.6819	.4324	.5384	.5575	.5043	.4027
C_2	.1065	.0949	.0986	.0892	.0945	.0649
C_3	.0315	.0325	.0260	.0292	.0339	.0224
iC_4	.0026	.0032	.0005	.0029	.0036	.0027
nC_4	.0008	.0012	.0064	.0068	.0085	.0084
iC_5	.0059	.0048	.0024	.0042	.0058	.0035
nC_5	.0145	.0133	.0082	.0110	.0127	.0095
C_6	.0165	.0944	.0130	.0152	.0162	.0252
C_7+	.1265	.3143	.2924	.2698	.3020	.4479

UL = Unsaturated Liquid
SL = Saturated Liquid
SV = Saturated Vapor

APPENDIX D

SUMMARY OF CORRELATED DATA

TABLE D1

COMPRESSIBILITY FACTOR AT SATURATION PRESSURE
nC_4 - nC_{10} SYSTEM

Experimental Data from Sage, et al[90]

Sample	nC_4 Mole Fraction	R_D cc/ Mole	Temperature °F	Pressure psia	Z Factor		Deviation	Per Cent Deviation
					Experimental	Calculated		
1	.1787	43.504	100	9.1	.00438	.00432	-.006	1.3
2	.1787	43.504	160	21.3	.00960	.00956	.00004	.4
3	.1787	43.504	220	39.9	.01700	.0170	0	0
4	.1787	43.504	280	63.6	.0263	.0260	-.0003	1.0
5	.1787	43.504	340	96.1	.0388	.0382	-.0006	1.5
6	.1787	43.504	400	140.0	.0561	.0548	-.0013	2.3
7	.1787	43.504	460	198.0	.0799	.0781	-.0018	2.2
8	.6617	30.052	100	33.4	.0120	.1143	.0057	4.7
9	.6617	30.052	160	76.8	.0262	.0249	.0013	4.9
10	.6617	30.052	220	145.0	.0477	.0463	.0014	2.9
11	.6617	30.052	280	245.0	.0794	.0775	.019	2.39
12	.6617	30.052	340	374.0	.1230	.1173	.0057	4.6
13	.6617	30.052	400	525.0	.1818	.1681	.0137	7.5
14	.6617	30.052	460	671.0	.2607	.2492	.0115	4.4
15	.8358	23.811	100	42.6	.0135	.0132	-.003	2.2
16	.8358	23.811	100	98.4	.0300	.0292	-.0008	2.6
17	.8358	23.811	220	191.0	.0574	.0574	0	0
18	.8358	23.811	280	331.0	.1002	.0966	.0034	3.4
19	.8358	23.811	340	511.0	.1645	.1612	-.0033	2.0
Average Percentage Deviation								2.65

TABLE D2

COMPRESSIBILITY FACTOR AT SATURATION PRESSURE
C_1 - nC_5 System

Experimental Data from Sage, et al[90]

Sample	C_1 Mole Fraction	R_D cc/ Mole	Temperature °F	Pressure psia	Z Factor		Deviation	Per Cent Deviation
					Experimental	Calculated		
1	.0288	24.595	100	100	.312	.302	-.010	3.2
2	.947	4.476	100	1000	.860	.883	.023	2.7
3	.3077	18.494	100	1000	.269	.276	.007	2.6
4	.7568	8.644	160	200	.935	.950	.025	2.7
5	.0480	24.174	160	200	.555	.619	.064	11.5
6	.4002	16.457	160	1500	.380	.395	.015	3.9
7	.6846	10.226	220	400	.875	.901	.026	3.0
8	.08696	23.320	220	400	.115	.1174	.0024	2.1
9	.7420	8.968	220	2000	.705	.715	.010	1.4
10	.5657	12.831	220	2000	.556	.532	-.024	4.3
11	.6429	11.139	280	1000	.762	.767	.005	.7
12	.2297	20.193	280	1000	.286	.285	-.001	.3
13	.2569	19.597	340	1000	.390	.363	.027	6.9
14	.2950	18.762	340	1025	.439	.410	-.019	4.3
Average Percentage Deviation								3.54

TABLE D3

COMPRESSIBILITY FACTOR AT SATURATION PRESSURE
C_1 - nC_4 - nC_{10} SYSTEM

$$C = \frac{nC_4}{nC_4 + nC_{10}} = .66 \text{ Mole Ratio}$$

Experimental Data from Reamer, et al[80]

Sample	C_1 Mole Fraction	R_D	Temperature °F	Pressure psia	Z Factor		Deviation	Per Cent Deviation
					Experimental	Calculated		
1	.1	27.420	160	420	.134	.127	-.007	5.2
2	.1	27.420	220	537	.167	.167	0	0
3	.1	27.420	280	673	.206	.206	0	0
4	.1	27.420	340	790	.246	.241	-.005	2.0
5	.1	27.420	400	873	.296	.271	-.025	8.5
6	.2	24.742	100	671	.212	.196	-.016	7.5
7	.2	24.742	160	802	.242	.238	-.004	1.7
8	.2	24.742	220	952	.279	.279	0	0
9	.2	24.742	280	1097	.318	.317	-.001	.3
10	.2	24.742	340	1185	.352	.345	-.007	1.98
11	.2	24.742	400	1203	.400	.390	-.010	2.57
12	.2	24.742	460	1112	.460	.459	-.001	2.17
13	.3	22.343	100	1057	.313	.297	-.016	5.1
14	.3	22.343	160	1230	.348	.342	-.006	1.7
15	.3	22.343	220	1392	.385	.382	-.003	.8
16	.3	22.343	280	1518	.419	.419	0	0
17	.3	22.343	340	1562	.449	.450	.001	.2

TABLE D4

COMPRESSIBILITY FACTOR AT SATURATION PRESSURE
C_1 - nC_4 - nC_{10} SYSTEM

$$C = \frac{nC_4}{nC_4 + nC_{10}} = .66 \text{ Mole Ratio}$$

Experimental Data from Reamer, et al[80]

Sample	C_1 Mole Fraction	R_D	Temperature °F	Pressure-psia	Z Factor		Deviation	Per Cent Deviation
					Experimental	Calculated		
18	.3	22.343	400	1497	.493	.482	-.011	2.2
19	.3	22.343	460	1270	.551	.564	.013	2.56
20	.4	19.386	100	1503	.415	.395	-.020	4.83
21	.4	19.386	160	1721	.457	.445	-.012	2.63
22	.4	19.386	220	1870	.490	.484	-.006	1.2
23	.4	19.386	280	1946	.517	.515	-.002	.4
24	.4	19.386	340	1921	.542	.541	-.001	0
25	.4	19.386	400	1744	.575	.586	.011	1.9
26	.5	15.919	100	2008	.515	.500	-.015	2.9
27	.5	15.919	160	2252	.561	.547	-.014	2.5
28	.5	15.919	220	2363	.588	.585	-.003	.5
29	.5	15.919	280	2363	.610	.628	.018	3.0
30	.5	15.919	340	2230	.628	.630	.002	.3
31	.5	15.919	400	1936	.657	.671	.014	2.1
32	.5	15.919	460	1377	.642	.757	.115	17.9
33	.6	14.029	100	2520	.605	.595	-.010	1.65
34	.6	14.029	160	2757	.650	.644	-.006	.92

TABLE D5

COMPRESSIBILITY FACTOR AT SATURATION PRESSURE

$C_1 - nC_4 - nC_{10}$ SYSTEM

$$C = \frac{nC_4}{nC_4 + nC_{10}} = .66 \text{ Mole Ratio}$$

Experimental Data from Reamer, et al[80]

Sample	C_1 Mole Fraction	R_D	Temperature °F	Pressure-psia	Z Factor		Deviation	Per Cent Deviation
					Experimental	Calculated		
35	.6	14.029	220	2830	.679	.672	-.007	1.03
36	.6	14.029	280	2743	.697	.705	.008	1.15
37	.6	14.029	340	2486	.715	.720	.005	.7
38	.6	14.029	400	2071	.744	.770	.026	3.5
39	.7	11.350	100	3026	.690	.674	-.016	2.3
40	.7	11.350	160	3218	.727	.720	-.007	.96
41	.7	11.350	220	3234	.766	.750	-.016	2.1
42	.7	11.350	340	2674	.803	.806	.003	.37
43	.7	11.350	400	2090	.830	.856	.026	1.93
44	.8	8.672	100	3467	.763	.742	-.021	2.75
45	.8	8.672	160	3550	.802	.792	-.010	1.25
46	.8	8.672	220	3470	.832	.830	-.002	.24
47	.8	8.672	280	3188	.848	.863	.015	1.77
48	.8	8.672	340	2677	.872	.888	.016	1.84
49	.9	5.993	100	3670	.817	.808	-.009	1.1
50	.9	5.993	160	3525	.857	.847	-.010	1.16
51	.9	5.993	220	3130	.877	.884	.007	.79
Average Per Cent Deviation								2.22

TABLE D6

MOLAL VOLUME OF BUBBLE POINT LIQUID
IN C_1 - nC_4 -C_{10} SYSTEM

$$C = \frac{nC_4}{nC_4 + C_{10}} = .66 \text{ Mole Ratio}$$

Mole Fraction Methane	Temperature °F	Pressure psia	Exp!	Molal Volume Cu.Ft./Lb. Mole		
				NGAA Correlation	Deviation	Per Cent Deviation
.1	100	332	2.031	2.184	.153	7.5
.1	160	420	2.138	2.175	.037	1.7
.1	220	537	2.266	2.341	.075	3.3
.1	280	673	2.431	2.567	.136	5.6
.1	340	790	2.672	3.002	.330	12.4
.1	400	873	3.126	4.403	1.278	40.8
.2	100	671	1.902	1.936	.034	1.8
.2	160	802	2.009	2.056	.047	2.3
.2	220	952	2.139	2.241	.102	4.8
.2	280	1097	2.301	2.535	.235	10.2
.2	340	1185	2.552	3.168	.616	24.1
.3	100	1057	1.778	1.826	.048	2.7
.3	160	1230	1.883	1.936	.053	2.8
.3	220	1392	2.020	2.135	.115	5.7
.3	280	1518	2.193	2.519	.326	14.9
.4	100	1503	1.658	1.842	.184	11.1
.4	160	1721	1.765	2.123	.358	20.2
.4	220	1870	1.910	2.812	.902	47.2
.6	100	2520	1.443	1.580	.137	9.5
.6	160	2758	1.567	1.971	.404	25.8
.7	100	3026	1.370	1.648	.278	20.3
Average					.299	13.1

TABLE D7

PREDICTION OF MULTICOMPONENT LIQUID DENSITIES

Group	Phase	Sample	R_D	Temperature °F	Pressure psia	Experimental	Calculated Density gm/cc		
							Proposed	Alani	NGAA (Standing)
A	UL	2	31.059	195.0	4015	.6165	.615	.5626	.601
A	UL	3	27.187	195.9	4025	.6233	.583	.5121	.575
AVERAGE PERCENTAGE DEVIATION OF FIRST TWO SAMPLES							3.35	13.4	4.8
A	SL	4	36.558	194.7	1095	.5041	.620	.5974	.608
A	SL	6	34.439	197.5	995	.5432	.604	.5762	.606
A	SL	10	36.523	196.7	830	.4995	.613	.5956	.614
A	SL	12	36.715	197.3	805	.5005	.6104	.5997	.613
A	SL	14	37.294	198.0	745	.5128	.619	.5991	.687
A	SL	16	38.304	197.7	705	.5085	.624	.6084	.6945
A	SL	20	41.294	198.2	685	.5440	.628	.6394	.480
A	UL	20	29.414	308.0	1655	.4650	.511	.4945	.485
A	UL	21	28.695	328.0	1840	.4770	.472	.4770	.482
A	UL	22	29.463	329.0	1745	.4400	.499	.4761	.458
A	UL	23	22.881	321.0	2245	.4251	.418	.4057	.311
AVERAGE PERCENTAGE DEVIATION OF ALL GROUP A							12.9	12.5	11.4
B	UL	1	23.557	197.6	4825	.5724	.561	.5703	.650
B	SL	2	39.061	199.9	1965	.6073	.615	.7237	.678
AVERAGE PERCENTAGE DEVIATION							1.6	10.2	12.6
C	UL	2	10.474	201.1	5058	.4040	.379	.2663	.419
C	SL	3	20.672	200.0	3621	.5438	.502	.5135	.578
AVERAGE PERCENTAGE DEVIATION							6.7	19.6	5.0
D	UL	1	11.837	201.1	6295	.4293	.404	.2879	.448
D	SL	2	24.537	200.6	3860	.5726	.557	.5437	.582
AVERAGE PERCENTAGE DEVIATION							4.5	20.1	3.1
E	UL	1	14.435	202.8	6180	.4726	.448	.3900	.537
E	SL	2	29.279	201.9	3296	.5774	.584	.6376	.650
AVERAGE PERCENTAGE DEVIATION							3.2	13.7	13.1

TABLE D8

PREDICTION OF MULTICOMPONENT LIQUID DENSITIES

Group	Phase	Sample	R_D	Temperature °F	Pressure psia	Experimental	Calculated Density gm/cc		
							Proposed	Alani	NGAA (Standing)
F	UL	1	15.625	202.0	6352	.5100	.475	.4504	.560
F	SL	2	32.746	200.2	3264	.5945	.609	.6271	.638
AVERAGE PERCENTAGE DEVIATION							2.0	8.6	8.6
G	UL	1	25.967	201.0	6359	.6463	.631	.6073	.655
G	SL	2	28.704	203.3	4445	.6047	.615	.6363	.656
AVERAGE PERCENTAGE DEVIATION							2.0	5.7	5.0
OVERALL AVERAGE PERCENTAGE DEVIATION OF ALL GROUPS							5.08	12.91	8.4
OVERALL AVERAGE PERCENTAGE DEVIATION OF ALL GROUPS EXCEPT GROUP A							3.78	12.98	7.88

UL = Unsaturated Liquid
SL = Saturated Liquid

TABLE D9

COMPARISON OF DENSITY PREDICTION METHODS 1, 2, AND 3

Group	Sample	Pressure psia	Temperature °F	Density g/cc	Prediction of Density					
					Method 1, G-A		Method 2, G-G		Method 3, H-H	
					Deviation	% Dev.	Deviation	% Dev.	Deviation	% Dev.
B	1	4825	197.6	.5724	-.0114	2.0	+.0044	.8	-.0124	2.1
C	1	5058	201.1	.4040	-.0250	6.2	-.0230	5.7	-.0540	13.3
C	3	3621	200.0	.5438	-.0418	7.6	-.0278	5.1	-.0338	6.2
D	1	6295	201.1	.4293	-.0253	5.9	-.0120	2.8	-.0423	9.8
D	2	3860	200.6	.5726	-.0156	2.7	-.0106	1.9	-.0126	2.2
E	1	6180	202.8	.4726	-.0306	6.4	-.0176	3.7	-.0456	9.6
E	2	3296	201.9	.5774	+.0066	1.1	+.0346	5.9	+.0186	3.2
F	1	6352	202.0	.5100	-.0350	6.9	-.0120	2.4	-.0420	8.2
G	1	6359	201.1	.6463	-.0163	2.5	+.0257	4.0	+.0157	2.4
G	2	4445	203.1	.6047	+.0103	1.7	+.0153	2.5	-.0047	.8
C_1-nC_4 -nC_{10}	1	537	220.0	.5633	-.0090	1.6	-.0033	.6	-.0123	2.2
nC_4 -nC_{10}	1	245	280.0	.5364	+.0026	.5	+.0056	1.0	+.0019	3.5
C_1-nC_5	1	1500	160.0	.4724	-.0144	3.0	-.0044	.9	-.0164	3.5
Average Percentage Deviation						3.70		2.86		5.15

TABLE D10

COMPARISON OF PSEUDOCRITICAL PROPERTIES BY METHOD 1, 2, & 3

Group	Sample	Pseudocriticals					
		Method 1, G-A		Method 2, G-G		Method 3, H-H	
		T_c'	P_c'	T_c'	P_c'	T_c'	P_c'
B	1	.910	10.11	.828	8.44	.873	8.17
C	1	1.290	8.21	1.22	7.34	1.32	7.52
C	3	.938	7.15	.872	6.18	.916	6.07
D	1	1.250	10.54	1.160	9.19	1.26	9.39
D	2	.892	8.25	.814	6.88	.856	6.65
E	1	1.17	11.04	1.07	9.25	1.17	9.33
E	2	.827	7.72	.752	6.38	.781	6.08
F	1	1.13	11.70	1.03	9.67	1.12	9.68
G	1	.879	14.04	.794	11.47	.834	10.99
G	2	.841	10.34	.763	8.50	.794	8.10
C_1-nC_4 -nC_{10}	1	.785	1.147	.773	1.104	.787	1.100
nC_4-nC_{10}	1	.812	.548	.806	.536	.819	.536
C_1-nC_5	1	.924	2.61	.904	2.496	.926	2.503

TABLE D11

COMPRESSIBILITY FACTOR OF MULTICOMPONENT VAPOR
IN COEXISTENCE WITH LIQUID

Vapor Sample	Group	Temperature ^{o}F	Pressure psia	Experimental	Compressibility Factor		
					Kay's Rule	Deviation	Percentage Deviation
1	A	100.4	817	.831	.748	-.083	10.0
2	A	194.7	1095	.810	.832	.022	2.8
3	A	197.5	995	.896	.821	-.075	8.4
4	A	196.0	865	.838	.842	.004	.5
5	A	196.7	830	.903	.829	-.074	8.2
6	A	197.3	805	.858	.776	-.082	9.6
7	A	198.0	745	.927	.889	-.038	4.3
8	A	197.7	705	.851	.870	.019	2.2
9	A	198.2	685	.916	.878	-.038	4.2
AVERAGE PERCENTAGE DEVIATION							5.6
1	B	199.9	1965	.494	.845	.351	71.0
1	C	201.6	3637	.888	.795	-.093	10.5
1	D	201.0	3835	.532	.865	.333	62.3
1	E	202.0	3296	.820	.751	.069	8.4
1	F	200.2	3264	1.100	.745	.355	32.2
1	G	203.0	4445	1.250	1.08	.170	13.6
OVERALL AVERAGE PERCENTAGE DEVIATION							16.5

APPENDIX E

SAMPLE CALCULATIONS

APPENDIX E

SAMPLE CALCULATIONS

System: Methane-Normal Pentane Ref. 88, p. 183.

Experimental Data:

Mole fraction methane = .4002

P = 1500 psia

T = 160°F

(Z) exp = .3801

(d) exp = .4724 g/cc

Physical Properties and Other Constants for the Compounds Used:

	P_c psia	T_c, °F	Z_c	$(R)_D$ at 25°C	Molecular Wt, M
Methane	673	344	.290	3.530	16.04
N-Pentane	485	847	.269	25.266	72.15

Preliminary Calculations:

1. $M_{mix} = X_1M_1 + X_2M_2 = .4002 \times 16.04 + .5998 \times 72.15 = 49.70$

2. Calculation of F, Equation (69)

$$F = \frac{1500 \times (.4002 \times 344 + .5998 \times 847)}{620 \times (.4002 \times 673 + .5998 \times 485)} = 2.77$$

Since $F \not> 2.0$ $\therefore$ $\alpha = 1.0$

3. Calculation of molar average molecular refraction to choose reference substance

$(R)_{D_{mix}} = .4002 \times 3.530 + .5998 \times 25.266 = 16.567 = (R)_D$Propane

∴ Reference Substance = Propane, according to Figure 1, Chapter III.

4. Critical properties of reference substance

P_c = 617 psia, $T_c = 666^{\circ}R$

Prediction Method 1

1. Calculation of pseudocritical properties - Equations (67) (68)

$$T_c' = \left[\frac{(.4002)^2 \times \left(\frac{.290 \times 344^2}{673}\right) + (.5998)^2 \times \left(\frac{.269 \times 847^2}{485}\right) + \frac{2 \times (.4002) \times (.5998) \times \left(\frac{.290 \times 344^2}{673}\right)^{1/2} \times}{2 \times (.4002) \times (.5998) \times \left(\frac{1}{2}\left[\frac{.24 \times 344}{673}\right]^{1/3} + \frac{\left(\frac{.269 \times 847^2}{485}\right)^{1/2}}{\frac{1}{2}\left[\frac{.269 \times 847}{485}\right]^{1/3}}\right)^3} \right]^{1/1} = 671^{\circ}R$$

$$P_c' = \frac{671 \times}{(.4002)^2 \times \left(\frac{.290 \times 344^2}{673}\right) + (.5998^2) \times \left(\frac{.269 \times 847^2}{485}\right) + \frac{(.4002 \times .290 + .5998 \times .269)}{2 \times (.4002) \times (.5998) \times \left(\frac{1}{2}\left[\frac{.290 \times 344}{673}\right]^{1/3} + \frac{1}{2}\right)}}{\left[\frac{.269 \times 847}{485}\right]^{1/3}\Big)^3} = 574.9 \text{ psia}$$

$$Tr = \frac{T}{T_c'} = \frac{620}{671} = .924$$

$$P_r = \frac{P}{P_c'} = \frac{1500}{574.9} = 2.609$$

Equivalent P and T of reference substance (Propane in this case)

$P = P_r \times P_c = 2.609 \times 617 = 1610$ psia

$T = T_r \times T_c = .924 \times 666 = 615.4^{\circ}F = 155.4^{\circ}F$

$\underline{V} = 1.54$ c.f./Lb. mole propane

$$Z = \frac{P\underline{V}}{RT} = \frac{1610 \times 1.54}{10.73 \times 615.4} = .375$$

$$d = \frac{M}{\underline{V} \times 62.43} = \frac{44.09}{1.54 \times 62.43} = .458 \text{ g/cc}$$

Prediction Method 2

1. Calculations of pseudocritical properties - Equations (93) (94)

$$T_c' = \left[\frac{(.4002)^2 \times \left(\frac{.290 \times 344^2}{673}\right) + (.5998)^2 \times \left(\frac{.269 \times 847^2}{485}\right) + 2 \times (.4002) \times (.5998) \times \left(\frac{.290 \times 344^2}{673}\right)^{1/2} \times \left(\frac{.269 \times 847^2}{485}\right)^{1/2}}{(.4002)^2 \times \left(\frac{.290 \times 344}{673}\right) + (.5998)^2 \times \left(\frac{.269 \times 847}{485}\right) + 2 \times (.4002) \times (.5998) \times \left(\frac{.290 \times 344}{673}\right)^{1/2} \times \left(\frac{.269 \times 847}{485}\right)^{1/2}} \right] = 686^{\circ}F$$

$$P_c' = \frac{686 \times (.4002 \times .290 + .5998 \times .269)}{(.4002)^2 \times \left(\frac{.290 \times 344}{673}\right) + (.5998)^2 \times \left(\frac{.269 \times 847}{485}\right) + 2 \times (.4002) \times (.5998) \times \left(\frac{.290 \times 344}{673}\right)^{1/2} \times \left(\frac{.269 \times 847}{485}\right)^{1/2}}$$

$= 601$ psia

$$T_r = \frac{T}{T_c'} = \frac{620}{686} = .904$$

$$P_r = \frac{P}{P_c'} = \frac{1500}{601} = 2.496$$

Equivalent P and T of reference substance (Propane in this case)

$$P = P_r \times P_c = 2.496 \times 617 = 1540 \text{ psia}$$

$$T = T_r \times T_c = .904 \times 666 = 602^{\circ}R = 142^{\circ}F$$

$\underline{V}$ = 1.51 c.f./Lb. mole propane

$$Z = \frac{PV}{RT} = \frac{1540 \times 1.51}{10.73 \times 602} = .360$$

$$d = \frac{M}{\underline{V} \times 62.43} = \frac{44.09}{1.51 \times 62.43} = .468 \text{ g/cc}$$

Prediction Method 3

1. Calculation of pseudocritical properties - Equations (97) (98)

$$T_c' = \left[\frac{(.4002)^2 \times (\frac{.290 \times 344^2}{673}) + (.5998)^2 \times (\frac{.269 \times 847^2}{485}) + 2 \times (.4002) \times (.5998) \times \frac{8\,(\frac{.290 \times 344}{673})\,(\frac{.269 \times 847}{485})\quad 2\,(344)^1 \times (847)^1}{[(\frac{.29 \times 344}{673})^{1/3} + (\frac{.269 \times 847}{485})^{1/3}]^3 \left[(344)^1 + (847)^1\right]}}{(.4002)^2 \times (\frac{.290 \times 344}{673}) + (.5998)^2 \times (\frac{.269 \times 847}{485}) + 2 \times (.4002) \times (.5998) \times \frac{8\,(\frac{.290 \times 344}{673})\,(\frac{.269 \times 847}{485})}{[(\frac{.29 \times 344}{673})^{1/3} + (\frac{.269 \times 847}{485})^{1/3}]} \right] =$$

$669^{\circ}R$

$$P_c' = \frac{669 \times}{(.4002)^2 \times \left(\frac{.290 \times 344^2}{673}\right) + (.5998)^2 \times \left(\frac{.269 \times 847^2}{485}\right) + 2 \times \frac{(.4002 \times .290 + .5998 \times .269)}{(.4002) \times (.5998) \times \frac{8 \times \left(\frac{.290 \times 344}{673}\right) \times}{\left[\left(\frac{.29 \times 344}{673}\right)^{1/3} + \frac{\left(\frac{.269 \times 842}{485}\right)}{\left(\frac{.269 \times 847}{485}\right)^{1/3}}\right]^3}}} = 599 \text{ psia}$$

$$P_r = \frac{P}{P_c'} = \frac{1500}{599.2} = 2.503$$

$$T_r = \frac{T}{T_c'} = \frac{620}{669} = .926$$

Equivalent P and T of the reference substance (Propane in this case)

$$P = P_r \times P_c = 2.503 \times 617 = 1544 \text{ psia}$$

$$T = T_r \times T_c = .926 \times 666 = 616.7 \text{ or } = 756.7^{\circ}F$$

$\underline{V}$ = 1.55 c.f./Lb. mole propane

$$Z = \frac{PV}{RT} = \frac{1544 \times 1.55}{10.73 \times 616.7} = .362$$

$$d = \frac{M}{\underline{V} \times 62.43} = \frac{44.09}{1.55 \times 62.43} = .456 \text{ g/cc}$$