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NONIDEAL BEHAVIOR OF GASES AND THEIR MIXTURES

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DEDICATED TO MY WIFE AND FAMILY

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INTRODUCTION

The naturally occurring fluids in petroleum reservoirs are complex mixtures of hydrocarbons often associated with nitrogen, carbon dioxide, hydrogen sulfide and other nonhydrocarbon components. Since the nonhydrocarbon substances are now being encountered in large proportions in many reservoir fluids, there is an increasing demand for more fundamental knowledge concerning the volumetric and thermodynamic properties of these mixtures.

The calculation of the P-V-T properties of gas mixtures, or even pure gases of diversified characteristics, has proved to be unusually complex. Ninety years have passed since van der Waals first proposed his famous equation of state. Yet today, we still are in serious need of improvements in the prediction and correlation of the volumetric behavior of mixtures as well as their pure components.

At present, a vast amount of experimental P-V-T data for many fluids in their pure states are available. Several methods are also available for predicting their volumetric properties with good accuracy. Systematic experimental data on mixtures, however, are inadequate. Considerable work has therefore been done in an attempt to develop methods of predicting the properties of mixtures. Although the various methods have been successful in limited cases, large errors are frequently encountered in "unexpected instatnces", demonstrating the basic weakness of purely empirical approaches. The occurrence of hydrogen sulfide in hydrocarbons may be cited as an example of such "unexpected instances".

Any valid method of predicting volumetric properties of mixtures must deal not only with the nonideal behavior of pure substances comprising the mixture but also with the nonideality of mixing itself. In recognition of the nonideality of pure substances, attempts are being made to classify compounds according to the structure and nature of their molecules. The concepts of acentric factors for non-polar molecules and dipole moments for polar compounds by several investigators are the products of such efforts. The nonideality of mixing can be better understood in the light of interactions of the dissimilar molecules of the constituents of a mixture. Available data on mixtures show that it is hopeless to obtain a general correlation technique that will adequately fit the wide range of compositions encountered. Even for the same mixture, accuracy is dependent upon its physical state, which is a function of pressure and temperature. For instance, most of the existing correlations in the literature show the largest deviation in the critical region. Thus the accuracy in predicting the properties of mixtures demands a classification scheme, depending upon the nature and structure of their constituents, even though such an effort may be limited to a specified range of pressure and temperature.

The objective of the present investigation is to provide improved methods of predicting the volumetric behavior of pure gases and their mixtures, and also to determine compressibility factors of several mixtures of methane, ethane, and hydrogen sulfide in the gaseous state using a modified Bean apparatus.

This study offers a real clue to the relative advantage of adding a third parameter, specific for a given substance, to the usual reduced pressure and reduced temperature for accurate estimation of the compressibility factor of a pure gas. It also reveals the need for classifying gas mixtures according to the nature of their constituents so that a method for precise calculation of compressibility factors of each of the classified systems can be used.

Mixtures of methane, ethane, and hydrogen sulfide were studied at the nominal temperatures of 100, 130 and 160 °F. up to a maximum pressure of 7,000 psig. The maximum amounts of ethane and hydrogen sulfide in the five mixtures studied were about 10 and 20 mole per cent, respectively.

CHAPTER II

THEORETICAL BACKGROUND

During the past 100 years various investigators have undertaken basically two approaches for the study of the volumetric properties of pure substances and their mixtures. The thermodynamical approach is concerned with mathematical relations connecting different experimental properties of macroscopic systems in equilibrium. The other one is statistical mechanical in nature which deals with molecular interactions. The purpose of this chapter is to survey the present knowledge of the P-V-T behavior of pure gases and their mixtures from both points of view.

A. Ideal Gas

The molecules of gases, unlike those of liquids and solids, are widely separated. Thus, the interactions between the molecules of a gas may be negligible except at high pressures. Especially at a very low pressure the molecules may act independently of one another. In such a case the gas may be called an ideal or perfect gas. As pointed out by Guggenheim (27) the perfect gas is not a reality but an abstraction corresponding to an approximate model.

Boyle's Law and Charles' Law may be combined to give the equation of state for an ideal gas:

$$P\underline{V} = RT \tag{2-1}$$

where P = absolute pressure

T = absolute temperature

$\underline{V}$ = specific molal volume

R = universal gas constant, the units of which depend upon the units of P, T, and $\underline{V}$

Equation (2-1) can also be deduced from the statistical mechanical considerations which will be discussed in the next section.

The real gases deviate in their behavior from that of the ideal gas, especially at high densities; however, Equation (2-1) may be considered as a limit which all gases approach as P approaches 0 and the temperature increases.

B. Pure Gases

To describe the volumetric properties of pure gases both the thermodynamists and the statistical mechanists have used empirical equations of state as well as the more fundamental theorem of corresponding states. The equations of state have been developed as a means of correlating experimental data. These are useful for interpolation but unsafe for extrapolation into uninvestigated region. The theorem of corresponding states has been used more or less as a predicting tool, although its accuracy is also limited.

1. Empirical Equations of State

Numerous equations of state have been proposed from the thermodynamical considerations since van der Waals (91) presented his famous two-constant equation in 1873. Some of them are specific for a particular pure gas in a specified range of pressure and temperature, while others have been generalized. There are two methods in common use for evaluating the coefficient of an equation of state. One method requires the coefficient to satisfy certain limiting conditions and general trends which have been observed experimentally to be characteristic of all pure fluids. For example,

$$P\underline{V} = RT \qquad \text{as } P \to 0$$

$$\left[\frac{\partial P}{\partial \underline{V}}\right]_{T_c} = 0 \tag{2-2}$$

$$\left[\frac{\partial^2 P}{\partial \underline{V}^2}\right]_{T_c} = 0$$

Here T_c is the temperature at the critical point. The other method consists in empirically evaluating the coefficients for a specified maximum deviation from the experimental data.

In statistical mechanics the equation of state is fundamentally related to the law of force between the individual molecules. The theory suggests the functional form of the potential of interaction, and experimental data are used to determine empirically the adjustable parameters. The important equations of state used in thermodynamics and statistical mechanics are now discussed.

a. Thermodynamics

The failure of the ideal gas law to describe the actual behavior of gases was first interpreted qualitatively by van der Waals. He postulated that the molecules of a gas have definite volume and furthermore are subjected to a force field which results in attractive or repulsive forces between them, depending upon their proximity to one another. His equation for a pure gas is given as follows:

$$\left(P + \frac{a}{\underline{V}^2}\right)\left(\underline{V} - b\right) = RT \qquad (2\text{-}3)$$

Rearranging $$P = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}^2} \qquad (2\text{-}4)$$

Here a and b are constants which are characteristic of a particular gas. The term $a/\underline{V}^2$ is the pressure correction due to the force field and b is the volume correction due to the definite volume of the molecules themselves. Although qualitatively correct, van der Waals' equation is unsatisfactory over a wide range of pressure and temperature for most gases, particularly near the critical region.

In an effort to improve van der Waals' equation, Berthelot and Dieterici have proposed the following two-constant equations of state (35):

Berthelot $$\left(P + \frac{a}{T\underline{V}^2}\right)\left(\underline{V} - b\right) = RT \qquad (2\text{-}5)$$

Dieterici $$\left(Pe^{a/\underline{V}RT}\right)\left(\underline{V} - b\right) = RT \qquad (2\text{-}6)$$

Equation (2-5) is reliable within moderate pressure and temperature ranges. The Dieterici equation is found to be remarkably accurate for many pure gases in the critical region and is the best empirical two-constant equation of state for general usage.

A somewhat more complex five-constant equation of state is due to Beattie and Bridgeman (22):

$$P\underline{V}^2 = RT\left(1 - \frac{c}{\underline{V}T^3}\right)\left(\underline{V} + B_o - \frac{bBo}{\underline{V}}\right) - Ao\left(1 - \frac{a}{\underline{V}}\right) \qquad (2\text{-}7)$$

The five constants Ao, Bo, a, b, and c have been empirically determined for a large number of pure gases. Although this equation is not reliable near the critical region, it provides the best empirical representation of the volumetric behavior of pure gases up to a maximum pressure of 250 atmospheres.

Benedict, Webb and Rubin (6) later refined the Beattie-Bridgeman equation of state. They proposed an eight-parameter equation which was necessary to fit the experimental P-V-T behavior of hydrocarbons up to densities of twice the critical density. Their equation is:

$$P = \frac{RT}{\underline{V}} + \frac{1}{\underline{V}^2}\left[RT\left(Bo + \frac{b}{\underline{V}}\right) - \left(Ao + \frac{a}{\underline{V}} - \frac{ad}{\underline{V}^4}\right) - \frac{1}{T^2}\left\{Co - \frac{c}{\underline{V}}\left(1 + \frac{f}{\underline{V}^2}\right)e^{-f/\underline{V}^2}\right\}\right] \qquad (2\text{-}8)$$

The constants Ao, Bo, Co, a, b, c, d, and f which are characteristic of a given substance are empirically determined from the observed data. This is by far the best equation available which can describe with reasonable accuracy the volumetric behavior of fluids in both the liquid and gas phases over a wide range of pressure and temperature.

The widely used empirical equation of state is the compressibility factor equation:

$$P\underline{V} = ZRT \qquad (2\text{-}9)$$

Here the dimensionless term Z is called the compressibility factor. It is useful in describing the departure in behavior of the real gases from the ideal gas law. The compressibility factor of a gas depends upon the pressure and temperature, the complexity of the structure, and the nature of the molecules in the gas phase.

b. Statistical Mechanics

The equation of state for pure gases may be expressed in terms of the partition function Q and the radial distribution function $g(r)$. The partition function is a measure of the way in which the energy of a system of molecules is partitioned among the molecular inhabitants. The radial distribution function, on the other hand, deals with the number of molecules whose separation lies between a distance r and $(r + dr)$. In terms of these quantities the equation of state is written as (9):

$$P = kT \left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} \tag{2-10}$$

$$P = \frac{NkT}{V} - \frac{N^2}{6V^2} \int g(r) r \frac{d\varphi}{dr} 4 \pi r^2 \, dr \tag{2-11}$$

where k = Boltzmann constant

V = total volume of the system

N = number of molecules in the system

φ = the potential energy of interaction

For an ideal monatomic gas, in which the molecules are indistinguishable and independent of each other, the following expression for Q may be obtained (33):

$$\ln Q = N \ln \left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{Ve}{N}\right] \tag{2-12}$$

where m = mass of a molecule

h = Plank's constant

Substitution of the Equation (2-12) for Q in Equation (2-10) gives:

$$PV = NkT \tag{2-13}$$

or

$$P\underline{V} = RT \tag{2-1}$$

where $R = k\overline{N}$

$\underline{V} = \dfrac{V}{N/\overline{N}}$

$\overline{N}$ = Avagadro's number

In the case of an ideal gas, Equation (2-11) reduces to Equation (2-1) because φ (r) and consequently $-\dfrac{d\varphi}{dr}$, giving an expression for the force acting between the two molecules, are zero.

The widely used virial equation of state which was originally proposed by Kammerlingh Onnes in 1901 as a means of fitting experimental data was developed later on the principles of molecular theory. This equation is generally expressed in the form of a power series in specific molal volume:

$$\frac{P\underline{V}}{RT} = 1 + \frac{B(T)}{\underline{V}} + \frac{C(T)}{\underline{V}^2} + \cdots \tag{2-14}$$

The temperature dependent coefficients B(T), C(T), etc., are called, respectively, the second, third, etc., virial coefficients. A very simple interpretation of the virial coefficients consists of the effects of the interactions of n- molecules. Thus, two-molecular interactions contribute to B(T), while three, etc., molecular interactions contribute to to C(T), etc., virial coefficients.

Some workers prefer to express the virial equation in terms of powers of the pressure:

$$\frac{P\underline{V}}{RT} = 1 + B'(T)P + C'(T)P^2 + \cdots \tag{2-15}$$

in which $B'(T) = B(T)/RT$ and $C'(T) = \{C(T) - B(T)^2\} / (RT)^2$.

In order to evaluate the virial coefficients the nature of the intermolecular forces must be known. Although the second virial coefficient has been established for some potential functions, the third and to a lesser extent the fourth virial coefficients are still under development.

The potential functions of molecules which have been the subject of intensive study in recent years depend upon the size, shape, nature and relative orientations of the molecules. At the present time the most widely used potential functions are due to Lennard-Jones for the simple non-polar molecules and Stockmeyer for polar molecules. These empirical functions are as follows:

Lennard-Jones (non-polar)

$$\varphi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{2-16}$$

Stockmeyer (polar)

$$\varphi\left(r, \theta_1, \theta_2, \phi_2 - \phi_1\right) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - \frac{\mu^2}{r^3}\left[(2 \cos\theta_1\theta_2 - \sin\theta_1\theta_2 \cos(\phi_2 - \phi_1)\right] \tag{2-17}$$

where ϵ = maximum energy of attraction

σ = collision diameter for encounters between two molecules with negligible kinetic energy

r = distance between two molecules

μ = dipole moment of a single molecule

Θ_1, Θ_2 = the angles which the dipoles make with the axis connecting them

$(\Phi_2 - \Phi_1)$ = the difference in their azimuthal angle

The terms σ and ϵ are the constant characteristics of the colliding molecules and commonly referred as force constants.

In the Lennard-Jones potential (Figure 1) the r^{-6} term is a good approximation to the long-range attractive forces, and the r^{-12} term is arbitrarily introduced to represent the short-range repulsive forces. The Lennard-Jones potential is satisfactory for representing the interaction between spherical non-polar molecules.

The Stockmeyer potential is a superposition of the Lennard-Jones potential and the interaction of two point dipoles. It is reasonably good for simple polar molecules for which dipole-quadrupole and higher multipole interactions are not important.

Several other potential functions have also been proposed by various investigators (35). Buckingham and Corner have proposed a four parameter potential function for spherical non-polar molecules. This potential function includes the induced-dipole-induced-dipole and the induced-dipole-induced-quadrupole interaction and has an exponential type repulsion. For non-spherical molecules several models which are extensions of the Lennard-Jones potential have been developed — one by Corner and a somewhat simpler one by Kihara. For polar molecules Rowlinson has suggested a modification of Stockmeyer potential function.

The following equation gives an expression for the second virial coefficient:

$$B(T) = 2\pi \bar{N} \int^{\infty} r^2 \left[1 - e^{-\varphi(r)/kT} \right] dr, \qquad (2\text{-}18)$$

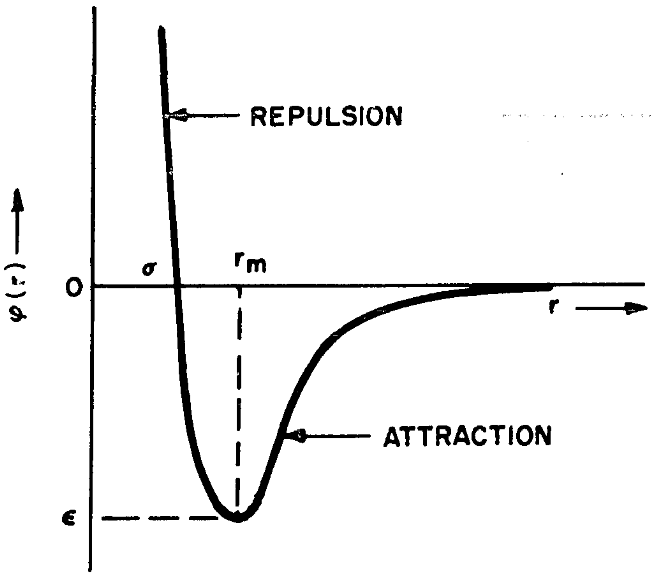

FIGURE I

LENNARD-JONES POTENTIAL ENERGY OF MOLECULAR INTERACTION AS A FUNCTION OF DISTANCE r BETWEEN THE TWO MOLECULES

In terms of the potential functions of Lennard-Jones and Stockmeyer the second virial coefficients are given as follows:

$$\text{Lennard Jones} \qquad B(T) = b_o \left\{ F(\epsilon/kT) \right\} \tag{2-19}$$

$$\text{Stockmeyer} \qquad B(T) = b_o \left\{ F(\epsilon/kT) + (\mu^*)^2 H(\epsilon/kT) + (\mu^*)^4 J(\epsilon/kT) + \ldots . \right\} \tag{2-20}$$

where

$$b_o = \left(\frac{2\pi \bar{N}}{3}\right) \sigma^3 \tag{2-21}$$

$$\mu^* = \frac{\mu^2}{\epsilon \sigma^3} \tag{2-22}$$

The functions $F(\epsilon/kT)$, $H(\epsilon/kT)$, $J(\epsilon/kT)$, etc. have been evaluated and reported in the literature (34).

2. Theorem of Corresponding States

van der Waals was the first to recognize the generalized P-V-T behavior of pure gases and laid down the foundation of the theorem of corresponding states. His theorem may be formally stated: all pure substances have corresponding molal volume at corresponding temperature and pressure if the reference point of correspondence is the critical point. The theorem of corresponding states, however, has assumed a modern form by the application of the principles of statistical mechanics. Pitzer (66) has observed from the point of view of molecular theory that a complete correspondence is feasible for only those substances which conform to the five requirements of perfection, as follows: 1) the validity of classical statistical mechanics, 2) spherical or freely rotating molecules, 3) intermolecular vibration is the same in liquid and gas, 4) potential energy depends only on intermolecular distances, and 5) universal shape of potential curve. The heavier rare gases Argon, Krypton, and Xenon follow the principle with respect to all these properties.

Guggenheim (26) has further shown that nitrogen, oxygen, carbon monoxide, and methane also follow the principle with fair accuracy. He pointed out that the departure of a particular pure substance from this ideal behavior must not be regarded as unsatisfactory flaws in the principle but rather as giving interesting information concerning fundamental differences between the molecules of the substances in question. The concept and applicability of the theorem from both the thermodynamic and statistical mechanics standpoint will be discussed in more detail in the following subsections.

a. Thermodynamics

The constants in van der Waals' equation for pure gases may be mathematically related to the critical properties, i.e., P_c, T_c, and $\underline{V}_c$. In terms of these quantities van der Waals' equation of state may be written as follows (84):

$$\left[\left(\frac{P_c\underline{V}_c}{RT_c}\right)\left(\frac{P}{P_c}\right)+\frac{9}{8}\left(\frac{\underline{V}_c}{\underline{V}}\right)^2\right]\left[\left(\frac{\underline{V}}{\underline{V}_c}\right)-1/3\right]=\left(\frac{T}{T_c}\right) \qquad (2\text{-}23)$$

where $\frac{P}{P_c} = P_r$ = reduced pressure (2-24)

$\frac{T}{T_c} = T_r$ = reduced temperature (2-25)

$\frac{\underline{V}}{\underline{V}_c} = \underline{V}_r$ = reduced specific volume (2-26)

The dimensionless group

$$Z_c = \frac{P_c \underline{V}_c}{R\,T_c} \qquad (2\text{-}27)$$

is known as the compressibility factor at the critical point. Combining Equations (2-24) through (2-27) with Equation (2-23), and assuming a common value of $Z_c = 3/8$ for all gases, a generalized reduced form of van der Waals' equation may be obtained:

$$\left(P_r + \frac{3}{\underline{V}_r^2}\right)\left(\underline{V}_r - 1/3\right) = 8/3\ T_r \qquad (2\text{-}28)$$

Equation (2-28) provides the basis of the theorem of corresponding states for pure gases which can be then expressed mathematically as:

$$\underline{V}_r = f_r(P_r,\ T_r) \qquad (2\text{-}29)$$

Where f_r is a universal function.

Combining Equations (2-9) and (2-27) the following expression may be obtained:

$$Z = \frac{P_r \underline{V}_r}{T_r}\ Z_c \qquad (2\text{-}30)$$

If Z_c has a common value for all gases and Equation (2-29) is valid, Z can be expressed as a universal function of P_r and T_r:

$$Z = f_r(P_r,\ T_r) \qquad (2\text{-}31)$$

Based upon the previous relationship, generalized compressibility factor charts for gases were prepared first by Cope and associates in 1931 (17) and later by Brown and co-workers in 1932 (12). However, the most widely used charts are those of Dodge (22), Nelson and Obert (60), Su (88), Hougen and Watson (41), and Standing and Katz (85). Su actually modified Equation (2-29) as follows:

$$\underline{V}_r'' = f_r(P_r, T_r) \tag{2-32}$$

where $$\underline{V}_r'' = \frac{\underline{V}}{(\underline{V}_c)_{ideal}} = \frac{\underline{V}\,P_c}{R\,T_c} = \text{ideal reduced volume} \tag{2-33}$$

Appreciable errors are often encountered in using the familiar generalized compressibility factor charts. This, however, is not too surprising. Several reasons may be advanced for this inadequacy: 1) the law of corresponding states as expressed by Equation (2-29) is only an approximation, 2) Z_c is not the same for all gases, and 3) generalized charts have been prepared by averaging the experimental data of a few pure gases.

Other early attempts to refine the compressibility factor prediction consisted of correcting T_c and P_c of a given substance. Newton (62) suggested that an empirical constant +8 be added to T_c(°K) and P_c (atmosphere) for hydrogen, helium, and neon. This was in fact an attempt to correct the quantum effects of these gases. Morgen and Childs (57) developed a more general method for correcting T_c and P_c of any substance whose P-V-T behavior could conform with their reference chart which was based upon data for ethylene and nitrogen.

In recent years increased efforts have been made to refine the prediction of gas compressibility factor by introducing a third and even a fourth parameter other than P_r and T_r. This has been done to account for deviations from perfect fluid behavior due to non-sphericity, polarity, and quantum effects.

Inasmuch as the compressibility factor at the critical point Z_c is not the same for all gases, Meissner and Saferian (53) proposed (in 1951) the following modified theorem of corresponding states:

$$Z = f_r(P_r, T_r, Z_c) \tag{2-34}$$

Later (in 1955) Lyderson and co-workers (52) used this modified theorem to prepare compressibility data in a tabular form for a large number of classified pure substances in both liquid and gaseous phases. In using Z_c as a third parameter, one, however is faced with the problem of accurately determining the Z_c of a given substance from the critical properties since $\underline{V}_c$ is very difficult to obtain. There is another fundamental weakness in using Z_c for generalized correlation. Although two substances may have the same Z_c, their molecular structure and nature may be completely different so that they cannot be expected to conform with the theorem of corresponding states as stated by Equation (2-34). It may, however, be expected that the use of Z_c would be quite helpful in predicting compressibility factor in the critical region.

Riedel proposed the slope, λ, of the vapor pressure curve at the critical temperature as the third parameter (41):

$$\lambda = \frac{d(\ln P)}{d(\ln T)} \quad \text{(at the critical point)} \tag{2-35}$$

Pitzer and co-workers (68) have undertaken basically the same approach as Riedel and introduced their acentric factor, ω, as the third parameter of the modified corresponding theorem. The acentric factor is postulated to be a measure of the deviation of a substance (excluding highly polar fluids) from the perfect fluid behavior. For perfect fluids ω was shown to be zero. By definition:

$$\omega = -\log P_r - 1 \tag{2-36}$$

where P_r is the reduced vapor pressure at $T_r = 0.7$. In terms of ω the compressibility factor is adequately given by:

$$Z = Z^o + \omega Z^1 \tag{2-37}$$

where

$$Z^o = f_r(P_r, T_r) \tag{2-38}$$

$$Z^1 = f_r'(P_r, T_r) \tag{2-39}$$

Generalized charts for Z^o and Z^1 were prepared by analyzing compressibility factor data on several pure fluids in the region $T_r = 0.8$ to 4.0 and $P_r = 0$ to 9. Agreement was obtained up to 0.5% over most regions with maximum deviations of about 2%.

Hooper and Joffe (40) have studied the accuracy of Z_c and ω as third parameters in generalized compressibility correlations. They selected for their study 15 different pure substances to cover a broad range of types. They found the acentric factor correlation to be more accurate than the critical compressibility factor correlation for compressibilities of non-polar or slightly polar saturated vapors and somewhat better for most superheated gases. The critical compressibility factor correlation was more accurate for saturated liquids and highly polar saturated vapors.

Hirschfelder and associates (37, 38) have presented a four parameter correlation covering both liquid and gaseous phases. Their method, which includes both Z_c and λ in addition to P_r and T_r, eliminates large errors near the critical region, which have been found when only either Z_c or λ is introduced.

Hall and Ibele (30) have employed the reduced dipole moment

$$\mu^* = \frac{\mu^2}{\epsilon \sigma^3} \tag{2-22}$$

$$\simeq \frac{\mu^2}{(KT_c)\ (\underline{V}_c/N)} \tag{2-40}$$

to extend the law of corresponding states for pure polar gases:

$$Z = f_r(T_r, \rho_r, \mu^*) \tag{2-41}$$

Where ρ_r is Su's ideal reduced density, i.e., $1/\underline{V}_r^{\#}$. They have presented charts which permit the calculation of compressibility factors for polar gases by applying a polarity correction to the compressibility as given by a standard chart. The group of rare gases argon, krypton, and xenon was selected as the standard.

Eubank and Smith (24) later introduced a fourth parameter in Pitzer's Equation (2-37) to account for the polar contribution to the compressibility factor. Thus

$$Z = Z^o + \omega Z^1 + p^* Z^2 \tag{2-42}$$

where Z^2 is still a function of P_r and T_r and the parameter p^* is given by

$$p^* = s(\mu^*)^{2t} \tag{2-43}$$

where s and t are constants within a chemical group. Their correlation, which was based upon alcohol data for P_r up to 0.9 and T_r up to 1.0, is expected to predict compressibilities for normal alcohols and methyl fluoride within 1 per cent deviation from experimental data.

b. Statistical Mechanics

The existence of the theorem of corresponding states for pure gases with spherical and non-polar molecules may be explained by the molecular theory. The reduced equation of state for such gases is as follows (35):

$$P^* = f^*(\underline{V}^*, T^*) \tag{2-44}$$

where the reduced parameters are given by

$$P^* = \frac{P\sigma^3}{\epsilon} \tag{2-45}$$

$$\underline{V}^* = \frac{\underline{V}}{\bar{N}\sigma^3} \tag{2-46}$$

$$T^* = \frac{kT}{\epsilon} \tag{2-47}$$

For long molecules Equation (2-44) may be modified as follows:

$$P^* = f^*(\underline{V}^*, T^*, l^*) \tag{2-48}$$

where

$$l^* = \frac{l}{\sigma} = \text{length to width ratio of the molecule} \tag{2-49}$$

Similarly, in order to account for the quantum effects of the noble gases a quantum mechanical parameter Λ^* may be introduced in Equation (2-44):

$$P^* = f^*(\underline{V}^*, T^*, \Lambda^*) \tag{2-50}$$

where

$$\Lambda^* = \frac{h}{\sigma\sqrt{m\epsilon}} \tag{2-51}$$

The value Λ^* is a measure of the importance of quantum effects for various substances. For most substances Λ^* is very small, and quantum effects are negligible except at low temperature and high pressure.

For substances containing polar molecules the reduced equation of state assumes the form

$$P^* = f^*(\underline{V}^*, T^*, \mu^*) \qquad (2\text{-}52)$$

where μ^* is the reduced dipole moment as defined by Equation (2-22).

The compressibility factor Z may be also expressed as universal function of $\underline{V}^*$ and T^*

$$Z = f^*(\underline{V}^*, T^*) \qquad (2\text{-}53)$$

Experimental verifications of this result are presented by Hirschfelder and associates (35) from data on argon, oxygen, nitrogen, and neon.

Nelson and Obert (60, 61) have presented a generalized compressibility chart for spherical and semispherical non-polar gases based upon the following law of corresponding states:

$$Z = f^*(T^*, P_o^*) \qquad (2\text{-}54)$$

where $P_o^* = \dfrac{P}{R(\epsilon/k\ b_o)}$ $\qquad$ (2-55)

They also noted extreme divergences in their correlation when the gases were highly polar or non-symmetric.

Guggenheim and McGlashan (28) have proposed a correspondence relationship for the second virial coefficient:

$$\frac{B(T)}{\underline{V}^{**}} = f^{**}\left(\frac{T}{T^{**}}\right) \qquad (2\text{-}56)$$

where f^{**} is the universal function for all substances, $\underline{V}^{**}$ is a characteristic volume proportional to σ, and T^{**} is a characteristic temperature proportional to ϵ/k. Except for the light molecules, $\underline{V}^{**}$ and T^{**} may be identified with $\underline{V}_c$ and T_c, respectively. For H_2 and D_2, Newton's law may be used to account for quantum effects. The previous relationship has been verified by plotting $B(T)/V^{**}$ versus T/T^{**} from experimental data on several substances (Ne, A, N_2, O_2, CO_2, CH_4, C_2H_6, n-C_4H_{10}, and H_2).

C. Gas Mixtures

In most industrial uses mixtures are more important than pure fluids. Experimental data on mixtures, however, are less abundant and special data on mixtures containing more than two components are extremely meager. Consequently, much effort is now being made to develop methods of predicting the properties of mixtures by relating them to the corresponding properties of the pure components.

Guggenheim (27) has shown from statistical mechanical considerations that the volumetric behavior of a mixture of ideal gases is identical with that of the pure components. Even though such a mixture is composed of molecules of different species, the molecules are independent of one another and therefore there are no interactions between them. On the contrary, the interactions in case of a mixture of real gases must be considered in order to accurately evaluate its volumetric properties.

The methods of extending the empirical equations of state and the theorem of corresponding states for pure gases are presented in more detail in the following sections.

1. Empirical Equations of States

In thermodynamics the various empirical equations of state of pure gases are extended to gaseous mixtures by combining empirically the constants or properties of individual components. The virial coefficients in statistical mechanics may be empirically related also to those of the pure components.

a. Thermodynamics

Beattie and Ikehara made a study of different methods of combining the constants in the equations of state of pure gases for mixtures. They recommended the linear combination of all constants having the dimension of $(\text{length})^3$ and the linear square root for those having the dimension of $(\text{length})^6$. Thus for van der Waals' Equation (2-3):

$$a' = \left[\sum_{i=1}^{n} x_i \, a_i^{\frac{1}{2}} \right]^2$$

$$b' = \sum_{i=1}^{n} x_i \, b_i \tag{2-57}$$

where x_i = mole fraction of the ith component in the mixture

Beattie proposed the following combination rules for the constants of the Beattie-Bridgemann Equation (2-7):

$$A_o' = \left[\sum_{i=1}^{n} x_i (A_o)_i^{\frac{1}{2}} \right]^2$$

$$B_o' = \sum_{i=1}^{n} x_i (B_o)_i$$

$$a' = \sum_{i=1}^{n} x_i\, a_i \tag{2-58}$$

$$b' = \sum_{i=1}^{n} x_i\, b_i$$

$$c' = \sum_{i=1}^{n} x_i\, c_i$$

Benedict and associates (7) used the following combination of constants for their Equation (2-8):

$$\begin{aligned}
A_o' &= \left[\sum_{i=1}^{n} x_i (A_o)_i^{\frac{1}{2}}\right]^2 & a' &= \left[\sum_{i=1}^{n} x_i\, a_i^{1/3}\right]^3 \\
B_o' &= \sum_{i=1}^{n} x_i (B_o)_i & b' &= \left[\sum_{i=1}^{n} x_i\, b_i^{1/3}\right]^3 \\
C_o' &= \left[\sum_{i=1}^{n} x_i (C_o)_i^{\frac{1}{2}}\right]^2 & c' &= \left[\sum_{i=1}^{n} x_i\, c_i^{1/3}\right]^3 \\
d' &= \left[\sum_{i=1}^{n} x_i\, d_i^{1/3}\right]^3 & f' &= \left[\sum_{i=1}^{n} x_i\, f_i^{\frac{1}{2}}\right]^2
\end{aligned} \tag{2-59}$$

Dalton's law of additive pressure and Amagat's law of additive volume which are valid for ideal gas mixtures may be extended for real gas mixtures (22):

$$P = \sum_{i=1}^{n} x_i\, \overline{P}_i \tag{2-60}$$

where $\overline{P}_i = \frac{Z_i RT}{\underline{V}}$ = pressure that would be exerted by the ith component at the temperature and molal volume of the mixture (2-61)

$$\underline{V} = \sum_{i=1}^{n} x_i \underline{V}_i \qquad (2\text{-}62)$$

where $\underline{V}_i = \frac{Z_i RT}{P}$ = molal volume of the ith component at the pressure and temperature of the mixture (2-63)

Of these two laws, Amagat's law may be generally expected to give better results.

Hirschfelder and Buehler (36) have proposed a method based upon the idea of partial molal volume for predicting the molal volume of binary gaseous or liquid mixture:

$$\underline{V} = x_1\underline{V}_1 + x_2\underline{V}_2 + x_1x_2^2\,(\underline{V}_{12} - \underline{V}_1) + x_1^2x_2\,(\underline{V}_{21} - \underline{V}_2) \qquad (2\text{-}64)$$

where subscripts 1 and 2 denote pure component 1 and 2, respectively.

12 and 21 denote component 1 immersed in almost pure 2 and vice versa.

The partial molal volumes may be determined from a knowledge of the volume increment, $\Delta\underline{V}$, for two compositions given by:

$$\Delta\underline{V} = x_1x_2^2\,(\underline{V}_{12} - \underline{V}_1) + x_1^2x_2\,(\underline{V}_{21} - \underline{V}_2) \qquad (2\text{-}65)$$

b. Statistical Mechanics

The virial equation of state, Equation (2-14) also may be used for multicomponent mixtures containing both non-polar and polar components. The second virial coefficient for a mixture made up of n components may be empirically expressed as follows:

$$B(T)_{mix} = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \; B(T)_{ij} \tag{2-66}$$

The quantity $B(T)_{jj}$ is the second virial coefficient for the pure jth substance, whereas the quantity $B(T)_{ij}$ is the second virial coefficient for a hypothetical substance, characterized by intermolecular potential parameters σ_{ij} and ϵ_{ij}, appropriate for the various interactions between pairs of dissimilar molecules in the gas. A method of evaluating $B(T)_{ij}$ for different kinds of mixtures is given by Bird, et al (9).

Semiempirical relationships for evaluating σ_{ij} and ϵ_{ij} of two dissimilar spherical molecules of the same general nature are given by:

$$\sigma_{ij} = \tfrac{1}{2}(\sigma_i + \sigma_j) \tag{2-67}$$

$$\epsilon_{ij} = \left(\epsilon_i \; \epsilon_j\right)^{\frac{1}{2}} \tag{2-68}$$

In mixtures where both non-polar molecules (i) and polar molecules (j) are present the following approximate combining rules may be used:

$$\sigma_{ij} = \tfrac{1}{2}(\sigma_i + \sigma_j) \quad (1 + \xi_{ij})^{-1/6} \tag{2-69}$$

$$\epsilon_{ij} = \left(\epsilon_i \epsilon_j\right)^{\frac{1}{2}} \left(1 + \xi_{ij}\right)^{\frac{1}{2}} \tag{2-70}$$

where the factor ξ_{ij} is given by:

$$\xi_{ij} = 1/4 \alpha_i^* \, (\mu_j^*)^2 \, (\epsilon_j / \epsilon_i)^2 \tag{2-71}$$

in which μ^* is the reduced dipole moment of the polar molecule (j) as given by Equation (2-22), and α^* is the reduced polarizability of the non-polar molecule (i) as given by:

$$\alpha^* = \frac{\alpha}{\sigma^3} \tag{2-72}$$

where α is the polarizability of the non-polar molecule.

2. Theorem of Corresponding States

Another useful method of predicting the compressibility factors of gas mextures involves the extension of the principle of corresponding states by utilizing the concept of pseudocritical properties proposed originally by Kay (43), and the use of reduced virial coefficient introduced by Guggenheim (27). The pseudocritical properties are based upon the hypothesis that there exists for each constant composition of the mixture a hypothetical pure substance with such criticals (pseudocritical properties) that it has thermodynamic properties identical with those of the mixture at the same P, $\underline{V}$, and T conditions.

a. Thermodynamics

In the thermodynamic approach of the extension of the theorem of corresponding states to mixtures, Equations (2-29) and (2-31) may be modified as follows:

$$\underline{V}_r' = f_r'(P_r', T_r') \tag{2-73}$$

$$Z = f_r''(P_r', T_r') \tag{2-74}$$

where the ratios

$$P_r' = \frac{P}{P_c'}, \qquad (2\text{-}75)$$

$$T_r' = \frac{T}{T_c'}, \qquad (2\text{-}76)$$

$$\underline{V}_r' = \frac{T}{\underline{V}_c'}, \qquad (2\text{-}77)$$

are the pseudoreduced pressure, temperature, and volume, respectively, and P_c', T_c', and $\underline{V}_c'$ are the pseudocritical pressure, temperature, and volume.

Various methods have been proposed for evaluating the pseudocritical properties in terms of critical properties of the individual components and their relative amounts present in the mixture. Kay (43) used the following simple molal average relations for mixtures of lighter hydrocarbons:

$$P_c' = \sum_{i=1}^{n} x_i (P_c)_i \qquad (2\text{-}78)$$

$$T_c' = \sum_{i=1}^{n} x_i (T_c)_i \qquad (2\text{-}79)$$

Kay, however, pointed out that the foregoing relationships would be in error if the mixture contained constituents differing greatly in molecular weight as well as in chemical nature.

Joffe (42) proposed the following rules for estimating P_c' and T_c' based upon van der Waals' equation of state:

$$\frac{T_c'}{(P_c')^{\frac{1}{2}}} = \sum_{i=1}^{n} x_i \frac{(T_c)_i}{(P_c)_i^{\frac{1}{2}}} \tag{2-80}$$

$$\frac{T_c'}{P_c'} = 1/8 \sum_{i=1}^{n} \sum_{j=1}^{n} x_i\ x_j \left[\left\{ \frac{(T_c)_i}{(P_c)_i} \right\}^{1/3} + \left\{ \frac{(T_c)_j}{(P_c)_j} \right\}^{1/3} \right]^3 \tag{2-81}$$

Prausnitz and Gunn (69, 70, and 71) have proposed several methods of finding the compressibility factor of gas mixtures. Their simplified method, which is an extension of the modified theorem of corresponding states proposed by Pitzer and associates, is as follows:

$$Z = f'(P_r', T_r', \omega') \tag{2-82}$$

where $\omega' = \sum_{i=1}^{n} x_i (\omega)_i$ (2-83)

The pseudocritical properties necessary for calculating P_r' and T_r' are given as follows:

$$T_c' = \sum_{i=1}^{n} x_i (T_c)_i \tag{2-84}$$

$$P_c' = \frac{RT_c' \sum_{i=1}^{n} x_i (Z_c)_i}{\sum_{i=1}^{n} x_i (\underline{V}_c)_i} \tag{2-85}$$

b. Statistical Mechanics

Guggenheim and McGlashan (28) have extended the reduced virial equation of state for pure gases expressed by Equation (2-56) to mixtures, as follows:

$$\frac{B(T)_{ij}}{\underline{V}_{ij}^{**}} = f^{**}\left(\frac{T}{T_{ij}^{**}}\right) \qquad (2\text{-}86)$$

Plots of Equation (2-86) from data on mixtures $N_2 - O_2$, $N_2 - H_2$, $A - H_2$, $H_2 - CO$, $CH_4 - C_2H_6$, and $CH_4 - n\text{-}C_4H_{10}$ are found to be identical with pure substances (Equation 2-56). Like pure components, $\underline{V}_{ij}^{**}$ is proportional to σ_{ij} or $(\underline{V}_c)_{ij}$ and T^{**} is proportional to ϵ_{ij} or $(T_c)_{ij}$. Semiempirical relationships for evaluating σ_{ij} and ϵ_{ij} are those given by Equations (2-67) and (2-68), respectively. The following equations present the empirical expressions for the corresponding parameters:

$$(V_c)_{ij} = \left[\tfrac{1}{2}(V_c)_i^{1/3} + \tfrac{1}{2}(V_c)_j^{1/3}\right]^3 \qquad (2\text{-}87)$$

$$(T_c)_{ij} = \left[(T_c)_i\,(T_c)_j\right]^{\frac{1}{2}} \qquad (2\text{-}88)$$

Leland, et al (47) have arrived at the following improved relationships for pseudocritical properties by a statistical mechanics approach:

$$T_c' = \left[\frac{\sum\limits_{i=1}^{n}\sum\limits_{j=1}^{n} x_i x_j \left(\frac{Z_c\,T_c^{\gamma+1}}{P_c}\right)_i^{\frac{1}{2}} \left(\frac{Z_c\,T_c^{\gamma+1}}{P_c}\right)_j^{\frac{1}{2}}}{\sum\limits_{i=1}^{n}\sum\limits_{j=1}^{n} x_i x_j \left[\tfrac{1}{2}\left(\frac{Z_c\,T_c}{P_c}\right)_i^{1/3} + \tfrac{1}{2}\left(\frac{Z_c\,T_c}{P_c}\right)_j^{1/3}\right]^3}\right]^{1/\gamma} \qquad (2\text{-}89)$$

$$P_c' = \frac{T_c' \sum_{i=1}^{n} x_i (Z_c)_i}{\sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left[\frac{1}{2} \left(\frac{Z_c\, T_c}{P_c} \right)_i^{1/3} + \left(\frac{Z_c\, T_c}{P_c} \right)_j^{1/3} \right]^3} \qquad (2\text{-}90)$$

where the exponent Υ is given by an empirical relationship as follows:

$$\Upsilon = f \left[\frac{P \sum_{i=1}^{n} x_i (T_c)_i}{T \sum_{i=1}^{n} x_i (P_c)_i} \right] \qquad (2\text{-}91)$$

Leland and coworkers (48) later reported the following relationship:

$$\Upsilon = -0.75 \left[\frac{P \sum_{i=1}^{n} x_i (T_c)_i}{T \sum_{i=1}^{n} x_i (P_c)_i} \right] + 2.44 \qquad (2\text{-}92)$$

For values of $P \sum_{i=1}^{n} x_i (T_c)_i \Big/ T \sum_{i=1}^{n} x_i (P_c)_i \geqslant 2.0$, Υ was set $= 1.0$, and for values $\leqslant 0.4$, Υ was set $= 2.2$.

They have used their pseudocritical constants in conjunction with the Benedict-Webb-Rubin equation of state for a reference substance which is taken as the paraffin hydrocarbon having a value of critical compressibility nearest to that of the mixture. The critical compressibility of the mixture is found by the relationship:

$$Z_c' = \sum_{i=1}^{n} x_i (Z_c)_i \tag{2-93}$$

The molal average pseudocritical compressibility factor is justified by the fact that the critical compressibility factors of pure substances do not differ greatly from one another. It should be noted that unlike many other existing methods their approach gives pseudocritical constants T_c' and P_c' which are not constant for a mixture of constant composition but vary with pressure and temperature. Their method was applied to predict the compressibility factors of saturated liquids and vapors of several binary hydrocarbon systems, and binary systems containing hydrocarbons and compounds other than hydrocarbons. The over-all average absolute per cent error was 2.3% for systems of hydrocarbons and non-polar compounds. The largest reported error for systems containing H_2S was 22.6%.

Steward and associates (86) has also used an empirical statistical mechanical approach to find 21 different sets of pseudocritical rules. These rules, in conjunction with the compressibility tables of Lyderson, et al (52) have been used to predict the compressibility factors of 39 binary systems (over 1,700 single-phase data on nearly equimolal mixtures of each of the systems). They have recommended the following method with a root-mean-square deviation of 4.32% of all systems and 3.26% of twenty three CO_2- and H_2S- free systems:

$$J = \frac{T_c'}{P_c'} = 1/3 \sum_{i=1}^{n} x_i \frac{(T_c)_i}{(P_c)_i} + 2/3 \left[\sum_{i=1}^{n} x_i \left\{ \frac{(T_c)_i}{(P_c)_i} \right\}^{\frac{1}{2}} \right]^2 \qquad (2\text{-}94)$$

$$K = \frac{T_c}{(P_c')^{\frac{1}{2}}} = \sum_{i=1}^{n} x_i \frac{(T_c)_i}{(P_c)^{\frac{1}{2}}} \qquad (2\text{-}95)$$

$$T_c' = \frac{K^2}{J} \qquad (2\text{-}96)$$

$$P_c' = \frac{T_c'}{J} \qquad (2\text{-}97)$$

$$Z_c' = \sum_{i=1}^{n} x_i (Z_c)_i \qquad (2\text{-}93)$$

It should be noted that the recommended method is an extension of Joffe's rule with the simplification of Equation (2-81). It is of interest to know that the three parameter extensions of Kay's rule for which the pseudocritical properties are given by Equations (2-78), (2-79), and (2-93) resulted in twice the deviation shown by the recommended method.

D. Summary

Undoubtedly, the present concepts concerning the behavior of real gases has long surpassed the realm of the ideal gas law. Numerous methods of interpretation and treatment of the nonideal behavior of pure gases, and their mixtures have been reviewed in this chapter. Included in the discussions are empirical equations and laws of corresponding states as used in thermodynamics and statistical mechanics. Prediction methods, based upon the theorem of corresponding states, have been more commonly used in engineering applications than empirical equations.

The fundamental differences in behavior between molecules of unlike pure substances have been finally accepted as commonplace rather than exceptions. Various methods of classification of pure gases depending upon sphericity, polarity, and quantum effects have been proposed by a number of investigators. Several thermodynamic methods are now available for accurately predicting compressibility factors of pure gases. Whereas the molecular theory is more fundamental than thermodynamics, its application is mainly limited to simple gases. Nevertheless, the concepts in statistical mechanics have been very useful in many thermodynamic approaches.

Unlike pure gases, any method of predicting the volumetric properties of a mixture has to deal with the interactions between dissimilar molecules in the system. Unfortunately, the present knowledge about the interactions in complex systems are limited; therefore existing methods lack accuracy which is not comparable to those of pure gases. In predicting the properties of mixtures, increased reliance is being placed on the modified theorem of corresponding states, since this approach does not require a knowledge of the constants in the equation of state and their combination rules for all components.

Kay's pseudocritical rules are commonly used in industrial applications to find compressibility factors of mixtures from a generalized chart. Various authors, however, have pointed out the unreliability of this method, especially when the mixtures contain gases of diversified character and structure. The limitations of most of the familiar charts have been also discussed in this chapter.

Leland and Steward have presented improved methods of predicting the compressibility factors of mixtures. These methods are based upon the statistical mechanics, remaining within the domain of engineering utility. These authors have used the critical compressibility factor Z_c as a characterizing parameter for different substances. A similar approach has been undertaken in the present study, with the exception of using Pitzer's acentric factor ω instead of Z_c. The choice of ω is justified, because ω may be related empirically to the nature and structure of molecules in a substance. The use of ω has been found also to be somewhat better than Z_c for correlating pure gas compressibility factors.

CHAPTER III

REVIEW OF EXPERIMENTAL INVESTIGATIONS

A. Apparatus and Procedure

In the natural gas industry the Bean and the Burnett apparatus are commonly used for determining the compressibility factors of gases. Both devices are fundamentally correct in principle, even though they differ in operating procedures.

The original Bean unit was developed in 1930 by Howard S. Bean (2) of the U. S. Bureau of Standards. The essential features of the apparatus consists of a steel cylinder of known capacity for holding a gas sample, a measuring burette or chamber, a mercury reservoir, a constant temperature bath, pressure and temperature recording devices, valves, and necessary connections.

The principle of operation of the Bean apparatus is to charge the steel cylinder with a high pressure gas sample and then to withdraw successively small portions of the sample into an evacuated burette where their volumes can be determined at atmospheric pressure and controlled temperature. This is continued until the whole sample has been reduced to atmospheric pressure. The sum of all the volumes is then compared with the volume to which the initial known volume of gas would have expanded had it been reduced to atmospheric pressure in accordance with Boyle's Law.

The Burnett unit which was originally designed by E. S. Burnett (14) of the U. S. Bureau of Mines requires no measurement of volume or mass of the gas sample. The apparatus essentially consits of two adjacent high pressure chambers of known volume ratio, a constant temperature bath, a vacuum pump, a diaphragm cell for separating the gas from the oil in the piston gauge, pressure and temperature recording devices, valves, and necessary connections.

The principle of operation is to expand the gas sample confined in the high pressure chamber into the adjacent evacuated chamber. Successive expansions are made after re-evacuation of the second chamber. The compressibility factor of the gas at a selected pressure and temperature is computed from a comparison of the volume ratio of the chambers to the pressure ratio before and after expansion.

In 1952, Bloomer (11) made a comparative study of the Bean and the Burnett methods to establish the relative accuracy of each, and the essential differences in their manipulation and performance. In this work, the compressibility factors of two typical natural gases and pure nitrogen were measured over the pressure range 0-1,000 psia for temperatures of 48.7 and 80.1 °F. For the Bean apparatus the maximum deviation from the literature data of any point of set was 0.2%, while for the Burnett unit the maximum deviation was 0.11%.

The Bean type of equipment is less expensive. The test points are more closely spaced, and larger number of points are obtained compared to the Burnett unit for the same pressure range. The primary disadvantage is its tedious operational procedure. It has delicate glass parts which are easy to damage resulting in considerable delay and probably recalibration of equipment. The commercially available unit is limited in its maximum working pressure. The unit which is obtainable from the Refinery Supply Company, Tulsa, Oklahoma, has a maximum pressure limit of 1,000 psig. Conversion of the apparatus for high pressure work increases the cost to the point where it costs as much as the Burnett type which is available from the same company for a maximum working pressure of 4,000 psig.

The Burnett type has the advantage of greater speed and simplicity of operation. It is more convenient for routine test work, and is also quite suitable for high pressure work (58, 45). The inherent disadvantage is its wide spread of test points at high pressure and close spacing at low pressure.

The Southern California Natural Gasoline Association (11) recommended a method of calibration of the Bean unit in which a test is run using a gas of known compressibility. The ratio of the volume of the steel cylinder to the volume of the burette required to give agreement of the test data with the known behavior of the gas is then calculated. This is all that is needed for the calculation of the compressibility factors. This calibration procedure greatly reduces the effect of the several sources of errors other than calibration of the burette and steel cylinder.

Recently, at the University of Oklahoma, a commercial Bean unit has been modified by Nassiri (59) for use up to a maximum working pressure of 7,000 psig. The constant volume cell and mercury-oil seal assembly of the original unit were replaced by a variable volume cell, operated by a high pressure mercury pump. The remaining Bean section of this equipment is merely used for determining the amount of gas after it is expanded from the high pressure cell. In addition to its higher working pressure, the modified apparatus may be used to determine the volumetric properties of a gas sample at a number of temperatures before the gas is expanded. This new feature of the modified equipment makes it more attractive than either of the two types of commercially available units, which are designed to take data on a sample at only one temperature. The accuracy of the modified unit, however, is found to be slightly lower than the others. This is due to the uncertainty involved in accurately measuring gas in a variable volume cell.

B. Volumetric Data

The volumetric properties of pure methane, ethane, and hydrogen sulfide, and their binary mixtures have been studied experimentally in some detail. A summary of the previous work is given in Table B1 in the Appendix. Although not listed in this table, Robinson and coworkers (77) have studied compressibility factors of a number of selected ternary mixtures of methane, carbon dioxide, and hydrogen sulfide over a temperature range from 40 to 160 °F and up to 3,000 psig.

CHAPTER IV

PRELIMINARY INVESTIGATIONS

A large volume of experimental compressibility factor data on a number of pure hydrocarbons and nonhydrocarbons is available in the literature. Data are also found on many binary mixtures. It was therefore possible to investigate several methods of correlating the existing data in an improved manner, before the experimental work of this research was carried out.

The preliminary study has served to develop: 1) a better understanding of the nonideality of pure gases while working with actual data, 2) an extension of Pitzer's compressibility tables for use at higher pressures, and 3) several combination rules for predicting pseudocritical properties of mixtures. Items 2 and 3 are discussed separately in the following chapters. This chapter deals with two typical correlations obtained during early investigations: 1) a reduced equation of state in statistical mechanics with acentric factor ω as a characterization parameter for a substance, and 2) a dimensionally reduced equation of state with a quantity F in addition to P_r, T_r, and Z_c. The dimensionless quantity F has been obtained by combining P_c, T_c, molar mass m, Plank's constant h and Boltzmann's constant k. Although no completely satisfactory results were obtained by these two correlations, they are presented to illustrate several interesting observations.

A. A Reduced Equation of State in Statistical Mechanics

The following equation of state for gases with spherical and nonpolar molecules was discussed in Chapter II:

$$P^* = f^* (\underline{V}^*, T^*) \tag{2-44}$$

To include the behavior of substances having nonspherical molecules and slightly polar molecules such as hydrogen sulfide, it was thought that the above equation might be modified as follows:

$$\underline{V}^* = f^* (P^*, T^*, \omega) \tag{4-1}$$

The success which Pitzer and co-workers had with their acentric factor ω to obtain a generalized correlation of the P-V-T data of pure fluids having molecules of diversified characteristics led to a choice of ω as the third independent variable in Equation (4-1).

Equation (4-1) was used to correlate the volumetric properties of pure methane, ethane, propane, n- butane, and hydrogen sulfide and three mixtures of methane and ethane. Table C1 in the Appendix shows the force constants ϵ and σ, and acentric factor of these substances. The force constants of pure methane, ethane, propane, and n- butane are for the Lennard-Jones potential as reported by Hirschfelder and co-workers (35). The force constants of hydrogen sulfide are for the Stockmeyer potential as given by the same authors. The force constants for a mixture were calculated by the following combination rules:

$$(\epsilon/k)_{mix} = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j (\epsilon/k)_{ij} \tag{4-2}$$

where $$(\epsilon/k)_{ij} = \left[(\epsilon/k)_i \quad (\epsilon/k)_j\right]^{\frac{1}{2}} \tag{4-3}$$

$$(\sigma)_{mix} = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \, (\sigma)_{ij} \tag{4-4}$$

where $$(\sigma)_{ij} = \tfrac{1}{2}(\sigma_i + \sigma_j) \tag{2-67}$$

The acentric factors of pure substances are due to Pitzer (68). The acentric factor of a mixture was obtained by the following combination rule:

$$(\omega)_{mix} = \sum_{i=1}^{n} x_i \, (\omega)_i \tag{2-83}$$

The reduced temperature T^* and pressure P^* were computed by applying the following relationships:

$$T^* = \frac{T}{1.8 \, \epsilon/k} \tag{4-5}$$

$$P^* = 68{,}950 \; \frac{P\sigma^3}{\epsilon} \tag{4-6}$$

where T is in °K

ϵ/k is in °K

P is in psi

σ^3 is in cm³/molecule

ϵ is in erg/molecule

Then the reduced volume was given by

$$\underline{V}^* = \frac{\underline{V}}{\overline{N}\,\sigma^3} = Z\,\frac{T^*}{P^*} \tag{4-7}$$

The compressibility factors of various systems obtained from the literature (46, 79, 80) were interpolated graphically to even values of T^* and P^*. Whenever experimental compressibility factors were not available, the correlation of Pitzer was used to compute these values. Table C2 in the Appendix shows the reduced properties of the fluids in question for the range of temperature and pressure indicated.

Figures 2 through 5 show V^* as functions of ω, at $P^* = 0.1$, 0.3, 0.5, and 1.0 and the values of $T^* = 1.6$, 1.8, and 2.0. At lower reduced pressures and higher temperatures, a reasonable agreement of Equation (4-1) with experimental data of pure hydrocarbons is observed. It is plausible that under these conditions the molecules of the compounds of this homologous series, although they are increasingly cylindrical in shape with increasing carbon atoms, may be adequately represented by a molecular model such as Lennard-Jones. At higher pressures, however, the constituent molecules are brought closer together and the actual structure and orientation of the molecules become more important in describing the forces of interactions. This may account for the poor correlation of data at higher reduced pressures. The computed reduced properties of the mixtures of methane and ethane are in fair agreement with those of their pure compounds. The failure of hydrogen sulfide to conform with the correlation is attributed to the fact that the molecules of this compound are different in nature and internal structure from

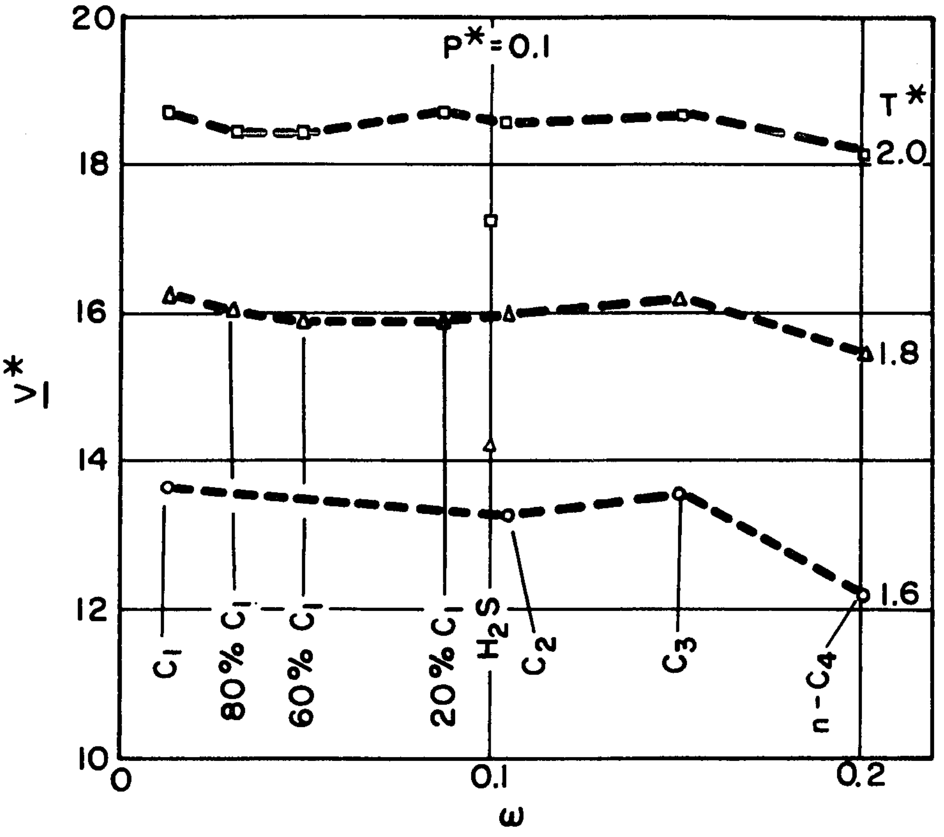

FIGURE 2

$\underline{V}^*$ AS A FUNCTION OF ω, AT $P^* = 0.1$
AND THE VALUES OF T^* INDICATED

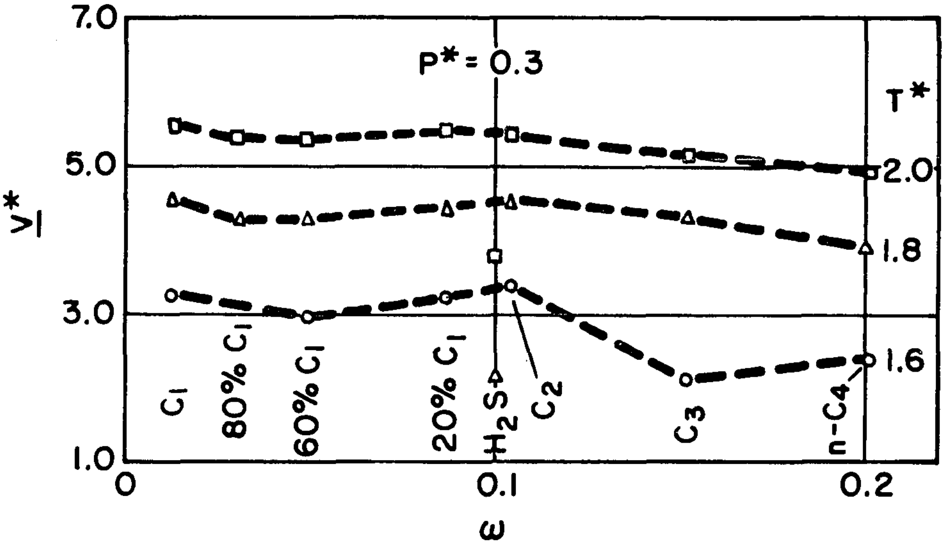

FIGURE 3

$\underline{V}^*$ AS A FUNCTION OF ω, AT $P^* = 0.3$
AND THE VALUES OF T^* INDICATED

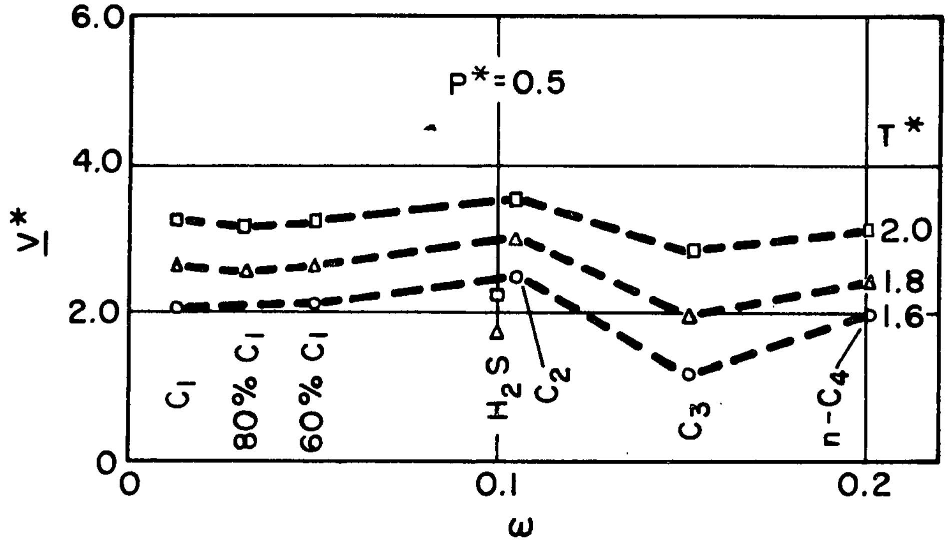

FIGURE 4

$\underline{V}^*$ AS A FUNCTION OF ω, AT $P^* = 0.5$
AND THE VALUES OF T^* INDICATED

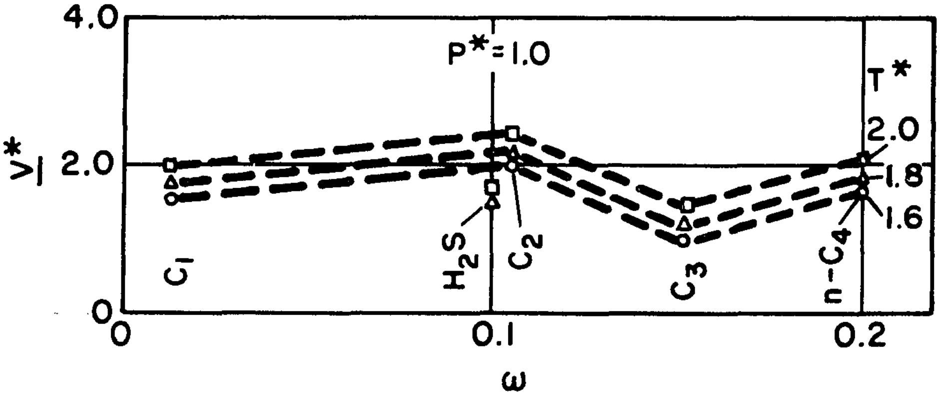

FIGURE 5

$\underline{V}^*$ AS A FUNCTION OF ω, AT $P^* = 1.0$
AND THE VALUES OF T^* INDICATED

those of the hydrocarbons. They have permanent electric moments and are too complex to be described by the parameters used in this correlation.

This analysis shows that it is difficult to obtain by statistical mechanical parameters a generalized correlation of volumetric data of pure gases over a wide range of pressure and temperature when the substances differ widely in molecular structure and chemical nature.

B. A Dimensionally Reduced Equation of State

An empirical equation of state based upon molecular parameters may be quite generally written as:

$$P = f\left(\underline{V}/\overline{N},\ kT,\ h,\ m,\ P_c,\ \underline{V}_c/\overline{N},\ kT_c\right) \qquad (4\text{-}8)$$

where P = pressure exerted in a system containing $\overline{N}$ molecules

$\underline{V}/\overline{N}$ = volume of a single molecule

kT = energy per molecule

h = Plank's constant

m = mass of a single molecule

$\underline{V}$ = specific volume

$\overline{N}$ = Avagadro's number

T = temperature

k = Boltzmann's constant

and subscript c indicates critical conditions.

Equation (4-8) assumes that $\underline{V}_c/\overline{N}$, kT_c, P_c and m are characteristics of molecular species. Then, the variables in Equation (4-8) may be dimensionally analyzed to obtain the following dimensionless groups:

$$P_r = \frac{P}{P_c} \tag{2-24}$$

$$T_r = \frac{kT}{kT_c} = \frac{T}{T_c} \tag{2-25}$$

$$\underline{V}_r = \frac{V/\bar{N}}{V_c/\bar{N}} \quad \frac{\underline{V}}{\underline{V}_c} \tag{2-26}$$

$$Z_c = \frac{P_c\ \underline{V}_c/\bar{N}}{kT_c} = \frac{P_c\underline{V}_c}{RT_c} \tag{2-27}$$

$$F = \frac{h\ P_c^{1/3}}{(kT_c)^{5/6}(m)^{\frac{1}{2}}} \tag{4-9}$$

$$Z = \frac{PV/\bar{N}}{kT} = \frac{P\underline{V}}{RT} \tag{2-9}$$

Since $\underline{V}_r$ is a function of P_r, T_r, and Z_c, the compressibility factor Z may be expressed as follows:

$$Z = f\ (P_r,\ T_r,\ Z_c,\ F) \tag{4-10}$$

Equation (4-10) is an extension of the theory of corresponding states formulated by Meissner and Saferian with an additional parameter F, which depends on the characteristics of the molecular species.

The validity of Equation (4-10) was investigated by correlating the volumetric properties of several pure substances, namely methane, ethane, propane, iso-butane, normal butane, normal pentane, carbon dioxide, and hydrogen sulfide. Table C3 in the Appendix lists the essential parameters for these substances. The critical temperatures, pressures, and compressibility factors of these compounds were obtained from the literature.(52). The parameter F, listed in Table C3, was computed by using the following equation:

$$F = 5.665 \frac{P_c^{1/3}}{(T_c)^{5/6}(M)^{\frac{1}{2}}} \qquad (4\text{-}11)$$

where P_c is in psi

T_c is in °R

M is molecular weight

The compressibility factors of various systems obtained from the literature (46, 79, 80) were interpolated, and in some cases extrapolated to even values of reduced pressure and temperature. The regions representing T_r from 1.0 to 2.0 and P from 0 to 14 were selected for detailed study. It is to be noted that at higher reduced pressures and temperatures, the data were relatively sparse. Two sets of data are shown in Tables C4 and C5 in the Appendix, which list the compressibility factors of fluids under consideration at the values of T_r indicated and P_r = 1.0 and 5.0, respectively. For the sake of simplicity and convenience, the parameters Z_c and F were combined as F/Z_c and the compressibility factors were plotted as a function of F/Z_c for a given P_r and and T_r. Two typical sets of these curves are shown in Figures 6 and 7. Most of the points fell on straight lines within one per cent. Among the two nonhydrocarbon components, H_2S shows better agreement than CO_2, which indicates larger errors at higher reduced pressures and temperatures. For example, CO_2 shows an error of -2.5% at P_r = 5.0 and T_r = 1.9.

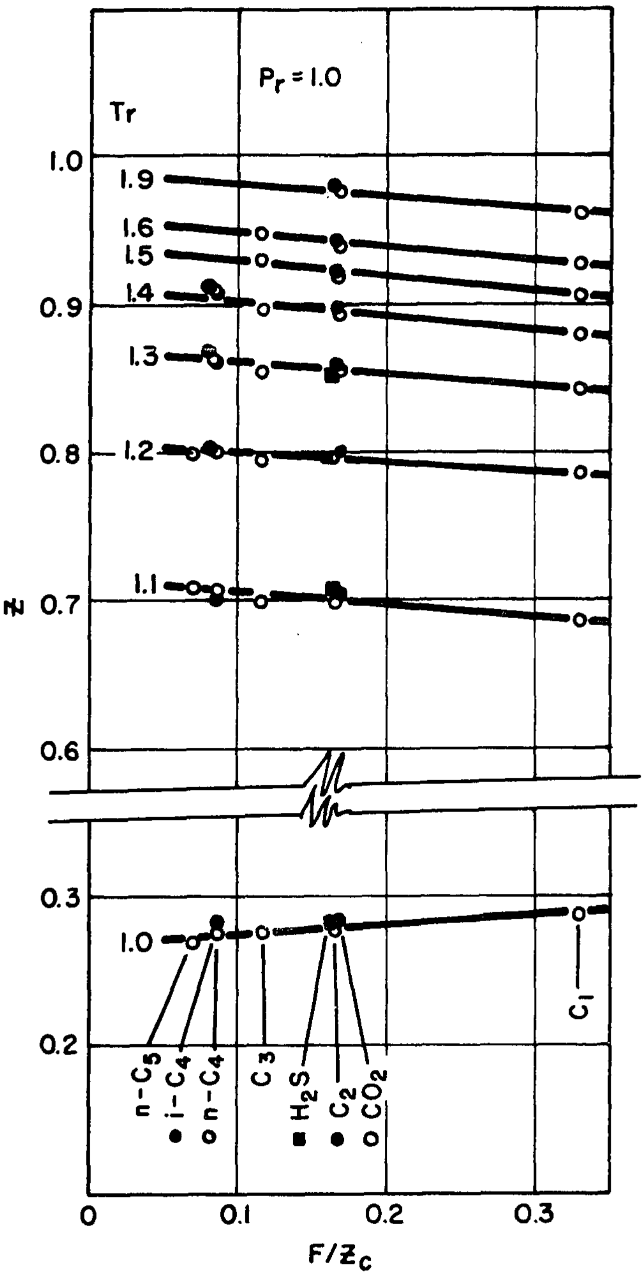

FIGURE 6

THE COMPRESSIBILITY FACTOR AS A FUNCTION OF F/Z_c AT $P_r = 1.0$ AND THE VALUES OF T_r INDICATED

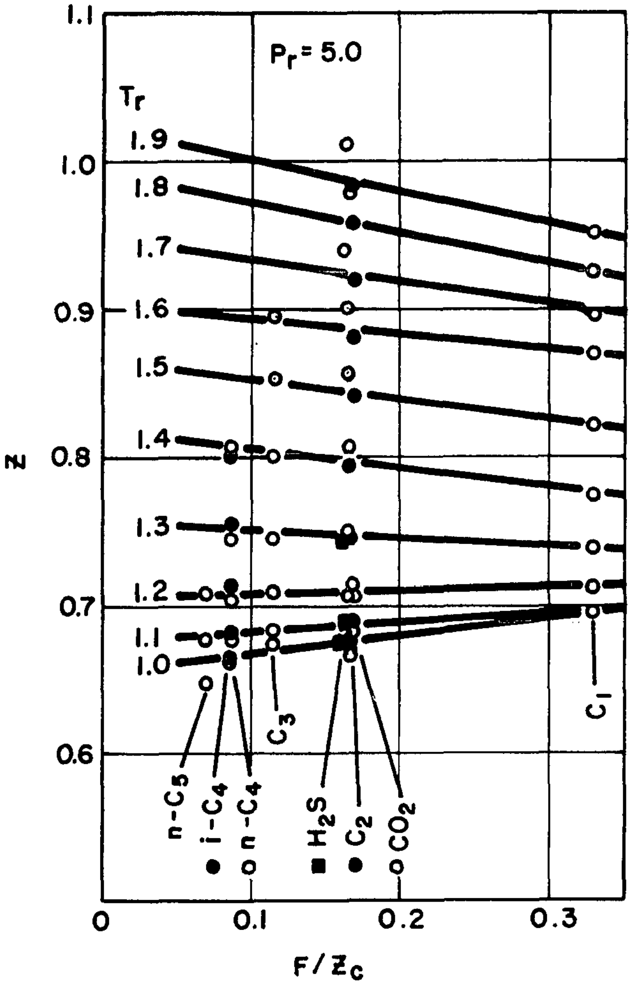

FIGURE 7

THE COMPRESSIBILITY FACTOR AS A FUNCTION OF F/Z_c AT $P_r = 5.0$ AND THE VALUES OF T_r INDICATED

For a given P_r and T_r the compressibility factors were also plotted as a function of the acentric factor, ω. These were obtained from the literature (68) and listed in Table C3 in the Appendix. Figures 8 and 9 show two typical curves for the same values of P_r and T_r that were used for Figures 6 and 7. The agreement of this correlation with the experimental data is somewhat better than the proposed correlation, especially in the case of CO_2 and H_2S.

The values of F/Z_c for different components were then compared with ω. Figure 10 shows the relationship of F/Z_c as a function ω for the pure components studied. Except for CO_2, an excellent correspondence can be noted between these quantities. The failure of CO_2 to agree with the other data may account for the errors involved in correlating generalized Equation (4-10) with the data of CO_2. It may be also observed that iso-butane shows some deviation from the general relationship.

It is not surprising to note that the correspondence between F/Z_c and ω is excellent for substances belonging to the same homologous series, since both of these quantities are measures of characteristics of molecular species. The parameter F represents, in a compact unit, the molecular mass and force constants ϵ and σ, which are correlative to T_c and $\underline{V}_c$, respectively. On the other hand, as demonstrated by Pitzer, the acentric factor is dependent upon the core radius of a globular molecule, the length of an elongated molecule, or the dipole moment of a slightly polar molecule.

It is probable that the extended theorem of corresponding states represented by Equation (4-10) is valid for a group of substances belonging to the same homologous series. However, further work beyond the

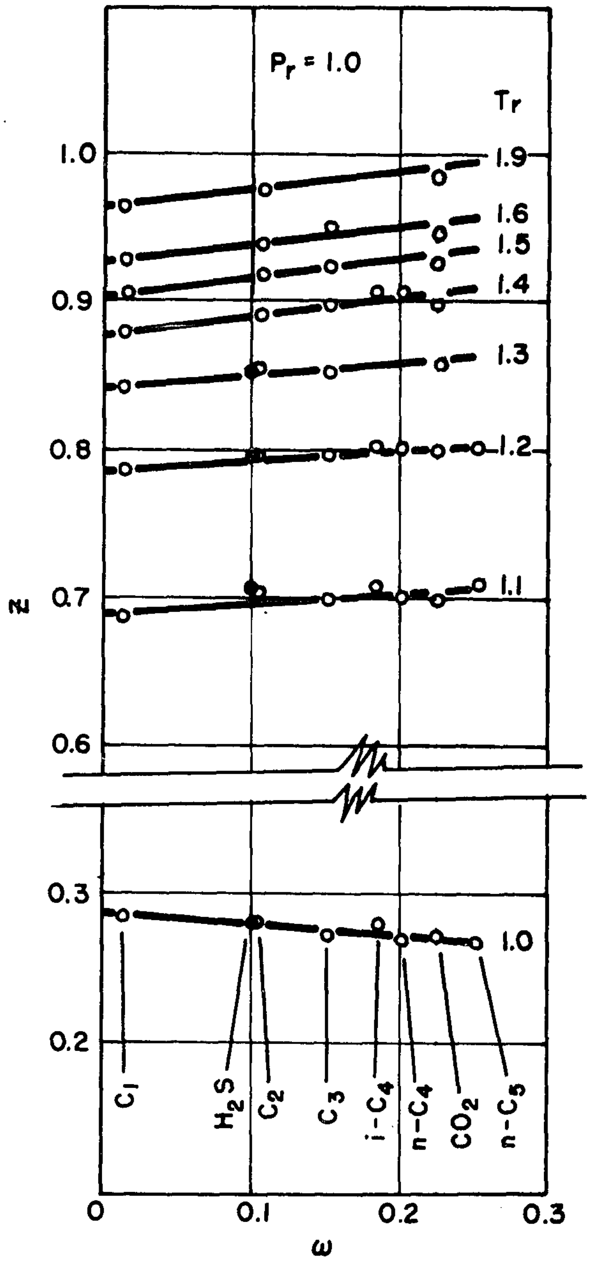

FIGURE 8

THE COMPRESSIBILITY FACTOR AS A FUNCTION OF ACENTRIC FACTOR AT $P_r = 1.0$ AND THE VALUES OF T_r INDICATED

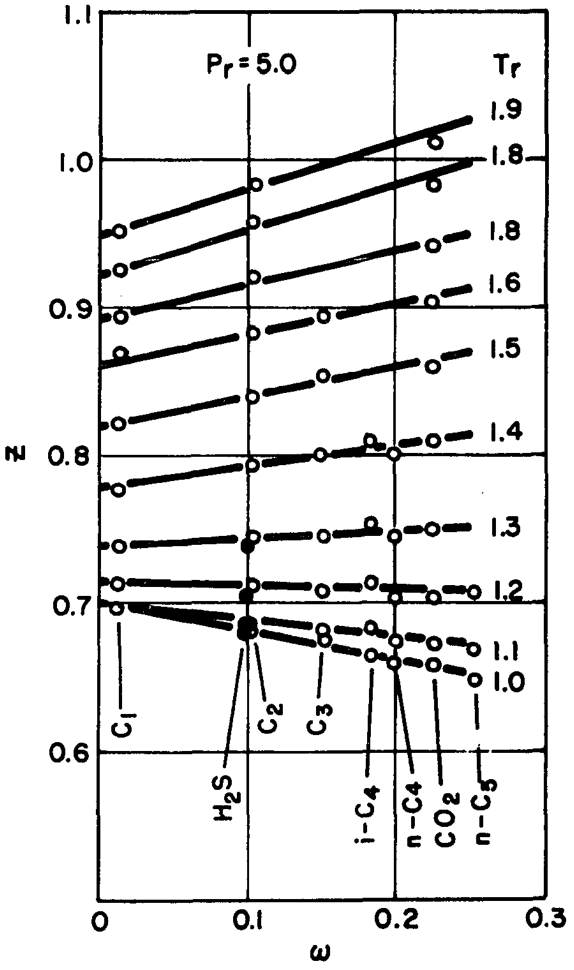

FIGURE 9

THE COMPRESSIBILITY FACTOR AS A FUNCTION OF ACENTRIC FACTOR AT $P_r = 5.0$ AND THE VALUES OF T_r INDICATED

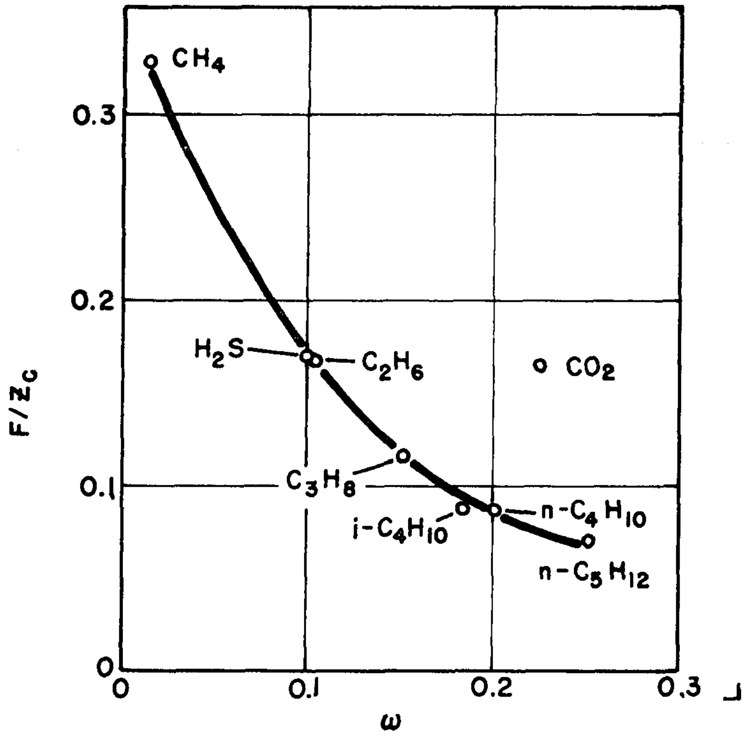

FIGURE 10

ACENTRIC FACTOR AS A FUNCTION OF F/Z_c

scope of this investigation would be required to substantiate this observation. The exact functional relationship between F and Z_c should be known in future work.

The excellent correlation found in Figures 6 through 10 was encouraging, for it confirmed that the acentric factor could be related to the statistical parameters. More important, it offered a real clue to the relative advantage of adding this as the third parameter in determination of the compressibility factor Z. Of the many approaches investigated in the preliminary work, all of which are not reported here, this was the only one which offered any practical advantage over the methods now used. Because of its inherent advantage, it was found appropriate to extend Pitzer's original tables and plot the results in convenient figures. The method of extension of these tables is presented in the following chapter.

CHAPTER V

EXTENSION OF THE COMPRESSIBILITY FACTOR TABLES OF PITZER, ET AL

The modified theorem of corresponding states as proposed by Pitzer and coworkers (68) has been presented in Chapter II. They have shown that the volumetric properties of pure, nonsimple fluids of nonpolar (or slightly polar) characteristics can be correlated with relatively high accuracy by introducing a third parameter (acentric factor ω). The theory requires that any group of substances with equal values of the acentric factor should conform among themselves to the principle of corresponding states. The new compressibility factor tables have an accuracy of 0.5% over most of the investigated region with a maximum deviation of about 2%. These tables, however, are limited to the region of $T_r = 0.8$ to 4.0, and P_r up to 9.0. Although this range covers the area of greatest practical utility, data beyond $P_r = 9.0$ are often required in engineering analysis to meet the demand for high pressure work. Thus, it was found appropriate to extend Pitzer's original tables even though some sacrifice in the good accuracy of the original tables resulted.

In extending the tables an approach similar to that used by the original authors was taken. The experimental compressibility factors of a number of pure substances, namely methane, ethane, propane, isobutane, normal butane, normal pentane, carbon dioxide, and hydrogen sulfide were interpolated, and in some instances extrapolated to whole values of reduced temperatures $T_r = 1.0$ to 2.0, and pressures $P_r = 0$ to 14.0. The compressibility factor for each point in this region was plotted as a function of acentric factors of the different substances. These points were then fitted with the best straight lines for evaluating Z^o, the value of Z at $\omega = 0$, and Z^1, the slope of the straight line.

The values of Z^o and Z^1 for $P_r = 0$ to 9.0, and $T_r = 1.0$ to 2.0 were found to be in good agreement with those reported by the original authors. The values of Z^o beyond this region up to $P_r = 14.0$ fell in line with the previously established range. This was evidenced by plotting on a large graph the values of Z^o as a function of P_r for various T_r. A similar plot of Z^1 showed some disagreement with the original table. This discrepancy was probably a result of the fewer points available at higher pressures for precisely defining the slope of the straight line. Fortunately the values of Z^o were not affected by the scarcity of data. The acentric factor of methane is so close to zero that regardless of the slope, the value of Z^o remained within a reasonable range of accuracy. Since Z^1 in Equation (2-37) is a corrective term, the final result may still be reasonably accurate, especially for gases having small values of acentric factor.

The final values of Z^o and Z^1 in the extended region of $P_r = 10.0$ to 14.0, and $T_r = 1.0$ to 2.0 are listed in Tables C6 and C7 in the Appendix. The original compressibility tables were extrapolated to $P_r = 14.0$ at $T_r = 0.8, 0.85, 0.90, 0.95, 2.5, 3.0$, and 4.0. The extrapolation was facilitated by using the curves of $T_r = 1.0$ and 2.0 as guidelines. These extrapolated values are also listed in Tables C6 and C7. Thus, it was possible to extend Pitzer's tables to $P_r = 14.0$ over the full original temperature range. The data of his original tables, which can be found in Reference (68), are not reported here. Graphical representations of the extended tables are shown in Figures 11 and 12 for $T_r =$ 1.0 to 2.0, and up to $P_r = 14$. These charts would be useful for correlating compressibility factors of pure gases and their mixtures encountered in most industrial applications. If it is necessary to find compressibility factor in regions covering $P_r = 0$ to 14.0, and $1.0 > T_r \geqslant 0.8$ and $4.0 \geqslant T_r > 2.0$, the original tables in conjunction with the extended tables of this work may be used.

To estimate the accuracy of the extended region of Pitzer's tables, 85 predicted values of compressibility factors of several gases, which were used in extending the original charts, were compared with the experimental values. The root mean square deviations of the predicted values were computed to be about 1.2%. Errors are generally found to increase with increasing pressures. In a later study, 1096 compressibility factors of several mixtures were predicted by using the extended Pitzer's tables. Many of these data points were in the extended region. It has been observed that the errors encountered in this region are substantially the same as those of the original region. This substantiates further the reasonable accuracy of the extended region.

In all systems tested with these charts, it was found that the basic accuracy was definitely superior to that obtained with our existing charts. It is therefore recommended that Figures 11 and 12 be used

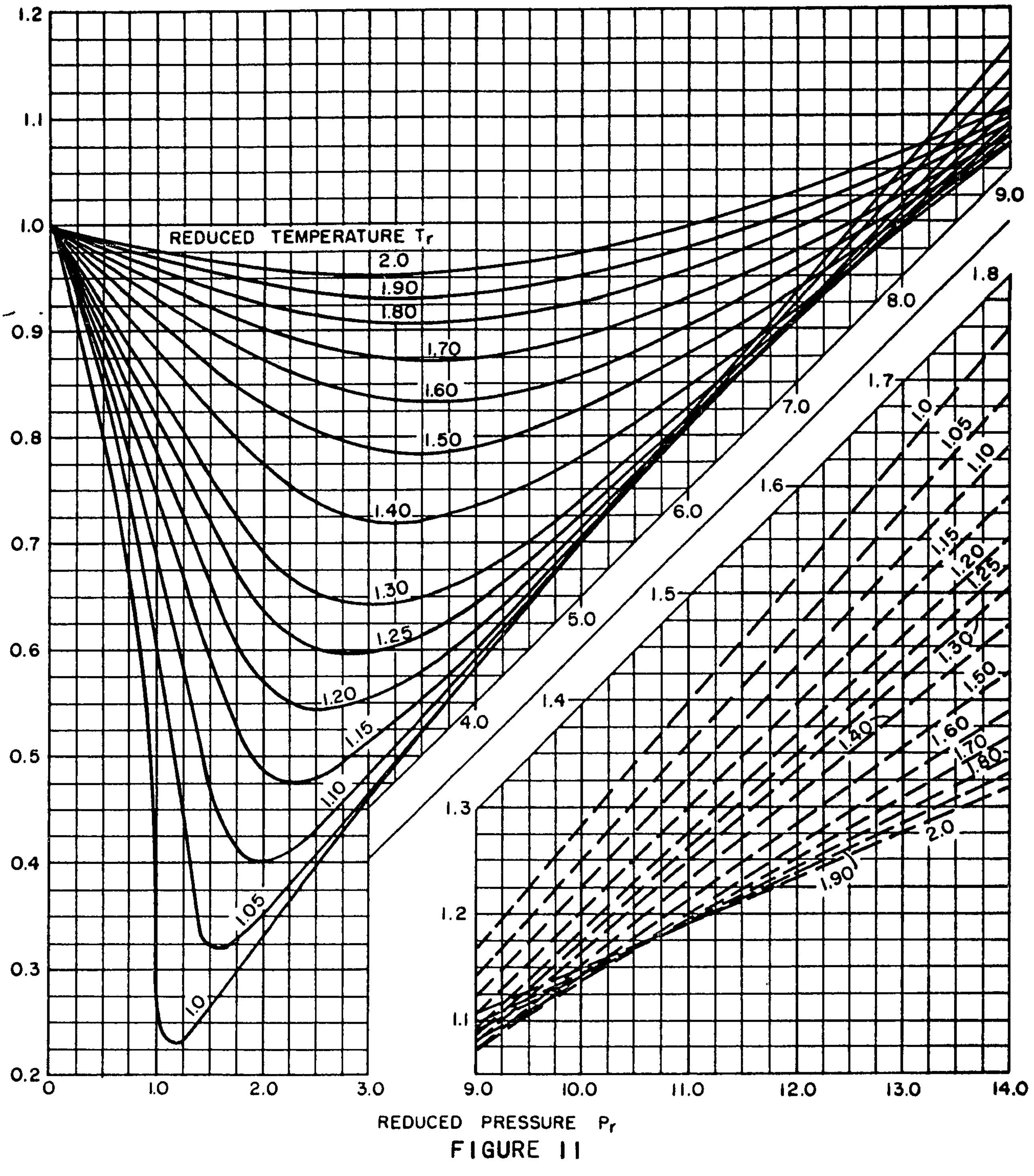

FIGURE 11

GENERALIZED COMPRESSIBILITY FACTORS Z^0
AT REDUCED TEMPERATURES AND PRESSURES

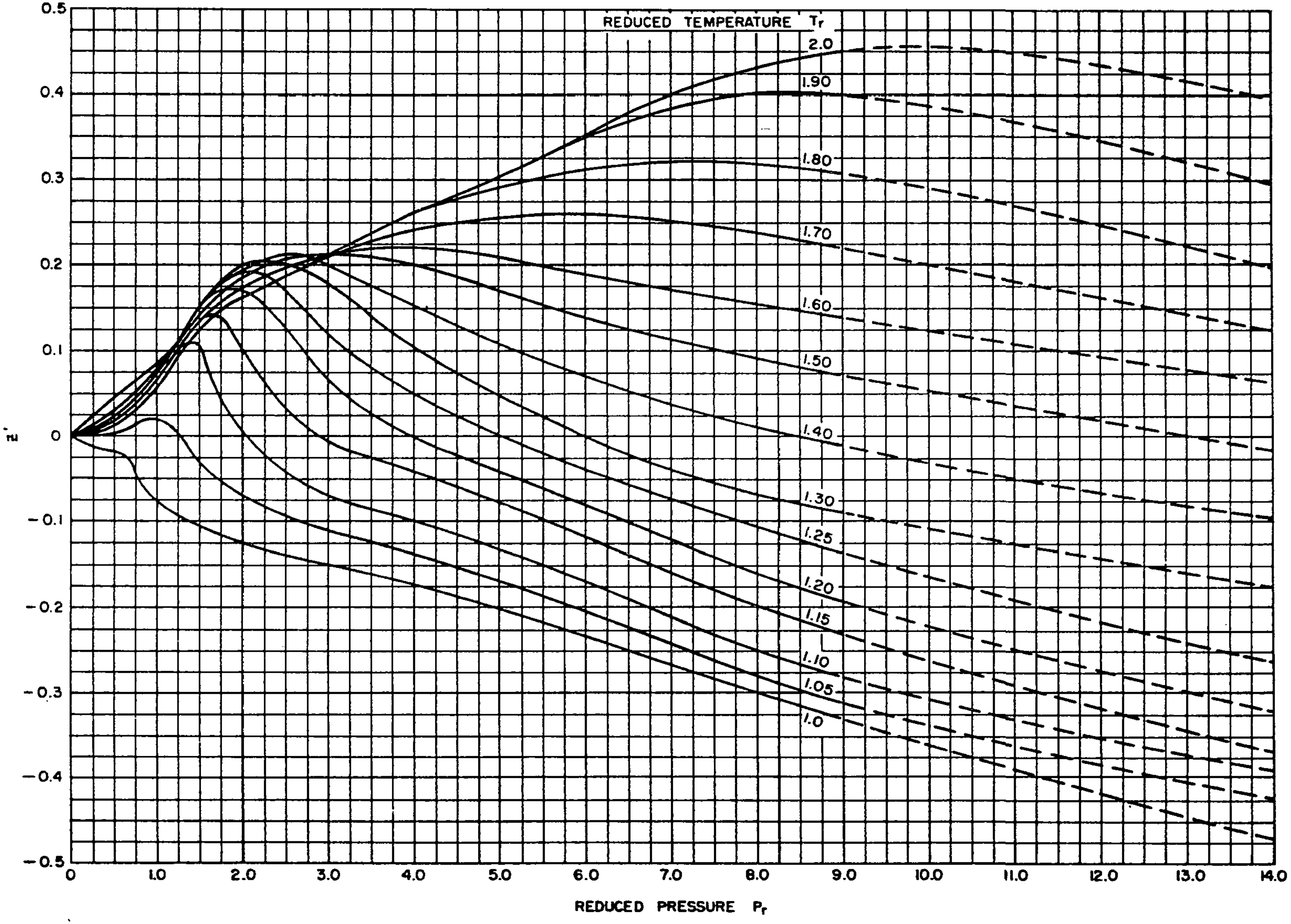

FIGURE 12

GENERALIZED COMPRESSIBILITY FACTORS Z'
AT REDUCED TEMPERATURES AND PRESSURES

as their replacement. These figures are used in the same manner as a regular Z-chart except that two steps are involved. Equations (2-36) through (2-39) specify the pertinent relationships. The values of Z^o and Z^1 are calculated from Figure 11 and Figure 12, respectively. The value of ω may be found from Equation (2-36). These three values are then substituted in Equation (2-37) to establish the value of Z for use in the conventional compressibility factor Equation (2-9).

CHAPTER VI

PROPOSED METHODS FOR PREDICTING VOLUMETRIC PROPERTIES OF MIXTURES

Any method of predicting the volumetric properties of mixtures must deal not only with the nonideality of pure components but also with the nonideality of mixing. Whereas the nonideality of pure gases can be treated successfully, the nonideality of mixing is not fully understood, and the various methods of predicting the properties of gaseous mixtures lack comparable validity. The most important factor which should be considered in dealing with the nonideal mixing of substances of diversified characteristics, is the nature of interactions of the dissimilar molecules in the system. Unlike Kay (43), recently Leland (47), Stewart (86), and Prausnitz (70) have considered interactions between dissimilar molecules in extending the theorem of corresponding states to mixtures. An improved approach similar to that of the latter authors has been taken in this study. Leland and Stewart used the critical compressibility factor for characterizing various substances. The acentric factor will be chosen as a characterization parameter in the present work. So far as this parameter is concerned, this method is the same as that of Prausnitz. The choice of the acentric factor is justified by the fact that it is a measure of the deviation of a substance from simple-fluid behavior. On the otherhand, critical compressibility factor is more empirical in nature for characterization purpose than the acentric factor.

In using the modified corresponding theorem of Pitzer, et al in the present study, several combination rules have been proposed to predict the pseudocritical properties, P_c' and T_c', of mixtures. Due to the complexity of the problem of finding the pseudocriticals, it is, however, believed that no single rule can be found for accurate prediction of compressibility factors of mixtures of diversified components and widely varying compositions. Even for the same mixture, the accuracy is dependent upon the physical state of the mixture, which in turn is a function of pressure and temperature. For example, it is apparent that most of the existing correlations show the largest deviation in the critical region. Mixtures are, therefore, conveniently classified in this work as consisting of only non-polar substances, and polar and non-polar components. Within this broad classification, a series of empirical rules of interactions between dissimilar molecules have been proposed in order to check their validity and learn more about the mechanism of nonideal mixing.

Pitzer's modified theorem of corresponding states is extended for mixtures as follows:

$$Z = f_r(P_r', T_r', \omega') \tag{6-1}$$

The previous equation may be also expressed in a manner following Pitzer:

$$Z = Z^0 + \omega' Z^1 \tag{6-2}$$

where $Z^o = f_r(P_r', T_r')$ (6-3)

$$Z^1 = f_r'(P_r', T_r') \qquad (6\text{-}4)$$

$$P_r' = \frac{P}{P_c'} \qquad (2\text{-}75)$$

$$T_r' = \frac{T}{T_c'} \qquad (2\text{-}76)$$

Under this scheme, the principal problem revolves around prediction of the pseudocritical properties P_c', T_c', and ω' for a mixture. After these pseudocritical properties are determined, pseudoreduced parameters can be computed from Equations (2-75 and (2-76). Pitzer's compressibility tables may be then used to find the compressibility from Equation (6-2). Various methods of predicting P_c', T_c', and ω', for mixtures of polar substances, and those containing polar and non-polar components are presented in the following sections.

A. Mixtures Containing Non-Polar Components

In predicting the pseudocriticals of gaseous mixtures containing non-polar components, the rules of Kay, Leland, and Stewart will be modified to adapt them to the proposed acentric factor correlation. A new method is also proposed in which the interactions of unlike molecules will be empirically treated.

1. Method 1: Modification of Kay's Rule

The simple molal average concept which has been suggested by Kay to predict P_c' and T_c' may be also extended to the pseudocritical acentric factor. The modified Kay's rule is then given by:

$$P_c' = \sum_{i=1}^{n} x_i (P_c)_i \tag{2-78}$$

$$T_c' = \sum_{i=1}^{n} x_i (T_c)_i \tag{2-79}$$

$$\omega' = \sum_{i=1}^{n} x_i \omega_i \tag{2-83}$$

Although Kay's combination rule is very simple, it is important to note that any error in evaluating one of the parameters may be compensated by errors involved in the others, so that the final result may be still reasonable.

2. Method 2: Empirical Statistical Mechanical Approach

This method, although empirical in nature, is based upon the nature of the interactions between unlike molecules in the system. The pseudocritical parameter, T_c' may be given by the empirical relationship:

$$T_c' = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j (T_c)_{ij} \tag{6-5}$$

whereas $(T_c)_{ij}$ for unlike molecules is given by the relationship suggested by Guggenheim and McGlasham:

$$(T_c)_{ij} = \left[(T_c)_{ii} \; (T_c)_{jj} \right]^{\frac{1}{2}} \tag{2-88}$$

Combining Equations (6-5) and (2-88), the expression for T_c' can be written as

$$T_c' = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left[(T_c)_{ii} \; (T_c)_{jj} \right]^{\frac{1}{2}} \tag{6-6}$$

The pseudocritical property $\underline{V}_c'$ may be given by a similar expression as represented by Equation (6-5):

$$\underline{V}_c' = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j (\underline{V}_c)_{ij} \tag{6-7}$$

$(\underline{V}_c)_{ij}$ for unlike molecules is given by the relationship also suggested by Guggenheim and McGlasham:

$$(\underline{V}_c)_{ij} = \left[\tfrac{1}{2}(\underline{V}_c)_{ii}^{1/3} + \tfrac{1}{2}(\underline{V}_c)_{jj}^{1/3} \right]^3 \tag{2-87}$$

In terms of critical properties of pure components, Equations (6-7) and (2-87) may be combined as follows:

$$\underline{V}_c' = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left[\tfrac{1}{2}\left(\frac{RZ_c T_c}{P_c} \right)_{ii}^{1/3} + \tfrac{1}{2}\left(\frac{RZ_c T_c}{P_c} \right)_{jj}^{1/3} \right]^3 \tag{6-8}$$

Since the value of Z_c does not vary much with simple components, the following mole average relationship for Z_c' may be reasonable:

$$Z_c' = \sum_{i\;1}^{n} x_i (Z_c)_i \tag{2-93}$$

Finally, knowing T_c', $\underline{V}_c'$ and Z_c' the pseudocritical property P_c' may be written as follows:

$$P_c' = \frac{RZ_c'T_c'}{\underline{V}_c'} \tag{6-9}$$

$$\text{or:}\quad P_c' = \frac{T_c' \sum_{i=1}^{n} x_i (Z_c)_i}{\sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left[\frac{1}{2}\left(\frac{Z_c T_c}{P_c}\right)_{ii}^{1/3} + \frac{1}{2}\left(\frac{Z_c T_c}{P_c}\right)_{jj}^{1/3} \right]^3} \tag{6-10}$$

The third pseudocritical parameter, ω' is computed by using Equation (2-83). This relationship is expected to give reasonable results since the acentric-factor correction for simple systems is relatively small.

3. Method 3: Based Upon Virial Approach of Stewart, Burkhardt, and Voo

As mentioned in Chapter II, Stewart, Burkhardt, and Voo recommended the following mixing rules for predicting T_c' and P_c':

$$J = \frac{T_c'}{P_c'} = 1/3 \sum_{i=1}^{n} x_i \left(\frac{T_c}{P_c}\right)_i + 2/3 \left[\sum_{i=1}^{n} x_i \left(\frac{T_c}{P_c}\right)_i^{\frac{1}{2}} \right]^2 \tag{2-94}$$

$$K = \frac{T_c'}{\left(P_c'\right)^{\frac{1}{2}}} = \sum_{i=1}^{n} x_i \left(\frac{T_c}{P_c^{\frac{1}{2}}}\right)_i \tag{2-95}$$

therefore,

$$T_c' = \frac{K^2}{J} \tag{2-96}$$

$$P_c' = \frac{T_c'}{J} \tag{2-97}$$

The foregoing rules are usable in the proposed scheme in conjunction with Equation (2-83) relating ω' with the pure component parameters.

4. Method 4: Based Upon Statistical Mechanical Approach of Leland and Mueller

The method proposed by Leland and Mueller has been discussed in Chapter II. In applying this method to the form demanded by the proposed acentric-factor correlation, a slight change will be made in the expression for T_c'.

Consider the following relationships derived by Leland and Mueller (47) for calculating pseudocritical conditions for mixtures:

$$\epsilon' = \left[\frac{\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j (\epsilon^{\gamma}\sigma^3)_{ij}}{\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j (\epsilon^{\psi}\sigma^3)_{ij}}\right]^{\frac{1}{\gamma-\psi}} \tag{6-11}$$

$$(\sigma')^3 = \left[\frac{\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j (\epsilon^{\psi}\sigma^3)_{ij}}{\left\{\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j (\epsilon^{\gamma}\sigma^3)_{ij}\right\}^{\psi/\gamma}}\right]^{\frac{\gamma}{\gamma-\psi}} \tag{6-12}$$

where ϵ, σ = parameters in the intermolecular potential function

Υ, Ψ = exponents in virial expansion

The previous equations were derived from strictly classical considerations and do not depend on any particular intermolecular potential as long as it satisfies the general expression of any two-parameter intermolecular potential function:

$$\varphi(r) = \epsilon\left[f\left(\frac{\sigma}{r}\right)\right] \tag{6-13}$$

The value of Ψ was taken as zero by Leland and Mueller and Υ was empirically correlated as given by Equation (2-91).

For determining pseudocriticals the following relations were used:

$$\epsilon \propto T_c \tag{6-14}$$

$$\sigma \propto V_c \propto \left(\frac{Z_c T_c}{P_c}\right) \tag{6-15}$$

The terms in the summations in Equations (6-11) and (6-12), when $i \neq j$, were based on approximations to the interaction constants between unlike molecules:

$$\left(\epsilon^{\Upsilon}\sigma^{3}\right)_{ij} = \left[\left(\epsilon^{\Upsilon}\sigma^{3}\right)_{ii}\left(\epsilon^{\Upsilon}\sigma^{3}\right)_{jj}\right]^{\frac{1}{2}} \tag{6-16}$$

$$(\sigma)^{3}_{ij} = \left[\tfrac{1}{2}\left(\sigma^{3}_{ii}\right)^{1/3} + \tfrac{1}{2}\left(\sigma^{3}_{jj}\right)^{1/3}\right]^{3} \tag{6-17}$$

In the present solution the following expression will be used in place of Equation (6-16):

$$(\epsilon)_{ij} = (\epsilon_i \epsilon_j)^{\frac{1}{2}} \qquad (2\text{-}68)$$

If the pseudocritical compressibility factor of a mixture is defined by Equation (2-93), and Equations (6-14), (6-15), (6-17), and (2-68) are substituted in Equations (6-11) and (6-12), the resulting equations are:

$$T_c' = \left[\frac{\sum_{i=1}^{n} \sum_{i=1}^{n} x_i x_j \left[(T_c)_{ii} \, (T_c)_{jj} \right]^{\gamma/2}}{\sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left[\frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_{ii}^{1/3} + \frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_{jj}^{1/3} \right]^3} \right.$$

$$\left. \frac{\left[\frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_{ii}^{1/3} + \frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_{jj}^{1/3} \right]^3}{} \right]^{1/\gamma} \qquad (6\text{-}18)$$

$$P_c' = \frac{T_c' \sum_{i=1}^{n} x_i (Z_c)_i}{\sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left[\frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_{ii}^{1/3} + \frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_{jj}^{1/3} \right]^3} \qquad (6\text{-}19)$$

These mixing rules are applicable along with acentric-factor combination formula given by Equation (2-83) to the proposed correlation scheme.

B. Mixtures Containing Polar and Non-Polar Components

The primary concern in predicting the volumetric properties of gaseous mixtures containing polar and non-polar substances has been to account for the interactions between polar and non-polar molecules. Methods 2 and 4 in the preceding section may be modified to meet this requirement.

The potential function which describes the intermolecular forces between one non-polar but polarizable molecule (i) and one polar molecule (j) may be written in the two-parameter form:

$$\left[\varphi(r)\right]_{ij} = \epsilon_{ij}\left[f'\left(\frac{\sigma_{ij}}{r}\right)\right] \tag{6-20}$$

where $\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj})\left(1 + \xi_{ij}\right)^{-1/6}$ (-269)

$$\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{\frac{1}{2}}\left(1 + \xi_{ij}\right)^2 \tag{2-70}$$

$$\xi_{ij} = 1/4\,\alpha_i^*\,(\mu_j^*)^2\left(\frac{\epsilon_{jj}}{\epsilon_{ii}}\right)^{\frac{1}{2}} \tag{2-71}$$

in which α_i^* and μ_j^* are given by Equations (2-72) and (2-22), respectively.

Equations (2-69) through (2-71) may now be expressed in terms of the criticals T_c, P_c, $\underline{V}_c$, and Z_c as follows:

$$(T_c')_{ij} = \left[(T_c)_{ii}\,(T_c)_{jj}\right]^{\frac{1}{2}}\left(1 + \xi_{ij}\right)^2 \tag{6-21}$$

$$(\underline{V}_c')_{ij} = \left[\frac{1}{2}\left(\frac{RZ_cT_c}{T_c}\right)_{ii}^{1/3} + \frac{1}{2}\left(\frac{RZ_cT_c}{P_c}\right)_{jj}^{1/3}\right]^3\left(1 + \xi_{ij}\right)^{-\frac{1}{2}} \tag{6-22}$$

with $$\xi_{ij} = 1/4\,\alpha_i^*\left(\mu_j^*\right)^2\left[\frac{(T_c)_{jj}}{(T_c)_{ii}}\right]^{\frac{1}{2}} \tag{6-23}$$

These relationships, when incorporated in method 2, yield the following expressions for T_c' and P_c':

$$T_c' = \sum_{i=1}^{n}\sum_{j=1}^{n} x_ix_j\left[(T_c)_{ii}\,(T_c)_{jj}\right]^{\frac{1}{2}}\left(1 + \xi_{ij}\right)^2 \tag{6-24}$$

$$P_c' = \frac{T_c'\sum_{i=1}^{n} x_i(Z_c)_i}{\sum_{i=1}^{n}\sum_{j=1}^{n} x_ix_j\left[\frac{1}{2}\left(\frac{Z_cT_c}{P_c}\right)_{ii}^{1/3} + \frac{1}{2}\left(\frac{Z_cT_c}{P_c}\right)_{jj}^{1/3}\right]_{jj}^3\left(1 + \xi_{ij}\right)^{-\frac{1}{2}}} \tag{6-25}$$

The third pseudocritical parameter ω' may be computed by Equation (2-83). In the limiting case, where the dipole moment of molecule j vanishes, $\xi_{ij} = 0$ and Equations (6-24) and (6-25) reduce to Equations (6-6) and (6-10).

For mixtures containing one polar compound three cases are encountered in the operation of the double summation term in Equations (6-24) and (6-25). In the case where $i = j$ the coefficient refers to the interactions between the molecules of the same species. The coefficient is then evaluated from the properties of the pure component with $\xi = 0$. In the case where i and j are dissimilar non-polar species, the coefficient reflects the interactions between two different non-polar molecules. In either instance ξ is still zero and the coefficient is computed by using the parameters of the two different species. Finally, there is the case where $i \neq j$ and i is a non-polar and j is a polar component. In this instance the coefficient encounters the interactions between non-polar and polar molecules. The quantity ξ is greater than zero, and is calculated from the properties of the two species.

The reduced dipole moment, μ^* of the polar molecule and polarizability α^* of the non-polar molecule may be expressed conveniently in terms of a particular unit if the force constants are expressed empirically in terms of the critical constants, as follows:

$$\epsilon = \frac{kT_c}{1.25} \tag{6-26}$$

$$\sigma^3 = \frac{V_c}{\pi \bar{N}} = \frac{kZ_cT_c}{\pi P_c} \tag{6-27}$$

Substitution of these relationships in the expressions for μ^* and α^* yield the following equations:

$$\mu^* = 3.7705 \times 10^{18} \left(\frac{\mu}{T_c}\right) \left(\frac{P_c}{Z_c}\right)^{\frac{1}{2}} \tag{6-28}$$

where μ is in e.s.u.

P_c is in psi

T_c is in $^{\circ}K$

and $$\alpha^{*} = 2.826 \times 10^{-21} \left(\frac{\alpha P_c}{Z_c T_c} \right) \qquad (6\text{-}29)$$

where α is in cm^3/molecule

P_c is in psi

T_c is in $^{\circ}R$

2. Method 6: Modification of Method 4

The concepts discussed in Method 5 are also applicable in modifying Method 4 to account for the presence of polar molecules in association with non-polar molecules. The following modified relationships for pseudocriticals may be obtained in this treatment:

$$T_c' \doteq \left[\frac{\sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left[(T_c)_{ii} (T_c)_{jj} \right]^{\gamma/2} \left[\frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_{ii}^{1/3} \right.}{\sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left[\frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_{ii}^{1/3} + \frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_{jj}^{1/3} \right]^3} \right.$$

$$\left. \frac{\left. + \frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_{jj}^{1/3} \right]^3 \left(1 + \xi_{ij} \right)^{\frac{4\gamma - 1}{2}}}{\left(1 + \xi_{ij} \right)^{-\frac{1}{2}}} \right]^{1/\gamma} \qquad (6\text{-}30)$$

$$P_c' = \frac{T_c' \sum_{i=1}^{n} x_i (Z_c)_i}{\sum_{i=1}^{n} \sum_{i=j}^{n} x_i x_j \left[\frac{1}{2}\left(\frac{Z_c T_c}{P_c}\right)_{ii}^{1/3} + \frac{1}{2}\left(\frac{Z_c T_c}{P_c}\right)_{jj}^{1/3} \right]^3}$$

$$\overline{\left(1 + \xi_{ij}\right)^{-\frac{1}{2}}} \qquad (6\text{-}31)$$

The third pseudocritical parameter ω' is, as usual, given by Equation (2-83).

3. Method 7: Another Modification of Method 2

It has been noted by Blanks and Prausnitz (10) that the modified force constants represented by Equations (2-69) and (2-70), and the slightly different form in Equation (2-71), tend to underestimate the second virial coefficient, $B(T)_{ij}$, of the polar-non-polar mixtures. Since the virial coefficient and compressibility factor are closely related, similar results may be expected in predicting compressibility factors. In the present study the expression $(1 + \xi_{ij})$ in the Equations (2-69) and (2-70) is changed to $(1 - \xi_{ij})$, while the expression for the third parameter is left unaltered. The net result of this is to decrease P_c' and T_c', which in turn are to increase P_r' and T_r'. Thus the predicted compressibility factors would be higher than those given by Method 5.

4. Method 8: Another Modification of Method 4

By the same token, as discussed for Method 7, the expression $\left(1 + \xi_{ij}\right)$ in Equations (6-30) and (6-31) is changed to $\left(1 - \xi_{ij}\right)$, while keeping the equation for ω' intact.

The proposed methods may be worked out with little effort with the help of a desk calculator. A sample calculation procedure for all 8 combination rules has been shown in Table D1 in the Appendix. As a part of preliminary investigations, these methods were used to find compressibility factors of several gaseous mixtures at selected pressures and temperatures. The predicted values were compared with experimental data available from the literature. These results were so encouraging that a large amount of additional data were analyzed using an IBM 7090 computer. Before discussing the results of this study, experimental methods and results of the ternary system composed of methane, ethane, and hydrogen sulfide will be presented in the next two chapters.

CHAPTER VII

EXPERIMENTAL METHOD

The experimental work of this investigation consisted in measuring the compressibility factors of five selected gaseous mixtures of methane, ethane, and hydrogen sulfide. The equipment used was a modified Bean unit. The reliability of the equipment and the experimental procedure was determined by obtaining data on pure methane and comparing the measured values of compressibility factors with those published in the literature (79). The presentation of the experimental method has been made in six sections of this chapter: A. Gases Used, B. Experimental Equipment, C. Calibration of Equipment, D. Experimental Procedure, E. Method of Calculating Compressibility Factors from the Measured Data, and F. Accuracy of the Experimental Method.

A. Gases Used

The gases used were pure methane, ethane, and hydrogen sulfide. The methane was Phillips Petroleum Company's pure grade with a nominal quoted purity of 99 mole per cent. The ethane, obtained from the same source, was of research grade with a nominal quoted purity of 99.9 mole per cent. The technical grade hydrogen sulfide was obtained from the Matheson Company. It had a minimum purity of 98.5 per cent. The most probable impurities in methane, ethane, and hydrogen sulfide were ethane, methane, and carbon dioxide, respectively.

The mixtures were prepared to the desired specification in the high pressure cell used for the P-V-T study. Detailed discussions of the mixing procedure will be made in Section D.

B. Experimental Equipment

The equipment used in this work consisted of a Bean type compressibility apparatus, 250 cc Ruska mercury pump, 500 cc high pressure P-V-T cell, and other necessary accessories. Figure 13 is a photograph of the experimental setup, while Figure 14 shows the flow diagram.

1. Bean Unit

The Bean apparatus used varies in detail but not in principle from that described by Dr. Bean (2). Since this unit was originally designed for a maximum pressure of 1,000 psig, certain modifications were made in order to adapt it to the higher pressure conditions of this investigation. The constant volume cell and mercury-oil seal assembly of the original apparatus were eliminated. This was used only as an expansion unit for measuring the volume of the gas expanded from the high pressure cell after the P-V-T measurement of gas sample was obtained.

In the modified form the Bean unit consisted of two glass burettes (1) and (2), needle valve (3) for admitting gas to (1), needle valve (4) for admitting pressure to (2), needle valve (5) for atmospheric relief for (2), manometer tube with scale (6) and constant temperature bath (7). The burette (1) was connected to a 3-way glass cock

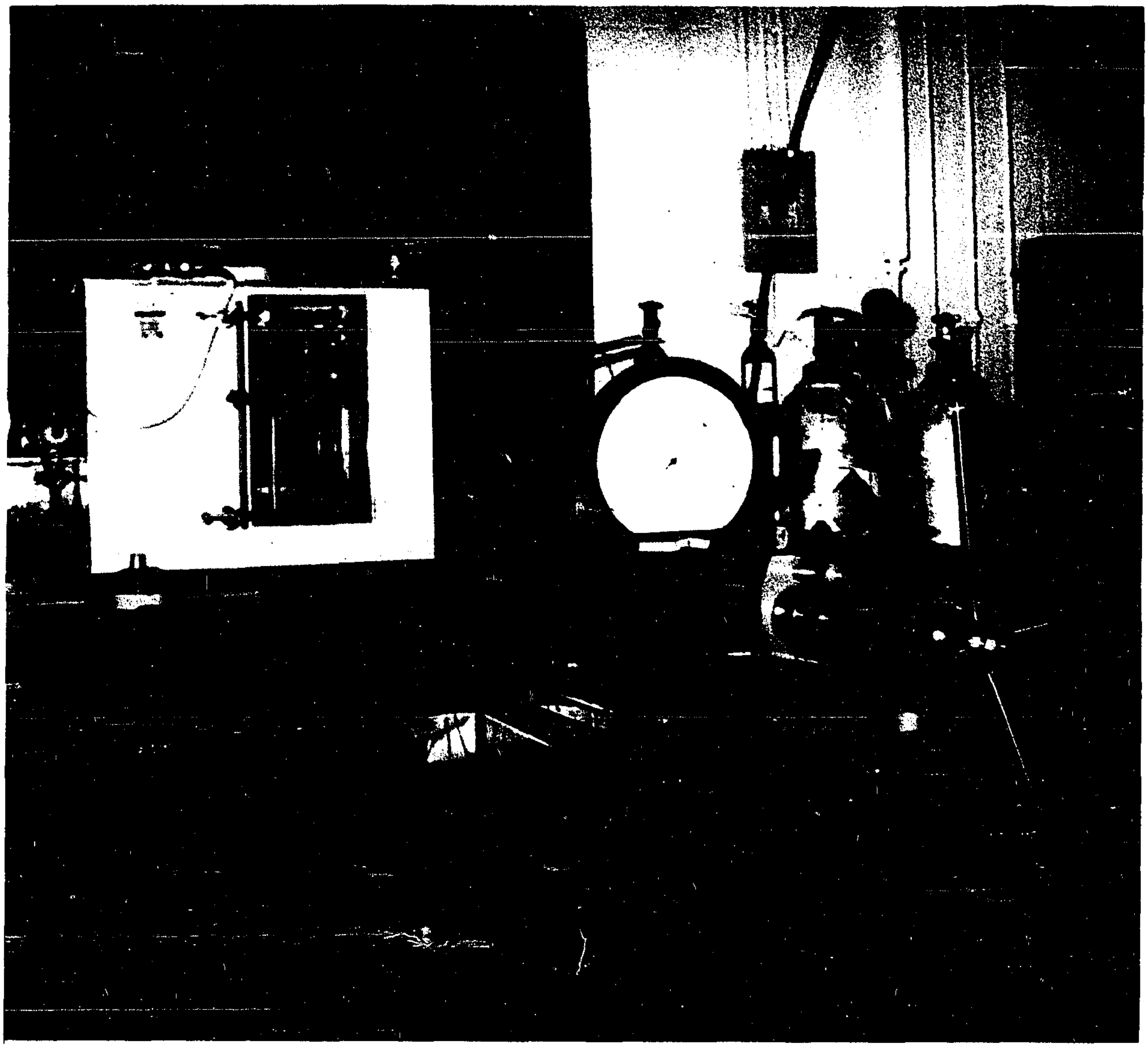

FIGURE 13

PHOTOGRAPH OF EXPERIMENTAL SETUP

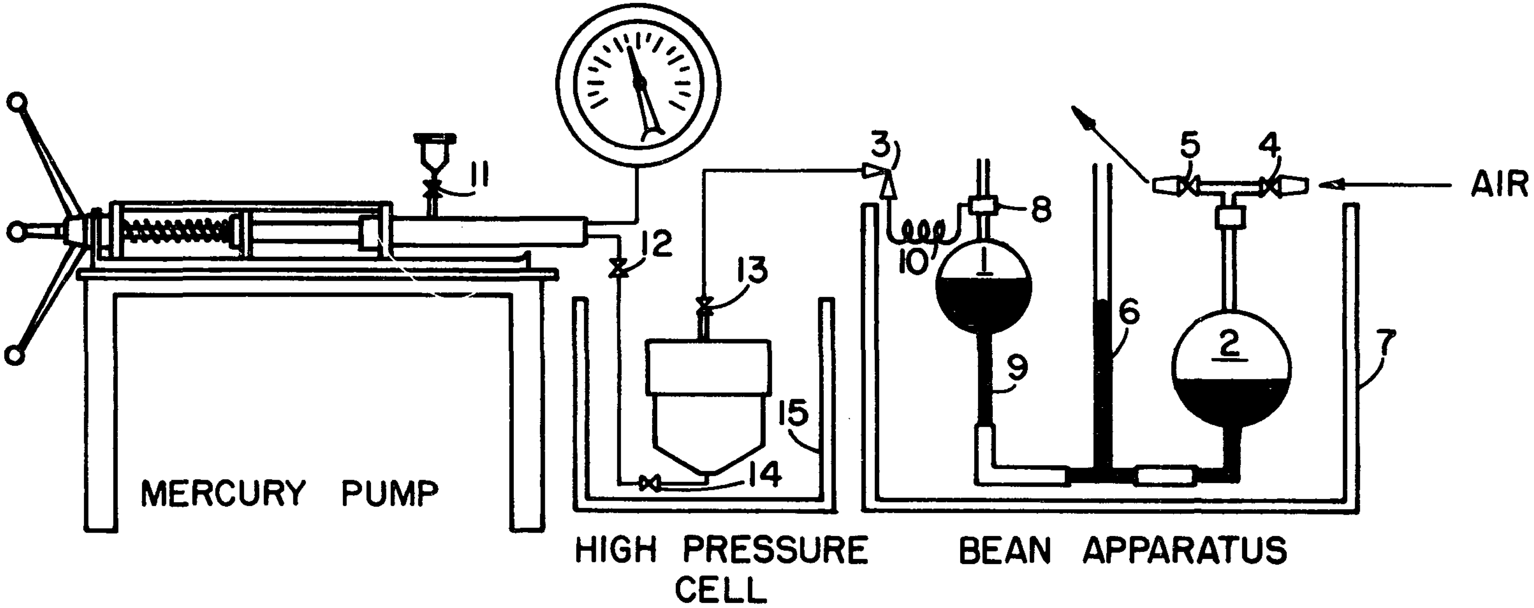

FIGURE 14

FLOW DIAGRAM OF EXPERIMENTAL EQUIPMENT

(8) at the top and had an etched line (9) about its lower neck. The constant temperature bath consisted of a stainless steel lined, glass wool insulated, metal shielded tank with large windows front and rear to enable observation of the manometer and burette (1). An electric stirrer and thermostatically controlled electric heaters (750 watt and 200 watt) were provided for maintaining constant temperature. The large heater was used only to bring the bath up to the controlled temperature after which it was turned off. The needle valve (3) was connected to the high pressure cell with 0.0595 inch I. D. stainless steel tubing before gas was expanded from the high pressure cell into the burette (1). In order to bring the expanded gas from the cell quickly up to the temperature of the bath, four feet of stainless steel tubing (10) were coiled and placed between the valve (3) and a short piece of rubber tubing which in turn was connected to the 3-way glass cock. All other connections necessary were of rubber tubing.

2. Ruska Mercury Pump

The Ruska mercury pump was designed for a maximum pressure of 10,000 psig. The maximum working displacement of this pump was 250 cc and the smallest division which could be read was 0.01 cc. Mercury from a cup could be introduced into the pump through valve (11).

This pump was connected to a 10,000 psig Heise Gauge with scale divisions of 10 psi. It was also connected to the high pressure cell through valve (12).

3. High Pressure Cell

The high pressure cell made by Ruska Instrument Corporation was a standard P-V-T cell with a capacity of 500 cc. Two high pressure stainless steel valves (13 and 14) served as inlet and outlet. A paddle suspended inside stirred the fluid while it was being rocked. The cell was placed on a stand in a constant temperature water bath (15). A circulating pump and thermostatically controlled electric heaters were provided for maintaining constant temperature.

4. Accessories

In addition to the above equipment, a dead weight tester provided with a diaphragm differential pressure indicator, mercury in glass thermometers, Cenco-Hyvac 2 vacuum pump, barometer, balances, graduated cylinders, and other accessories were used in course of the experimental work.

C. Calibration of Equipment

Accurate calibrations were needed for the following items: 1) the volume of burette (1), 2) the volume of high pressure cell, 3) the expansibility of the high pressure cell, 4) the calibration of the Heise Gauge, and 5) thermometers. Also needed was the volume of the lines connecting the mercury pump to the high pressure cell, and that joining the latter to burette (1). The distance from the center of the cell to the center of the Heise Gauge was measured to determine the difference in pressure between the cell and the gauge due to the change in elevation.

1. Burette (1)

The burette was cleaned with dilute hydrocholoric acid, carbon tetrachloride and finally, distilled water. It was then dried and filled with mercury from the stopcock to the etched mark. The mercury was displaced and weighed. The volume was found by dividing the weight of the mercury by its density. The measurement was also checked by filling the burette with weighed distilled water and then dividing the weight of water by its density. Several determinations were made at room temperature as well as at 100 °F. The burette was placed in the constant temperature bath in the latter case. The different determinations agreed within a fraction of a cubic centimeter. No change in volume of burette from room temperature to 100 °F. could be detected. The average value of the different measurements was 996.07 cc.

2. High Pressure Cell

The high pressure cell was cleaned with dilute hydrochloric acid, carbon tetracholoride, and acetone in sequence. It was cleaned until clear effluent was obtained, after which it was air-dried. It was then evacuated and filled with mercury to determine its volume in the same manner as the burette. The volume was found to be 501.50 cc.

The volumes of the line connecting the mercury pump to the cell and that joining the latter to the burette were calculated from their dimensions. They were found to be 2.37 and 4.83 cc, respectively.

3. Expansibility of the High Pressure Cell

The combined effect of isothermal expansion of the high pressure cell and compression of mercury contained in the cell was experimentally determined at different temperatures. Table E1 in the Appendix shows the results of these determinations. These values, at the same pressure, showed some irregularity with temperature. Thus, temperature-average values were calculated. Figure E1 in the Appendix shows the average correction as a function of pressure. The data for the compressibility of mercury were obtained from the literature (54) and presented in Table E2 in the Appendix. The correction for cell expansibility with increasing pressure could then be obtained by calculating the difference between the total correction and the compressibility of mercury.

4. Heise Gauge

The Heise Gauge was calibrated using a dead weight tester provided with a diaphragm differential pressure indicator. After the dial of the gauge was adjusted, no difference in gauge pressure readings from those of the tester could be observed. It should be noted, however, that the gauge pressure readings were considered accurate only within 10 psi, which was the smallest reading on the gauge. The readings were taken at 100, 200, 500, 1,000, 1,500, and 2,000 psig, and then in increments of 1,000 to 8,000 psig. The procedure was repeated while lowering the pressure in similar steps. No calibration chart was required.

After the equipment was assembled, the distance from the center of the cell to the center of the Heise Gauge was measured. The pressure difference was found to be 12 psi.

5. Thermometers

The thermometers used were made by Schaar and Company, Chicago, Illinois. The smallest divisions of these thermometers were 0.1 °F. The freezing point of the thermometers were checked with melting ice prepared from distilled water, and found to be accurate within 0.1 °F. Since this difference in terms of absolute values of the experimental temperatures is insignificant, no corrections were made for observed experimental temperature.

The data on the calibration of the experimental system, except the compressibility of the high pressure cell, are summarized in Table E4 in the Appendix.

D. Experimental Procedure

After the apparatus was assembled, it was necessary to make a few adjustments and take precautionary measures before the equipment was ready for use. The burettes of the Bean unit were filled with mercury such that mercury was on the plane of the etched line of the burette (1) and the zero of the manometer tube, while the system was exposed to atmospheric pressure. The final adjustment involved lowering or raising the manometer tube and withdrawing or adding mercury to the system. Since all the experimental runs in Bean unit were conducted at approximately 100 °F., the adjustment of the mercury level as specified above was performed at 100 °F.

After the mercury pump was connected with the high pressure cell, this system was evacuated for several hours and then filled with mercury. All possible measures were taken to make this system completely leakproof. In a final test, the system was raised to a pressure of 8,000 psig and maintained at that condition for 24 hours as a positive proof that no leaks or air pockets were present in the system. In fact, the pressure slightly increased or decreased depending upon the room temperature during the test period.

1. P-V-T Measurement

Before the high pressure cell was charged with the gas sample, the cell was evacuated through valve (13). This valve was then closed and the cell was filled with mercury from the pump with valve (11) open. It should be noted that a level of mercury was always maintained in the mercury cup at the top of the pump. This was necessary to avoid any communication between atmospheric air and inside of the mercury pump while valve (11) was open.

The water bath containing the high pressure cell was brought to a constant predetermined temperature. Valves (11) and (12) were then closed. The pressure in the mercury pump was raised to a base pressure of 3,000 psig, and the pump reading corresponding to zero gas volume in the cell was noted. All subsequent volume measurements were made similarly at this base pressure, thus reducing any error due to pump play and substantially eliminating the expansion of the pump body and compressibility of mercury in the pump. In measuring the gas volume in the cell under pressure, the valve (12) was closed isolating the cell from the pump. The pressure in the pump was reduced to zero psig and then raised to the base pressure.

Before connecting the gas bottle to the cell, the line was purged with the sample gas. The valve (13) was then opened, admitting gas to the cell while withdrawing mercury with the pump. In case the charge was more than the capacity of the pump, the charging operation was carried out in two steps. When the pump capacity was first reached, the valve (12) was closed and a volume reading was taken at the base pressure. The mercury pump was brought to zero psig and valve (11) opened. The mercury was then withdrawn from the pump into the cup and finally into another container. Valve (11) was closed, and a volume reading at the base pressure was again taken. Thus, this reading became the new volume reading of the gas in the cell. The pressure in the pump was raised to that of the cell and valve (12) was opened. Further, gas was then admitted into the cell and the final volume measurement taken.

Sufficient time was allowed for the gas sample to reach equilibrium before the P-V-T measurements of the sample were taken. The gas was compressed from its initial pressure to about 1,000 psig and then in increments of 1,000 psig to 7,000 psig. In each step, volume measurements were taken as outlined previously. In the case of an initial sample of approximately 400 cc, it was necessary to introduce more mercury into the pump when the pressure in the cell was 2,000 psig. In such cases, a new volume reading of the gas in the cell had to be taken. Normally, 30 to 45 minutes were sufficient for attaining equilibrium conditions. When the maximum pressure of 7,000 psig was reached in the cell, the pressure was decreased using the same steps as before and P-V-T measurements were repeated. As previously mentioned, at the pressure of 2,000 psig, mercury had to be withdrawn from the system for further expansion of gas in cell. For each sample of gas, P-V-T data were obtained at nominal temperatures of 100, 130, and 160 °F. Barometric pressures were noted before and after each set of experiments at the indicated temperatures.

When desired P-V-T data were obtained for a particular sample, the gas, initially at approximately 1,000 psig, was expanded in several steps from the high pressure cell into the Bean apparatus. An approximate temperature of 100 °F. was maintained at both water baths. The cell was connected to the Bean unit and gas was allowed to reach the needle valve. The 3-way cock was turned to open burette (1) to the atmosphere while closing the tube to the needle valve. Air was then admitted at a pressure of about 10 psig to the burette (2), thus forcing mercury into the other burette. Just as the mercury reached the edge of the 3-way cock, air supply was stopped. Gas was then expanded into the burette (1) while releasing air from the system. Expansion was continued until the mercury was on the plane of the etched line and the zero of the manometer scale. It required usually some manipulation to obtain this condition. This was, however, not absolutely necessary as long as the pressure of the gas in the burette could be read by the manometer.

This cycle of expansion was repeated. When the pressure in the cell dropped to about 100 psig, it was divided by the average fall of pressure during the three or four immediately preceding cycles. If the quotient was very nearly a whole number, it was evident that this whole number of additional cycles, similar to those immediately preceding, would reduce the pressure in the cell so nearly to zero that it would be within the range of the manometer. No change from the previous rate of withdrawal of gas from the cell was required in such instances. Otherwise, the rate of withdrawal for the remaining cycles was increased or decreased sufficiently so that a whole number of cycles would leave the final residual pressure within the range of the manometer. Some adjustment of the pressure in the system at the last expansion run was also possible by varying the volume of gas in the cell with the help of the mercury pump. After the last filling of the burette, the high pressure cell and the burette were opened to each other. The pressure in the burette was then determined as before, and this was also the pressure of the gas finally remaining in the cell and the line connecting the cell to the burette. Barometric and temperature readings were taken before and after the expansion operation.

2. Preparation of Mixture

A mixture was prepared by introducing gases into the evacuated high pressure cell in the following sequence--hydrogen sulfide, ethane, and methane. The cell volume and temperature were held constant during this operation. The amount of each gas delivered into cell was determined by the predetermined mixing pressure at the end of each stage of mixing. A sample calculation of the predetermined mixing pressure for Mixture B is given in Table D2 in the Appendix. In making the calculation of mixing pressures, it was noted that the maximum delivery pressure of hydrogen sulfide was limited to 100 psig, the maximum final pressure of mixture was to be around 1,000 psig, and the maximum cell volume was about 500 cc. After the mixture was prepared, it was allowed to stand for two days. During this time, the cell was rocked occasionally so that the paddle inside the cell could stir the gases. At the end of this period, a sample of the mixture was collected in an evacuated sample bottle at essentially atmospheric pressure. The remaining mixture in the high pressure cell was used for the P-V-T measurement at the various pressures and temperatures, as outlined in the preceding section. Five mixtures were prepared and a volumetric determination made. The mixture samples were sent to the Continental Research Laboratory at Ponca City, Oklahoma, for analysis. Table F3 in the Appendix shows the results of these determinations.

E. Method of Calculating Compressibility Factors from the Measured Data

It is necessary that the experimental calculation is consistent with the procedure. The largest source of error was the gross volume of gas as measured by the mercury pump at the base pressure and room temperature. The measured volume of mercury withdrawn from or introduced into the cell had to be corrected for the condition of pressure and temperature in the cell by using the following formula (54):

$$\Delta V_1 = V_1 \left[\left(1 + \beta_1 P_1\right) \left(\frac{v_2}{v_1}\right) \left(1 - \beta_2 P_2\right) - 1 \right] \qquad (7\text{-}1)$$

where V_1 = volume of mercury withdrawn from or introduced into the cell and measured by the pump at the base pressure P_1 and room temperature T_1

P_2 = pressure in the cell at temperature T_2

β_1, β_1 = compressibility of mercury at T_1 and T_2, respectively

v_1, v_2 = volumes of mercury at T_1 and T_2, respectively, relative to volume at 60 °F. and 1 atmosphere

The expansion of the cell and the compression of mercury remaining in the cell introduced further errors in the measured volume of the gas. The following equations were used to correct these errors:

$$\Delta V_2 = (\beta_3 - \beta_2)\, V_{cell}\, P_2 \tag{7-2}$$

where β_3 = the combined correction factor for cell expansion and mercury compression as determined experimentally

V_{cell} = volume of cell and the line connecting cell to the mercury pump

$$\Delta V_3 = \beta_2 (V_{cell} - V_3) P_2 \tag{7-3}$$

where V_3 = volume of gas in the cell

Another source of error was the expansion of mercury remaining in the cell when the sample was heated from one experimental temperature to another. The effect of this was to reduce the gas volume. The following formula, neglecting the slight pressure change which occurred, was used to make this correction:

$$\Delta V_4 = \left(V_{cell} - V_3\right) \left(\frac{v_3}{v_2} - 1 \right) \tag{7-4}$$

where v_3, v_2 = are relative volumes of mercury at experimental temperatures T_3 and T_2, respectively

The amount of gas present in the cell was found by expanding the gas into burette (1) of the Bean apparatus as outlined in a previous section. For each expansion, the moles of gas were found from a knowledge of the volume of the burette, pressure as recorded by the manometer, temperature, and by the application of the ideal gas law. For the last run, the combined volumes of cell, burette, and the line connecting the cell to the burette were taken into account. Finally, the compressibility factor of gas at a pressure P and temperature T was found by using the following formula:

$$Z = \frac{PV}{n_g RT} \qquad (7\text{-}5)$$

where n_g = moles of gas as determined from the Bean unit

V = corrected volume of gas at a pressure P and temperature T

Table D3 in the Appendix shows a sample calculation of compressibility factor using the experimental data on a sample of pure methane.

F. Accuracy of the Experimental Method

To determine the reliability of the equipment and procedures used in this work, compressibility factor data were obtained for pure methane and compared with the published values. The data on four samples of methane at nominal temperatures of 100, 130, and 160 °F. and up to a maximum pressure of 7,026 psia are reported in Table F1 in the Appendix. Included in this table are also the values which were found by interpolation of the compressibility factors of methane published by Sage, et al (79).

Figure 15 shows the literature compressibility curves and the experimental points from Sample C at the various temperatures and pressures. A good agreement between the data of these two different sources can be observed. The consistency of the values of the present work is also apparent. It may be noted that the experimental data deviate comparatively more from the published values at higher pressures and temperatures. These observations are also generally true for the data from the other samples.

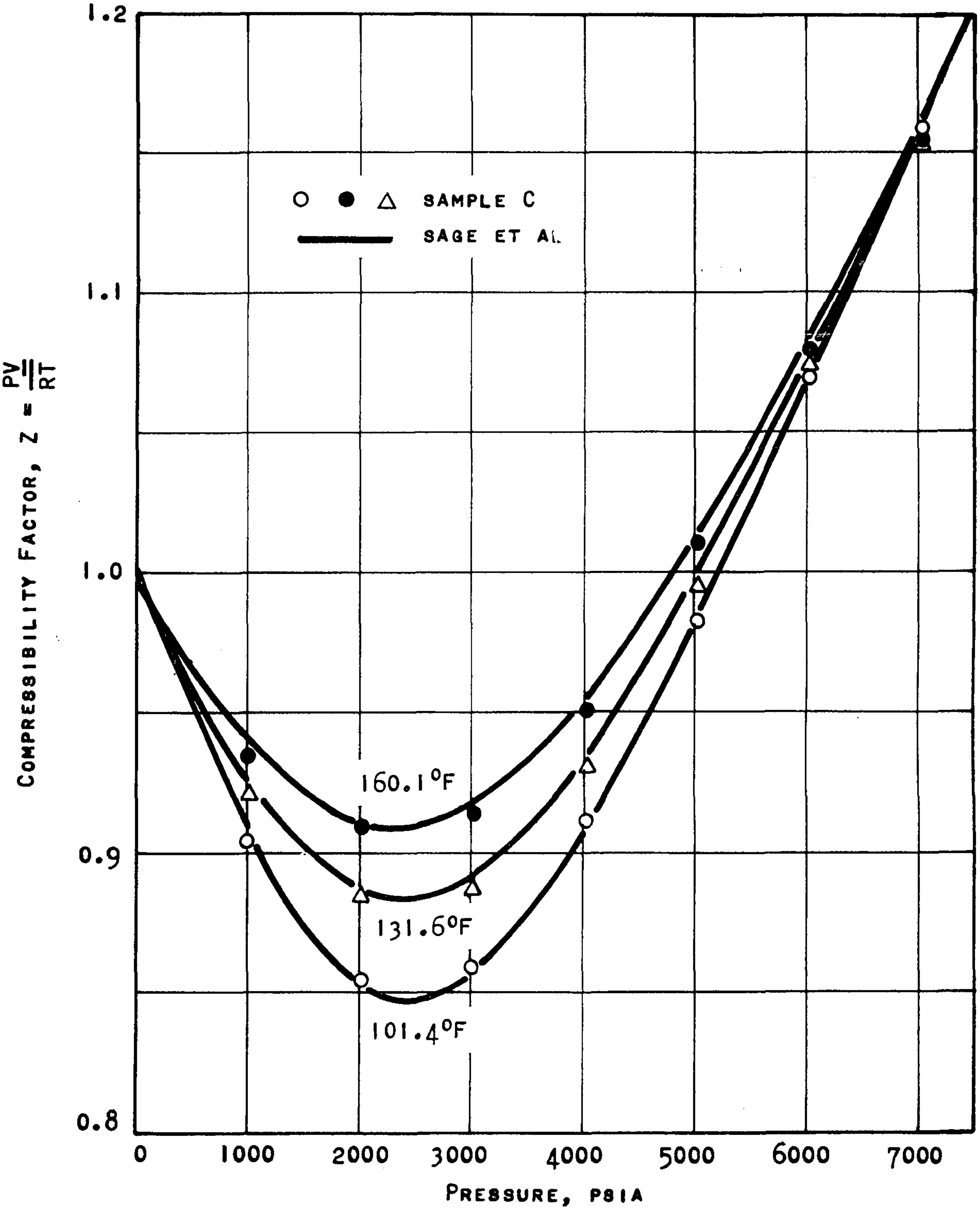

FIGURE 15

COMPRESSIBILITY FACTOR OF METHANE

A quantitative analysis of error, involved in the present method, was also made. The root mean square deviations of the experimental values of the four samples (at isothermal conditions) from the literature values were calculated. The results are given in Table F2 in the Appendix. A minimum root mean square deviation of 0.0017 is found for Sample C at 101.4 °F., whereas a maximum value of 0.0080 is noted for Sample D at 161.2 °F. The deviation of all points of the four samples is found to be 0.0050. The deviation of all points of any sample is also of the same order of magnitude.

Several factors contributing to the deviation of the experimental points from the literature values may now be discussed. The high degree of purity of the methane (99.9 mole per cent), which was used by Sage, could account for some deviation. The uncertainty of measuring the pressure was another source of error, especially at the low pressure range. The compressibility of varying amounts of mercury present in the pump at different points of the experiment could be another contributing factor. The change in room temperature and pressure during the course of the experiment could partly account for the discrepancy in the experimental results. The most important source of error was, however, due to uncertainty in measuring the actual gas volume in the high pressure variable volume cell. The greater uncertainty of measuring the smaller gas volumes at higher pressures could have had some adverse effect on the final results.

It was concluded by Nassiri (59) in his work that an initial large volume of gas sample should be used in order to decrease the error in measuring gas volumes at higher pressures. In the present study, an improved method was developed for calculating true gas volume from the experimentally measured gross volume. Consequently, this investigation does not support the conclusion of the previous investigator. Although Samples A, B, and C had an initial volume of approximately 400 cc at 1,000 psig and 100 °F., Sample D was of 200 cc at the same conditions. The results with the latter sample were found to be in good agreement with those of the others.

As a result of the calibration study, the experimental equipment and procedure were proved to be sound and reliable. The proposed method of measuring compressibility factors of gases is more versatile, within its range of accuracy, than either the original Bean or the Burnett equipment. This is because the present technique has the advantage of greater speed, simplicity of operation, and most important of all, the capability of taking data on a single sample at various temperatures and any increment of desired pressures.

After the reliability of this method was established, the volumetric properties of five selected mixtures of methane, ethane, and hydrogen sulfide were determined. The result of these determinations will be presented in the following chapter.

CHAPTER VIII

EXPERIMENTAL RESULTS

The experimental program included an investigation of the P-V-T behavior of five ternary mixtures of methane, ethane, and hydrogen sulfide in the gaseous phase. These new data were obtained at nominal temperatures of 100, 130, and 160 °F. and up to a maximum pressure of 7,026 psia. The compositions of all mixtures studied are reported in Table F3, while the compressibility factors are given in Table F4 in the Appendix.

The selected mixtures of this study could be representative of sour gases found in petroleum reservoirs. To provide data on a systematic series of mixtures, an attempt was made to keep ethane content constant at 5 mole per cent in Mixtures A and B while varying hydrogen sulfide composition from 5 to 10%. In Mixtures C, D, and E, an effort was made to maintain the ethane content at 10% for hydrogen sulfide contents of 5%, 10%, and 20%. This objective, however, was not entirely accomplished due to the impracticability of preparing an exact mixture of predetermined composition.

The compressibility factors of the five mixtures of this investigation are shown in Figures 16, 17, and 18 as a function of pressure at nominal temperatures of 100, 130, and 160 °F., respectively. Data obtained for the pure components are also illustrated in the same figures.

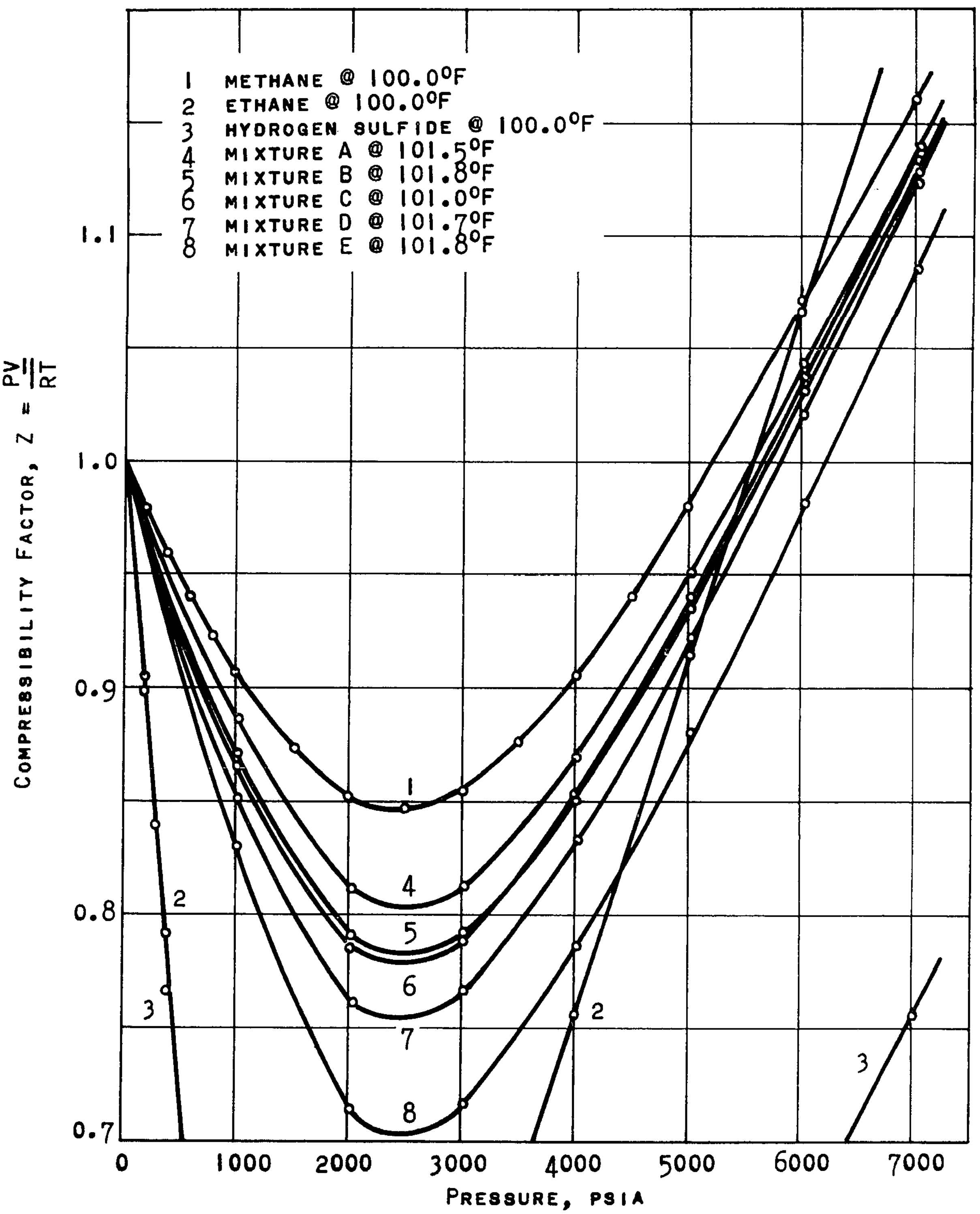

FIGURE 16

EXPERIMENTAL COMPRESSIBILITY FACTOR OF MIXTURES AT A NOMINAL TEMPERATURE OF 100° F

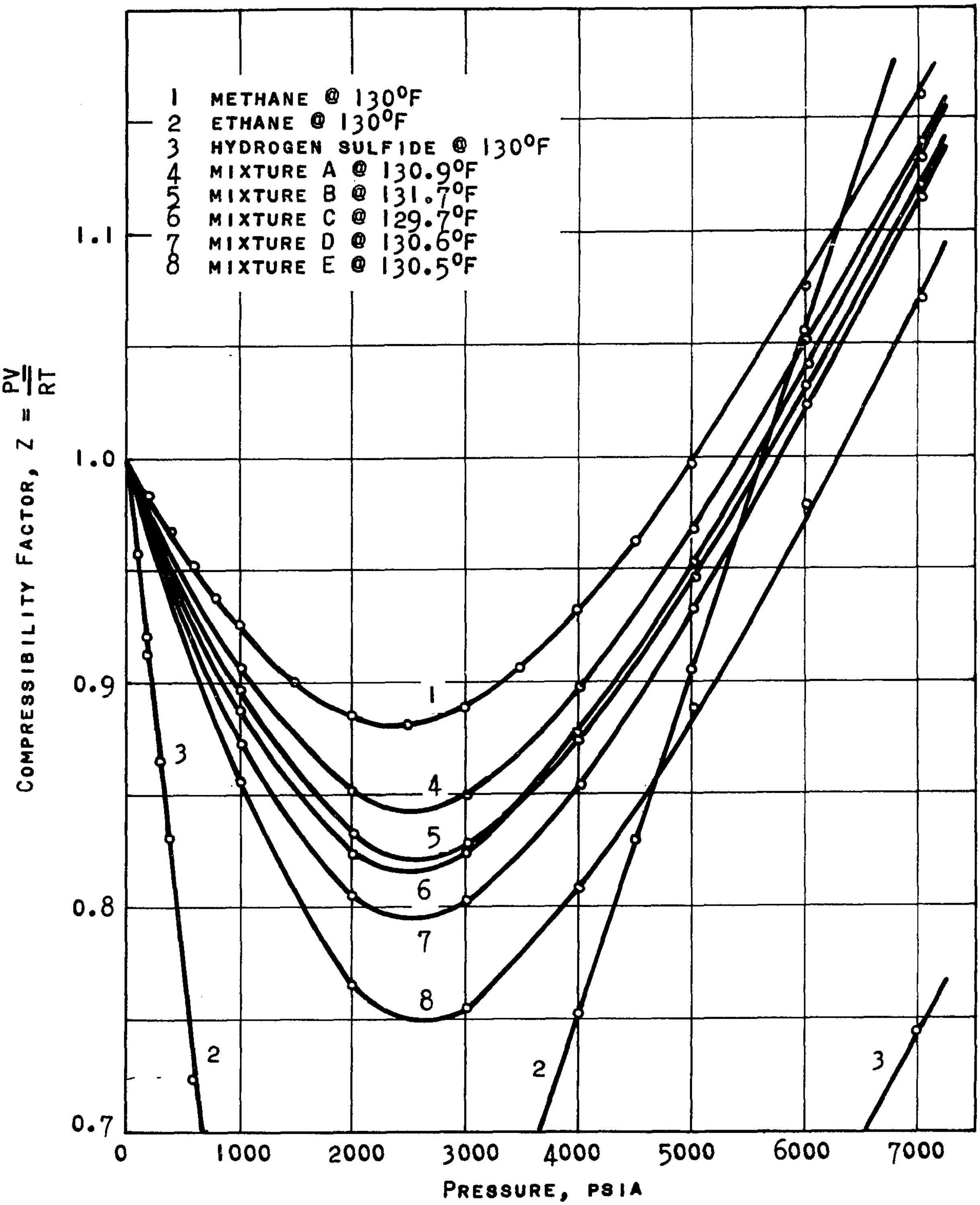

FIGURE 17

EXPERIMENTAL COMPRESSIBILITY FACTOR OF MIXTURES AT A NOMINAL TEMPERATURE OF 130° F

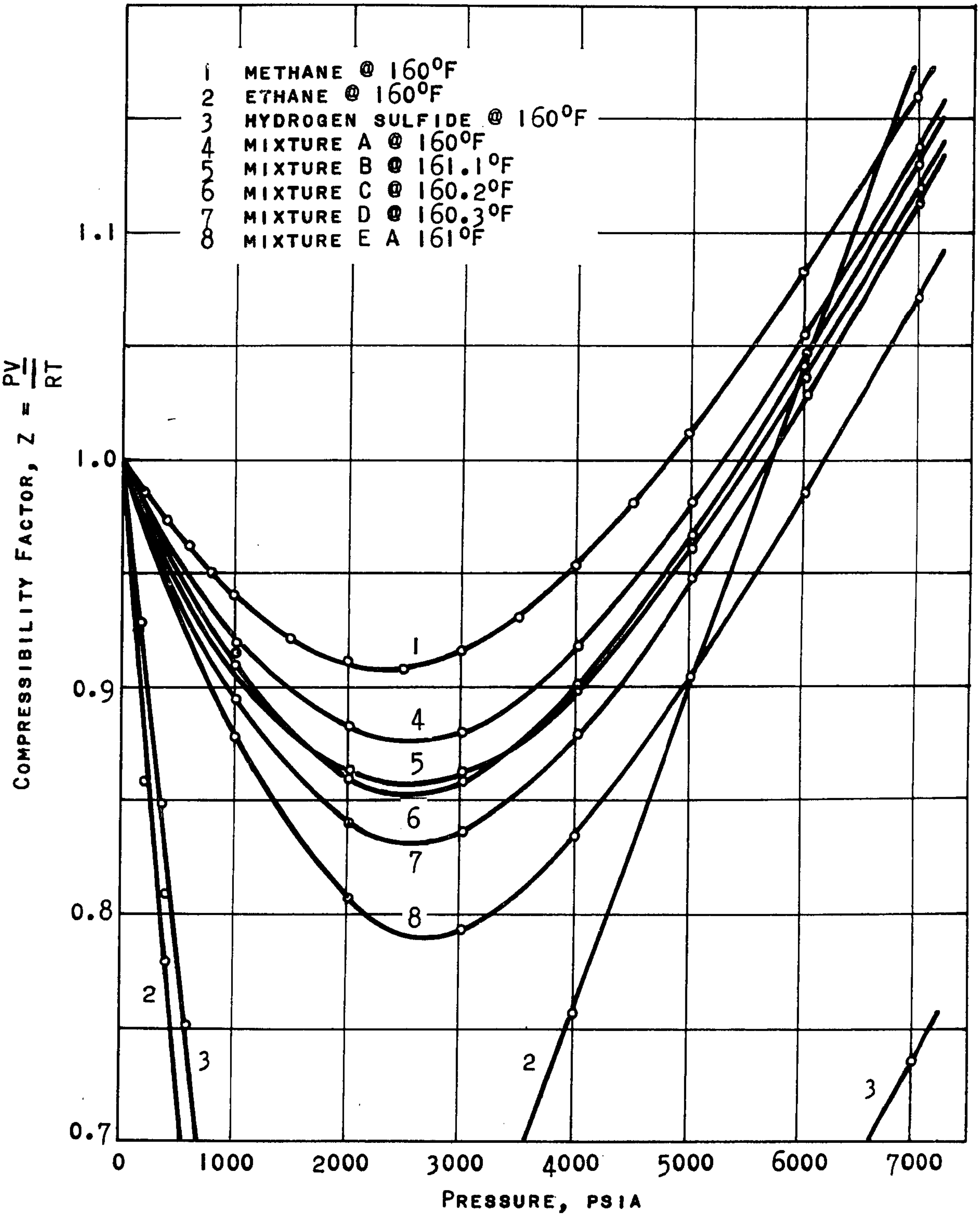

FIGURE 18

EXPERIMENTAL COMPRESSIBILITY FACTOR OF MIXTURES AT A NOMINAL TEMPERATURE OF 160° F

As expected, the experimental data fell on smooth curves, demonstrating their internal consistency. Based upon the calibration data of pure methane, the accuracy of these data is considered to be within 1.0%.

It is noted from these figures that the compressibility factor of a mixture at a given temperature and pressure decreases with decrease in methane content. The overlapping of the curves for Mixtures B and C may be due to nearly equal amounts of methane content of these mixtures, even though ethane and hydrogen sulfide were present in different quantities in both cases. This observation indicates that the presence of a small amount of hydrogen sulfide may be treated for correlation purpose by regarding it as ethane. This treatment may be further justified in the light of Pitzer's acentric factor. Interestingly enough, both ethane and hydrogen sulfide have practically the same acentric factor of 0.1. It should be emphasized, however, that the effect of hydrogen sulfide contamination on the volumetric properties of a natural gas cannot be entirely evaluated from the limited number of ternary mixtures of the present study.

The proposed methods of predicting the P-V-T data of gaseous mixtures have been used to calculate the compressibility factors of the experimental ternary mixtures. The result of comparison of the predicted values with the experimental data will be discussed in the next chapter. Included also in the next chapter are the discussions on the results of comparison of the predicted and experimental values of nine binary systems obtained from the literature.

CHAPTER IX

DISCUSSION OF THE PREDICTED RESULTS

It has been emphasized during this study that the understanding of the nature of interactions between dissimilar molecules in a heterogenous system is the key to developing any valid method of predicting its volumetric properties. Whereas interactions between molecules of diversified characteristics have not been fully understood, recent advancements in statistical mechanics have been useful in this work for developing several methods of predicting the compressibility factors of gaseous mixtures. These methods were discussed in Chapter VI. Mixtures may be considered under three broad classifications: 1) Non-Polar Mixtures, 2) Polar Mixtures, and 3) Mixtures Containing Polar and Non-Polar Components. The natural gases commonly encountered in petroleum reservoirs belong in either the first or the last group.

The validity of the proposed methods of prediction has been determined in the present study. The predicted and experimental values of nine binary systems obtained from the literature (79, 80) and the ternary system of this investigation were compared. Included in the binary systems were four non-polar systems of hydrocarbons, three non-polar mixtures of hydrocarbons and carbon dioxide, and two systems of non-polar hydrocarbons and polar hydrogen sulfide. The ternary system consisted of methane, ethane, and hydrogen sulfide. In order to place a severe test on the proposed prediction techniques, a wide range of substances of varying complexities were selected. In each binary system, 0.8, 0.5, and 0.2 molal mixtures were considered ranging in temperature from 70 °F. to 340 °F. and up to a maximum pressure of 10,000 psia. Five ternary mixtures contained as much as 0.1 and 0.2 mole fraction of ethane and hydrogen sulfide, respectively. The compressibility factors of these mixtures were investigated at 100, 130, and 160 °F. and up to a maximum pressure of 7,026 psia. A total of 1,096 single phase data were analyzed by each prediction method. The calculations were made by using Pitzer's original compressibility tables, along with the extended tables of this work, in an IBM 7090 computer in the research center of the Continental Oil Company at Ponca City, Oklahoma. A summary of the results of these calculations is shown in Table G1 in the Appendix. Included in this table are the absolute and standard deviations of the predicted results from the experimental values of various mixtures. The range of pressures and temperatures, number of experimental points observed, the greatest positive or negative deviations, and the reduced temperature and pressure at which the maximum deviation occurs for each mixture are also given.

In the vast majority of cases, the analysis shows very good agreement between the predicted and experimental values. It is observed that the maximum deviation tended to occur in the pseudocritical region; that is, $T_r^{'} = 1$ and especially when $P_r^{'}$ is about 1.

The inaccuracy of the predicted results in the pseudocritical region may be due to several reasons. The variation of the compressibility factor with reduced pressure and temperature is extremely sensitive in the critical range (see Figure 11). A slight error in predicting one of the pseudocritical properties of a mixture can then easily yield a large discrepancy. In particular, the compressibility factors in the critical region are so low in magnitude that any per cent error calculation is usually adversely magnified. Lohrenz (51) has pointed out some "second level" inconsistencies in this area in the original Pitzer Z^0 table, which could contribute to large deviations. For example, in the region of $P_r = 0.8$ to 1.2 and $T_r = 0.98$ to 1.05, the differences in sequential values of Z^0 are not smooth but have some fluctuation. This can cause even more fluctuation in the computer interpolation.

In addition to the mechanical problem, the real problem is more fundamental in nature. An error as high as 50%, which was observed in the critical area, could not be remedied by the introduction of additional parameters other than Pitzer's acentric factor. The real solution probably lies in accurate prediction of the pseudocritical properties of a mixture in the critical region. This, in turn, would require more precise information concerning interactions between unlike molecules of pair, triplet, or even higher order collisions. This subject, which would require an extensive study, was beyond the scope of this investigation.

The systems of this investigation were classified as mixtures of A) hydrocarbons, B) hydrocarbons and carbon dioxide, and C) hydrocarbons and hydrogen sulfide. As may be noted, the mixtures of the groups A and B belong to the same general class of non-polar mixtures. Further subclassification was made, since carbon dioxide differs in molecular nature and structure from those of the hydrocarbons. The mixtures of hydrocarbons and hydrogen sulfide belong to the general class of non-polar and polar mixtures. In order to determine the best of the proposed prediction methods for each group of mixtures, Figures 19, 20, and 21 were prepared. These figures show the standard and maximum deviation of the predicted values by each method from the experimental values as a function of acentric factors of equimolal mixtures of each group. Table G2 in the Appendix can also be used as a basis for comparing one prediction method with another for a given class of mixtures. The results of these comparisons and the validity of the best prediction method for different classes of systems for a specified range of temperatures and pressures will now be presented.

A. Mixtures of Hydrocarbons

Four systems of hydrocarbons consisting of methane as the common component, and ethane, propane, n-butane, and n-pentane as the other components were studied. Figure 19 shows the relative accuracy of the four prediction methods which were used for this class of mixtures. In consideration of the standard and maximum deviations of the predicted compressibility factors given by different methods from the experimental values, it is evident that Method 3 is the most accurate prediction tool for these mixtures. The trend which is observed in the case of these equimolal mixtures is also good for other mixtures of these systems studied. Table G2 lists the standard deviations of the predicted values by each method from 359 experimental compressibility factors. It should be noted that Method 3 yields a standard deviation of 2.03%, which is better than the 3.26% reported by Stewart, et. al. in their correlation. At only one out of 359 experimental points, a maximum deviation of -24.18% was noted for 0.2 molal methane-ethane mixture in the critical region.

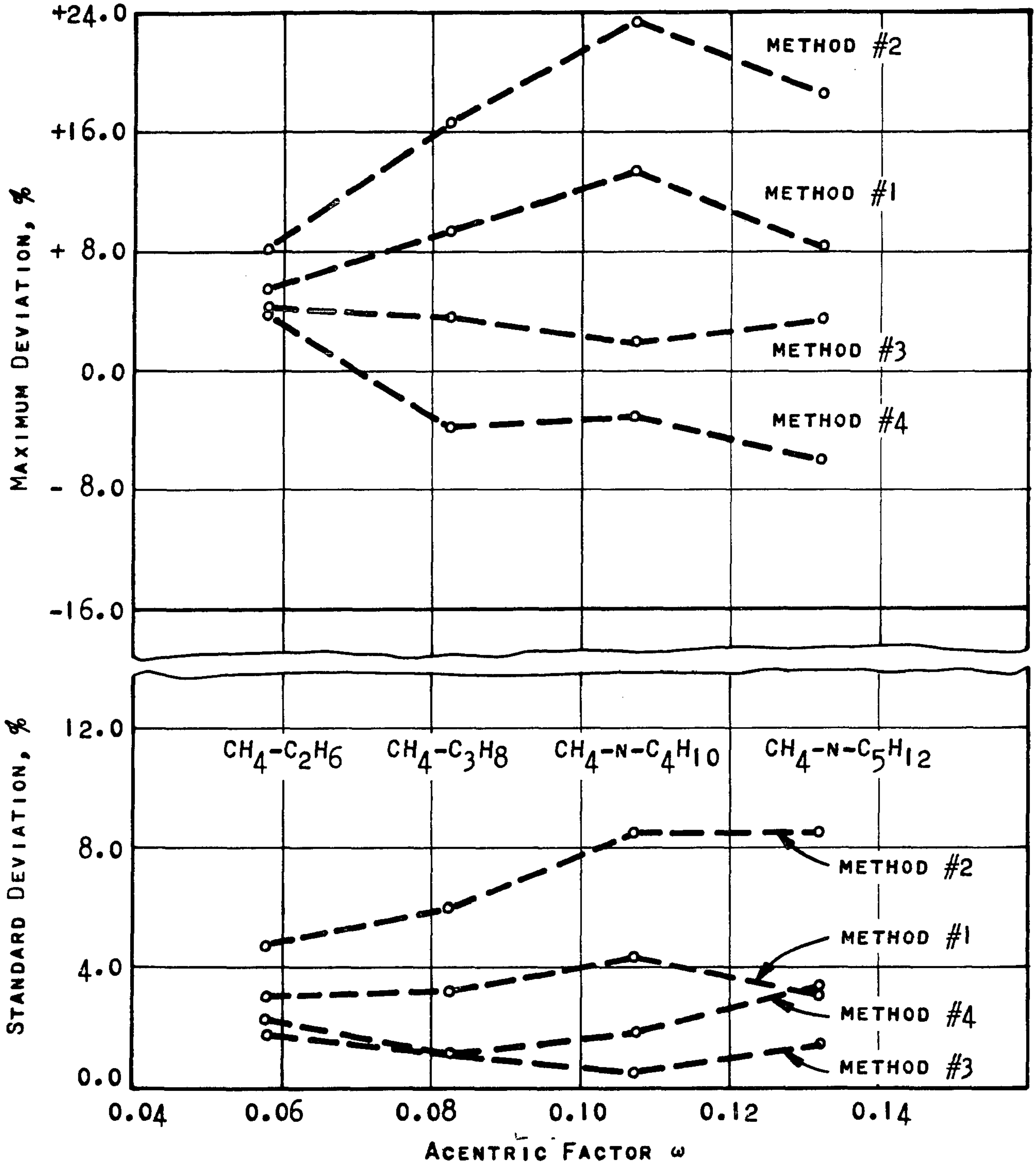

FIGURE 19

COMPRESSIBILITY FACTOR DEVIATION OF EQUIMOLAL HYDROCARBON MIXTURES

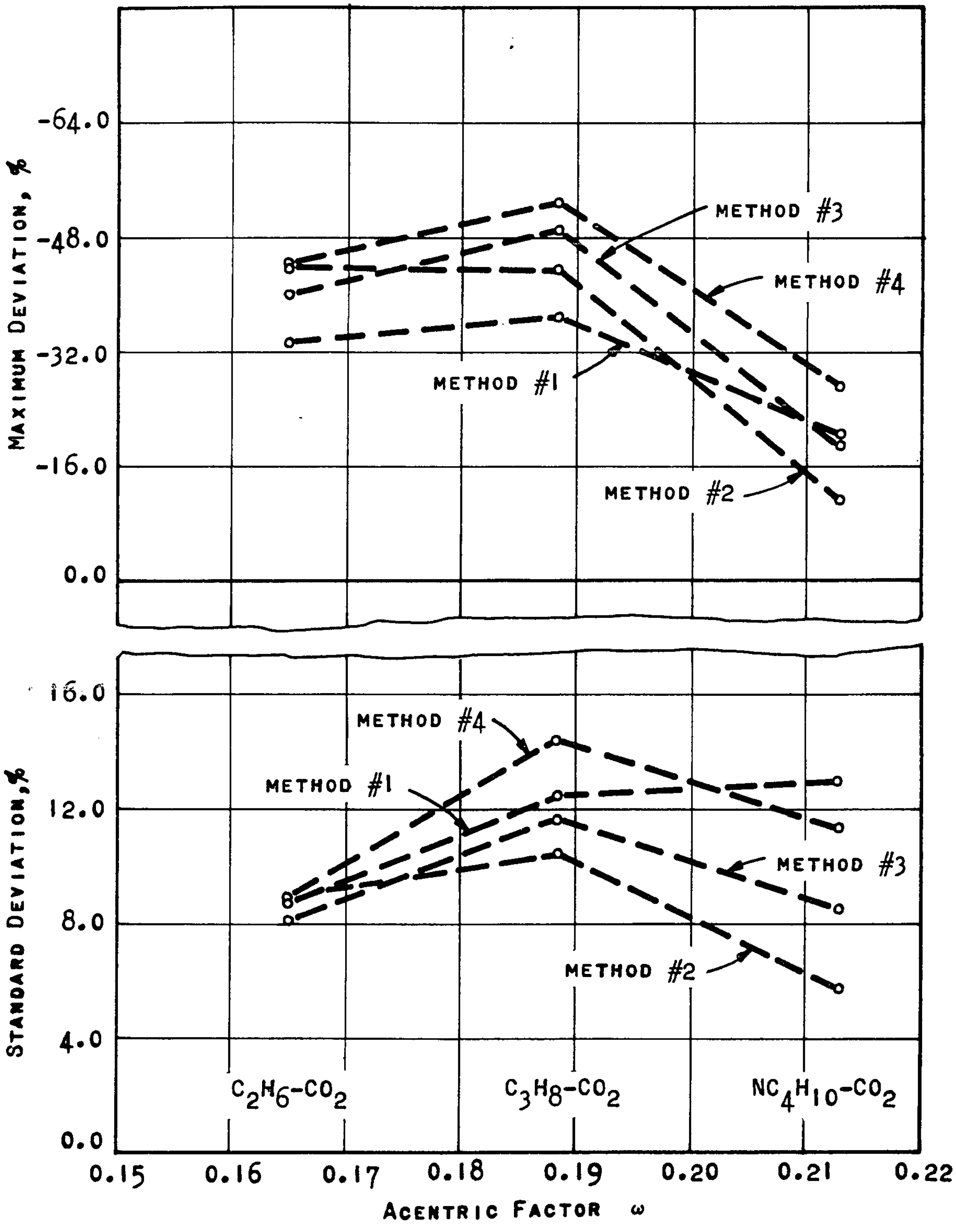

FIGURE 20

COMPRESSIBILITY FACTOR DEVIATION OF EQUIMOLAL HYDROCARBON-CARBON DIOXIDE MIXTURES

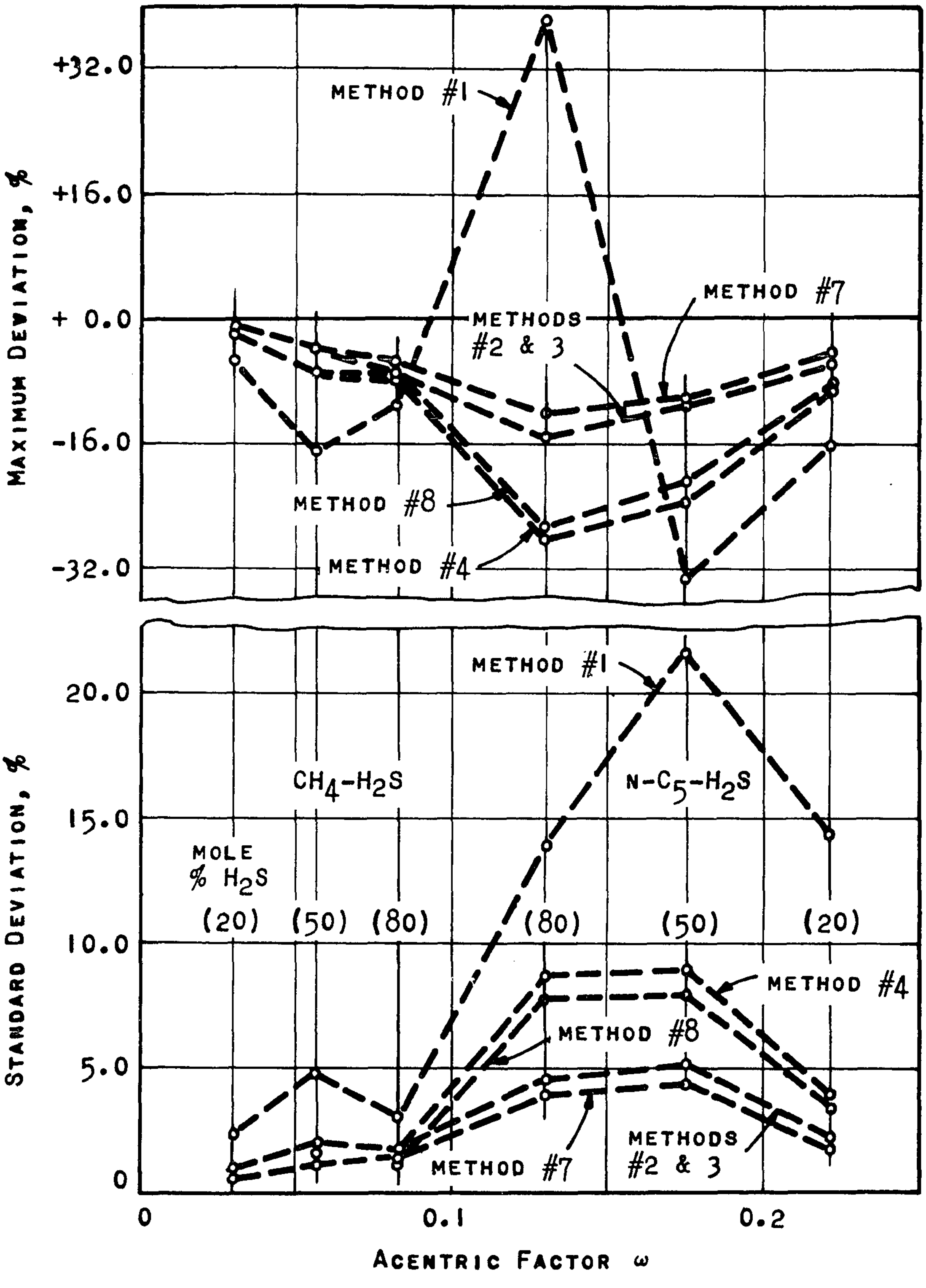

FIGURE 21

COMPRESSIBILITY FACTOR DEVIATION OF HYDROCARBON-HYDROGEN SULFIDE MIXTURES

If this point is excluded, a revised standard deviation of 1.58% is obtained for this method. It is interesting to note that the validity of this method is comparable to that of Pitzer's compressibility charts for pure gases.

Method 1, which is based upon Kay's mole average rule, shows standard deviations of 3.14%. In case of mixtures of the same homologous series, the modified Kay's rule seems to be sufficiently accurate for predicting interaction between unlike molecules of different sizes such as in the methane-n-pentane system. A good agreement may be thus obtained between the experimental data and predicted values given by this method. Method 4 gives nearly equal accuracy as that of Method 3, whereas Method 2 is the least accurate of all.

B. Mixtures of Hydrocarbons and Carbon Dioxide

Three binary systems of carbon dioxide and ethane, propane, and n-butane have been investigated in the present study. Although these systems are non-polar in nature, like mixtures of hydrocarbons, Methods 1 through 4 were found to be less accurate for predicting the compressibility factors of this class of gases. Figure 20 shows that Method 2 is the best of the four prediction methods. Table G2 shows a standard deviation of 7.27% of Method 2 for 381 observed points. A reason for this higher discrepancy may be found from the tabulated data of maximum deviation in Table G1. An error as high as 50% is noted. It is also observed that the maximum deviations occur in the critical area. In order to determine the accuracy of the different methods in areas other than the critical range, all data in the region bounded by $0.9 \leqslant T_r \leqslant 1.15$ and $0.8 \leqslant P_r \leqslant$

2.0 were discarded and new values of standard deviations were calculated. Table G2 shows the results of this investigation. An elimination of about 7% of the original 381 experimental points has increased considerably the accuracy of the different methods. Method 2 is still found to be the most accurate of all, with a standard deviation of 4.68% for 353 experimental points. The other methods in order of their accuracy are, Method 3 (5.5%), Method 4 (6.83%) and Method 1 (7.97%). It is proper to point out that the compressibility factors of the mixtures of this class, under all temperature and pressure conditions, were underestimated by the four methods used.

Stewart, et. al. have also observed higher errors for systems of hydrocarbons and carbon dioxide than hydrocarbon mixtures. Lohrenz has used an acentric factor of 0.1912 for carbon dioxide (compared to the value of 0.225 as reported by Pitzer) to obtain a better correlation of compressibility factor data for pure carbon dioxide within 0.52% of the experimental values. This revised acentric factor was used to recalculate a few compressibility factors of the various mixtures at the points of maximum deviations given by the original approach. The results were unsatisfactory since a slight change in acentric factor is insufficient to account for an error as high as 50% in the critical region.

C. Mixtures of Hydrocarbons and Hydrogen Sulfide

The compressibility factors of two binary systems having the common component hydrogen sulfide, and the second components methane and n-pentane, and a ternary system consisting of methane, ethane, and hydrogen sulfide, were compared with the predicted values given by eight different methods. As with the non-polar mixtures of carbon dioxide and hydrocarbons, the predicted results of the non-polar and polar mixtures were, in most instances, lower than the experimental values. Figure 21 and Table G2 show that the most accurate method for the binary systems is Method 7, which is a modification of Method 2 for interaction between unlike polar and non-polar substances. Method 7 gives a standard deviation of 2.5% for 251 experimental data, including those also in the critical region. Methods 2 and 3 show nearly equal agreement with deviations of 3.00 and 2.88%, respectively. The maximum error for Method 7 was -12.13% in the critical range compared to -15.41% and -15.65% for Methods 2 and 3, respectively.

Method 1 was found to be the least accurate of all methods, with the highest standard deviation of 11.13%. The maximum deviation of -22.34% is also noted for the equimolal mixture of the n-pentane-hydrogen sulfide system. Like all other methods, this method results in lower standard deviations in the case of methane-hydrogen sulfide than n-pentane-hydrogen sulfide system; however, in the latter case, the errors in Method 1 were increased to more than five times those of the former system. It is apparent that the mole average rule of Method 1 is entirely unsatisfactory to account for the interaction between nearly spherical but polar molecules of hydrogen sulfide and long-chain and non-polar molecules of n-pentane.

For the ternary mixtures of methane, ethane, and hydrogen sulfide, all methods offer excellent agreement between the predicted and experimental data. The accuracy which was observed for the different methods could be attributed to the low content of ethane and hydrogen sulfide in the ternary mixtures. It may also be recalled that a maximum error of 1% is probably involved in the measured values of compressibility factors of the ternary mixtures.

As shown in Table G2, Method 7 is the most accurate method for predicting the compressibility factors of ternary mixtures, with a standard deviation of 0.76%. Table G1 shows that the maximum error involved in this method was -1.88%, in case of the mixture containing as high as 10% ethane and 20% hydrogen sulfide. Figure 22 has been prepared by using data of Table G3 in the Appendix. It shows an excellent agreement between the experimental points of this mixture at the various temperatures and pressures and the predicted compressibility curves by Method 7.

D. Recommended Prediction Methods for Different Classes of Gas Mixtures

The foregoing discussion has shown that no single method was found in this investigation for accurately predicting the compressibility factors of gaseous mixtures of widely varying compositions in all ranges of pressures and temperatures. The following methods, however, are recommended for engineering applications:

1. Non-Polar Gas Mixtures:
    a. Hydrocarbons with negligible contamination

        Method 3 for all ranges of pressures and temperatures

    b. Hydrocarbons and Carbon Dioxide

        Method 2, excluding the region bounded by $0.9 \leqslant T_r \leqslant 1.15$ and $0.8 \leqslant P_r \leqslant 2.0$

        Simpler Method 3 may be used with slightly less accuracy than Method 2 under the same conditions as above.

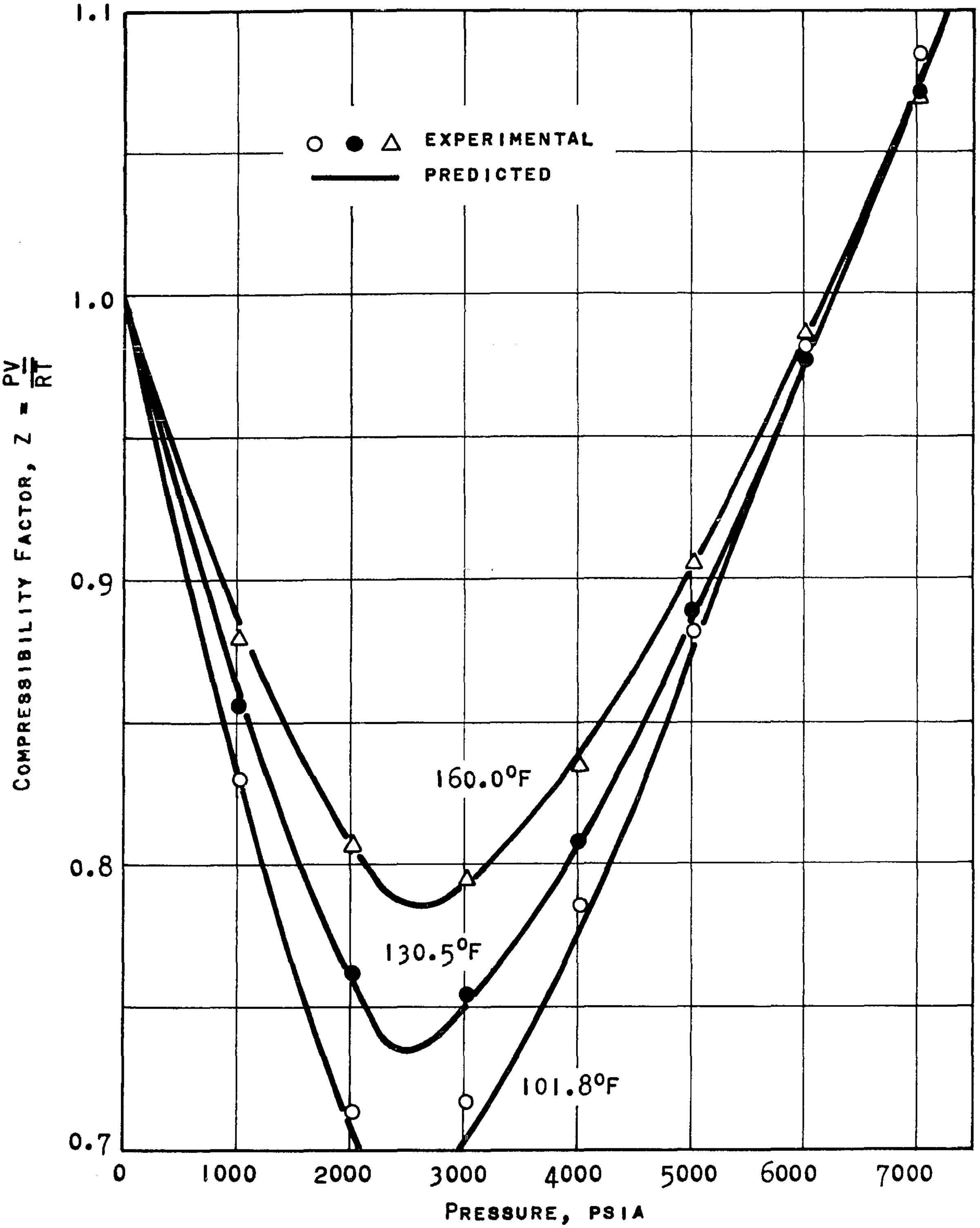

FIGURE 22

PREDICTED AND EXPERIMENTAL COMPRESSIBILITY FACTOR OF MIXTURE E

2. Non-Polar and Polar Gas Mixtures:

   a. Hydrocarbon and Hydrogen Sulfide

      Method 7. Less accuracy may occur in the critical region

      Method 3 for slightly less accuracy than Method 7

E. Recommendations for Future Work

The following recommendations may be made for future work:

1. A study of the nonideal behavior of gaseous mixtures, in general, around the critical region.
2. A study to eliminate the larger errors observed in the case of non-polar hydrocarbons and carbon dioxide mixtures compared to hydrocarbons only.
3. A study to remove possible inconsistency of Pitzer's Z^o chart in the critical region.

CHAPTER X

CONCLUSION

An understanding of the fundamental differences between the molecules of various pure gases is required for the accurate prediction of their volumetric properties. This study shows that the acentric factor can be used for characterizing a substance. It is also found that this factor is an important addition to the usual reduced pressure and reduced temperature to calculate the proper value of the compressibility factor of a pure gas. Because of the inherent advantage of this modified theorem of corresponding states, first proposed by Pitzer, the original compressibility factor tables were extended from P_r of 9 to 14, and results were plotted in convenient figures. In all systems tested, the basic accuracy was definitely superior to that obtained with our existing charts. It is therefore recommended that the new figures be used for their replacement.

This investigation also provides a real insight into the problem of predicting the P-V-T properties of gas mixtures which are affected by the nonideality of pure components, their relative amounts, and the interactions between unlike molecules in the systems. As a result of this extensive study, it is concluded that mixtures are needed to be classified according to the nature and molecular structure of their constituents if reasonable accuracy in predicted results is to be achieved. In extending Pitzer's modified theorem of corresponding states to gas mixtures, mixtures were therefore classified as systems of hydrocarbons alone, hydrocarbons and hydrogen sulfide, and hydrocarbons and carbon dioxide. Based upon an analysis of 991 experimental literature data and 105 values of this study, a method is recommended for predicting compressibility factors of each of the classified systems. These methods were found to be definitely superior to the widely used Kay's rule.

A commercial Bean apparatus was modified for use up to a maximum working pressure of 7,000 psig. An interesting feature of this modified unit was that volumetric data on a single gas sample could be obtained at various temperatures and any increment of desired pressures. Accurate volumetric data on five mixtures of methane, ethane and hydrogen sulfide in the gaseous state were taken using this equipment. The mixtures were studied at the nominal temperatures of 100, 130 and 160 $^{\circ}$F. up to the maximum working pressure of the unit. The amounts of ethane and hydrogen sulfide in these mixtures were about 10 and 20 mole per cent, respectively.

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APPENDIX A

NOMENCLATURE

TABLE A1

NOMENCLATURES

A_o = Constant in equations of state of pure gases (Equations 2-7 and 2-8)

A_o' = Constant in equations of state of gas mixtures (Equations 2-58 and 2-59)

a = Constant in equations of state of pure gases (Equations 2-7 and 2-8)

a' = Constant in equations of state of gas mixtures (Equations 2-58 and 2-59)

$B(T)$ = Second virial coefficient of the virial equation expressed in the form of power series in specific volume

$B'(T)$ = Second virial coefficient of the virial equation expressed in the form of power series in pressure

B_o = Constant in equations of state of pure gases (Equations 2-7 and 2-8)

B_o' = Constant in equations of state of gas mixtures (Equations 2-58 and 2-59)

b = Constant in equations of state of pure gases (Equations 2-7 and 2-8)

b_o = Kinetic constant given by Equation 2-21

$C(T)$ = Third virial coefficient of the virial equation expressed in the form of power series in specific volume

$C'(T)$ = Third virial coefficient of the virial equation expressed in the form of power series in pressure

C_o = Constant in equations of state of pure gases (Equations 2-7 and 2-8)

C_o' = Constant in equations of state of gas mixtures (Equations 2-58 and 2-59)

c = Constant in equations of state of pure gases (Equations 2-7 and 2-8)

c' = Constant in equations of state of gas mixtures (Equations 2-58 and 2-59)

d = Constant in equations of state of pure gases (Equation 2-8)

d' = Constant in equations of state of gas mixtures (Equation 2-59)

e = Exponential

F = Dimensionless molecular parameter

$F(k/T)$ = Function in Equation 2-20

^{o}F = Degree Fahrenheit

f = Constant in equations of state of pure gases (Equation 2-8)

f' = Constant in equation of state of gas mixtures (Equation 2-59)

$g(r)$ = Radial distribution function

$H(k/T)$ = Function in Equation 2-20

h = Plank's constant

i = Subscript denoting ith component or molecule

J = T_c'/P_c' (Equation 2-94)

$J(k/T)$ = Function in Equation 2-20

j = Subscript denoting jth component or molecule

K = $T_c'/(P_c')^{\frac{1}{2}}$ (Equation 2-95)

^{o}K = Degree Kelvin

k = Boltzmann's constant

l = Length of a molecule

l^* = Length to width ratio of a molecule

M = Molecular weight

m = Mass of a molecule

N = Number of molecules in a system

$\bar{N}$ = Avagadro's number

n = Number of components in a system

n_g = lb mole of a gas

P = Absolute pressure

$\bar{P}$ = Absolute pressure that may be exerted by a component at the temperature and molal volume of a mixture

P^* = Reduced pressure given by Equation 2-45

P_o^* = Reduced pressure given by Equation 2-55

P_c = Critical pressure

P_c' = Pseudocritical pressure

P_r = Reduced pressure given by Equation 2-24

P_r' = Pseudoreduced pressure given by Equation 2-75

p^* = Parameter given by Equation 2-43

Q = Partition function

R = Universal gas constant

^{o}R = Degree Rankine

r = Distance between two molecules

s = Constant in Equation 2-43

T = Absolute temperature

T^* = Reduced temperature given by Equation 2-47

T^{**} = Characteristic temperature proportional to ϵ/k

T_c = Critical temperature

T_c' = Pseudocritical temperature

T_r = Reduced temperature given by Equation 2-25

T_r' = Pseudoreduced temperature given by Equation 2-76

t = Constant in Equation 2-43

V = Total volume of a system

$\underline{V}$ = Specific molal volume

$\bar{V}$ = Specific molal volume of a component at the pressure and temperature of a mixture

$\underline{V}^*$ = Reduced volume given by Equation 2-46

$\underline{V}^{**}$ = Characteristic volume proportional to σ

$\underline{V}_c$ = Critical specific molal volume

$\underline{V}_c'$ = Pseudocritical specific molal volume

$\underline{V}_r$ = Reduced volume given by Equation 2-26

$\underline{V}_r'$ = Pseudoreduced volume given by Equation 2-77

$\underline{V}_r$ = Ideal reduced volume given by Equation 2-33

v = Volume of mercury at any temperature relative to volume at 60 °F

W = Z_cT_c/P_c

x = Mole fraction of a component in a mixture

Z = Compressibility factor

Z^o = Compressibility factor of an ideal substance with zero acentric factor

Z^1 = Slope of the compressibility factor vs. acentric factor curve at a given reduced temperature and pressure

Z^2 = Factor accounting for the polar contribution to the compressibility factor of a substance

Z_c = Critical compressibility factor given by Equation 2-27

Z_c' = Pseudocritical compressibility factor given by Equation 2-93

Abs = Absolute

cal = Calculated

expt = Experimental

mix = Mixture

P. M. D. = Point at which maximum deviation occurs

std = Standard

α = Polarizibility of a nonpolar molecule

α^* = Reduced polarizibility given by Equation 2-72

β = Compressibility of mercury

γ = Exponent in virial expansion of Equation 6-11

ϵ = Parameter in the intermolecular function. It is the maximum energy of interaction

θ = Angle which the dipoles make with the axis connecting them

λ = The slope of the vapor pressure curve at the critical temperature given by Equation 2-35

μ = Dipole moment of a polar molecule

μ^* = Reduced dipole moment given by Equation 2-22

ξ = Factor given by Equation 2-71

ρ_r = Su's ideal reduced density given by $1/\underline{V}_r$

σ = Parameter in the intermolecular potential function. It is the collision diameter for encounters between two volecules with negligible kinetic energy

ϕ = Azimuthal angle

ψ = Exponent in virial expansion of Equation 6-11

ω = Acentric factor given by Equation 2-36

ω' = Pseudoacentric factor of a mixture given by Equation 2-83

Λ = Measure of the importance of quantum effect given by Equation 2-51

φ = Intermolecular potential function

APPENDIX B

SURVEY OF EXPERIMENTAL DATA

TABLE B1

SURVEY OF EXPERIMENTAL DATA ON METHANE, ETHANE AND HYDROGEN SULFIDE AND THEIR BINARY MIXTURES

System	Investigators	Temperature Range °F	Pressure Range Psig
CH_4	Amagat (1)	58.5- 212.2	573- 4,410
	Freeth, et al (25)	32 - 68	253- 3,160
	Keys, et al (44)	32 - 392	475- 3,740
	Kvalnes (47)	-94 - 392	0-14,700
	Michels, et al (55, 56)	32 - 302	294- 5,586
	Mueller (58)	-200 - 50	0- 7,000
	Olds, et al (63)	70 - 460	0-10,000
C_2H_6	Beattie, et al (4)	90.0- 90.1	707- 710
	Beattie, et al (5)	122 - 527	882- 5,145
	Beattie, et al (3)	77 - 482	163- 2,827
	Quint (72)	57.2- 122	470- 823
	Reamer, et al (73)	100 - 460	0-10,000
	Sage, et al (81)	70 - 250	0- 3,528

TABLE B1--Continued

H_2S	Reamer, et al (74)	40 - 340	0-10,000
	West (92)	-76.4-1300	0- 1,014
CH_4-C_2H_6	Sage, et al (78)	70 - 250	0- 3,000
CH_4-H_2S	Reamer, et al (75)	40 - 340	0-10,000

APPENDIX C

CRITICAL AND REDUCED PROPERTIES OF FLUIDS USED FOR GENERALIZED CORRELATION

TABLE C1

FORCE CONSTANTS AND ACENTRIC FACTORS OF FLUIDS USED FOR GENERALIZED CORRELATIONS OF P-V-T DATA

System	$\sigma \times 10^8$ (cm)	ϵ/k ($^\circ K$)	ω
CH_4	3.817	148.2	0.013
C_2H_6	3.954	243.0	0.105
C_3H_8	5.637	242.0	0.152
n-C_4H_{10}	4.971	297.0	0.201
H_2S	3.733	221.1	0.100
CH_4-C_2H_6 (80 mole % CH_4)	3.845	165.3	0.031
CH_4-C_2H_6 (60 mole % CH_4)	3.872	183.3	0.050
CH_4-C_2H_6 (20 mole % CH_4)	3.928	222.2	0.087

TABLE C2

STATISTICAL MECHANICALLY REDUCED PROPERTIES OF FLUIDS

System	Temperature Range °F.	Pressure Range Psia
CH_4	-33-74	533-5330
C_2H_6	240-415	786-7860
C_3H_8	237-411	270-2705
n-C_4H_{10}	395-609	484-4840
H_2S	252-336	850-8500
CH_4-C_2H_6 (80 mole % CH_4)	75-134	582-2906
CH_4-C_2H_6 (60 mole % CH_4)	68-200	632-3160
CH_4-C_2H_6 (20 mole % CH_4)	179-339	734-3670

TABLE C2--Continued

V*					
P* = 0.1			P* = 0.3		
T* = 1.6	T* = 1.8	T* = 2.0	T* = 1.6	T* = 1.8	T* = 2.0
13.653	16.277	18.725	3.245	4.532	5.589
13.157	15.988	18.564	3.400	4.568	5.398
13.557	16.204	18.684	2.105	4.232	5.139
12.198	15.431	18.185	2.414	3.837	4.898
	14.208	17.286		2.158	3.777
	16.024	18.464		4.268	5.375
13.126	15.900	18.407	2.984	4.197	5.343
12.950	15.882	18.705	3.230	4.419	5.468

V*					
P* = 0.5			P* = 1.0		
T* = 1.6	T* = 1.8	T* = 2.0	T* = 1.6	T* = 1.8	T* = 2.0
2.040	2.629	3.261	1.571	1.772	1.998
2.500	3.021	3.593	2.006	2.212	2.438
1.145	1.964	2.810	0.958	1.156	1.427
1.979	2.439	3.105	1.687	1.876	2.106
	1.734	2.222		1.514	1.683
	2.554	3.153			
2.123	2.619	3.210			

TABLE C3

CRITICAL CONSTANTS AND OTHER PROPERTIES OF COMPOUNDS USED FOR GENERALIZED CORRELATIONS OF COMPRESSIBILITY FACTORS

Compound	Molecular Weight	T_c (^oR)	P_c (Psia)	Z_c	F
CH_4	16.042	343.26	673.08	0.290	0.0956
C_2H_6	30.069	549.72	708.35	0.285	0.0480
C_3H_8	44.095	665.82	617.23	0.277	0.0322
$i-C_4H_{10}$	58.121	734.58	529.06	0.283	0.0246
$n-C_4H_{10}$	58.121	765.31	550.66	0.274	0.0241
$n-C_5H_{12}$	72.147	845.64	489.38	0.269	0.0191
CO_2	44.010	547.56	1071.34	0.275	0.0456
H_2S	34.076	672.48	1306.47	0.284	0.0467

TABLE C3--Continued

F/Z_c	ω	μ (debey)	μ^*	$\alpha \times 10^{25}$ (cm^3)	α^*
0.330	0.013			26.0	0.050
0.168	0.105			44.7	0.057
0.116	0.152				
0.087	0.184				
0.088	0.201			104.0	0.063
0.071	0.252				
0.166	0.225				
0.164	0.100	1.02	0.698		

TABLE C4

THE COMPRESSIBILITY FACTORS OF PURE FLUIDS AT P_r = 1.0 AND THE VALUES OF T_r INDICATED

	Z			
T_r	CH_4	C_2H_6	C_3H_8	$i\text{-}C_4H_{10}$
1.0	0.290	0.285	0.277	0.283
1.1	0.688	0.705	0.700	0.707
1.2	0.786	0.799	0.795	0.803
1.3	0.844	0.854	0.854	0.864
1.4	0.880	0.892	0.896	0.909
1.5	0.908	0.918	0.926	
1.6	0.929	0.939	0.950	
1.7	0.943	0.956		
1.8	0.955	0.968		
1.9	0.965	0.976		
2.0	0.972	0.985		

TABLE C4--*Continued*

Z			
n-C_4H_{10}	n-C_5H_{12}	CO_2	H_2S
0.274	0.269	0.275	0.284
0.700	0.710	0.698	0.707
0.802	0.800	0.800	0.796
0.860		0.860	0.854
0.906		0.898	
		0.925	
		0.945	
		0.961	
		0.973	
		0.983	
		0.990	

TABLE C5

THE COMPRESSIBILITY FACTORS OF PURE FLUIDS AT P_r = 5.0 AND THE VALUES OF T_r INDICATED

	Z			
T_r	CH_4	C_2H_6	C_3H_8	i-C_4H_{10}
1.0	0.696	0.680	0.674	0.665
1.1	0.697	0.689	0.683	0.684
1.2	0.713	0.712	0.708	0.715
1.3	0.740	0.746	0.746	0.755
1.4	0.775	0.794	0.800	0.809
1.5	0.822	0.840	0.855	
1.6	0.870	0.882	0.895	
1.7	0.895	0.921		
1.8	0.925	0.958		
1.9	0.952	0.985		

TABLE C5--Continued

Z			
$n\text{-}C_4H_{10}$	$n\text{-}C_5H_{12}$	CO_2	H_2S
0.660	0.649	0.660	0.680
0.675	0.669	0.673	0.685
0.704	0.709	0.704	0.705
0.745		0.750	0.736
0.801		0.808	
		0.858	
		0.902	
		0.940	
		0.978	
		1.012	

TABLE C6

VALUES OF Z^o FOR COMPRESSIBILITY FACTOR CALCULATION

(EXTENSION OF PITZER'S CORRELATION)

T_r	Z^o				
	P_r				
	10.0	11.0	12.0	13.0	14.0
0.80	1.417	1.551	1.686	1.819	1.952
0.85	1.367	1.493	1.619	1.745	1.871
0.90	1.330	1.451	1.573	1.694	1.815
0.95	1.303	1.421	1.539	1.657	1.775
1.00	1.281	1.398	1.514	1.631	1.748
1.05	1.249	1.358	1.467	1.576	1.686
1.10	1.224	1.327	1.430	1.533	1.636
1.15	1.201	1.299	1.395	1.492	1.589
1.20	1.183	1.275	1.365	1.458	1.549
1.25	1.172	1.261	1.348	1.435	1.524
1.30	1.162	1.248	1.332	1.418	1.504
1.40	1.150	1.230	1.311	1.390	1.471
1.50	1.141	1.212	1.283	1.354	1.425
1.60	1.137	1.200	1.262	1.325	1.388
1.70	1.137	1.194	1.251	1.307	1.364
1.80	1.141	1.181	1.244	1.293	1.345
1.90	1.144	1.190	1.238	1.284	1.330
2.00	1.149	1.191	1.234	1.276	1.318
2.50	1.167	1.198	1.230	1.261	1.291
3.00	1.173	1.198	1.222	1.247	1.271
3.50	1.168	1.189	1.210	1.230	1.250
4.00	1.160	1.179	1.197	1.216	1.235

TABLE C7

VALUES OF Z^1 FOR COMPRESSIBILITY FACTOR CALCULATION

(EXTENSION OF PITZER'S CORRELATION)

T_r	Z^1				
	P_r				
	10	11	12	13	14
0.80	-0.400	-0.430	-0.460	-0.490	-0.520
0.85	-0.390	-0.420	-0.450	-0.480	-0.510
0.90	-0.380	-0.410	-0.440	-0.470	-0.500
0.95	-0.370	-0.400	-0.430	-0.460	-0.490
1.00	-0.360	-0.390	-0.418	-0.445	-0.470
1.05	-0.336	-0.361	-0.384	-0.404	-0.424
1.10	-0.307	-0.330	-0.352	-0.371	-0.391
1.15	-0.262	-0.290	-0.318	-0.343	-0.368
1.20	-0.220	-0.248	-0.274	-0.298	-0.320
1.25	-0.164	-0.190	-0.215	-0.240	-0.261
1.30	-0.108	-0.125	-0.140	-0.157	-0.175
1.40	-0.030	-0.049	-0.065	-0.081	-0.095
1.50	+0.054	+0.036	+0.019	+0.001	+0.017
1.60	+0.125	+0.109	+0.094	+0.080	+0.064
1.70	+0.201	+0.183	+0.163	+0.145	+0.125
1.80	+0.290	+0.270	+0.247	+0.223	+0.199
1.90	+0.385	+0.368	+0.346	+0.321	+0.295
2.00	+0.454	+0.448	+0.435	+0.416	+0.395
2.50	+0.530	+0.537	+0.527	+0.510	+0.487
3.00	+0.545	+0.590	+0.601	+0.596	+0.580
3.50	+0.545	+0.590	+0.630	+0.670	+0.665
4.00	+0.545	+0.590	+0.630	+0.670	+0.709

APPENDIX D

SAMPLE CALCULATIONS

TABLE D1

CORRELATION SAMPLE CALCULATIONS

System: Methane-Hydrogen Sulfide

Let Methane be Component 1 and Hydrogen Sulfide Component 2

Experimental Data:

$x_1 = 0.5$ $x_2 = 0.5$

$P = 6000$ psia $T = 160^\circ F = 619.69\ ^\circ R$

$(Z)_{expt.} = 0.8485$

Critical Constants and Other Physical Properties and Parameters of the Compounds Used:

	Comp. 1	Comp. 2
T_c	343.26 °R	672.48 °R
P_c	673.08 psia	1306.47 psia
Z_c	0.290	0.284
ω	0.013	0.100
α^*	0.050	0.000
μ^*	0.000	0.698
$W = \dfrac{Z_c T_c}{P_c}$	0.1479	0.1462
$W^{1/3}$	0.5288	0.5268

$$\left[(T_c)_{11}\ (T_c)_{22}\right]^{\frac{1}{2}} = 480.45$$

From Equation (2-83)

$$\omega' = x_1\omega_1 + x_2\omega_2 = 0.0565$$

From Equation (2-93)

$$Z_c' = x_1(Z_c)_1 + x_2(Z_c)_2 = 0.287$$

From Equation (6-23)

$$\xi_{12} = \frac{1}{4} \alpha_1^* (\mu_2^*)^2 \left[\frac{(T_c)_2}{(T_c)_1}\right]^{\frac{1}{2}} = 0.008524$$

Method 1:

From Equation (2-78)

$$P_c' = x_1(P_c)_1 + x_2(P_c)_2 = 989.78 \text{ psia}$$

From Equation (2-79)

$$T_c' = x_1(T_c)_1 + x_2(T_c)_2 = 507.87\ ^\circ\text{R}$$

$$\omega' = 0.0565$$

$$P_r' = \frac{P}{P_c'} = 6.062 \qquad T_r' = \frac{T}{T_c'} = 1.220$$

From the compressibility charts (Figures 11 and 12)

$$Z^o = 0.818 \qquad Z^1 = -0.060$$

$$Z = Z^o + \omega' Z^1 = 0.815$$

Method 2:

$$\omega' = 0.0565 \qquad Z_c' = 0.287$$

From Equation (6-6)

$$T_c' = x_1^2(T_c)_{11} + 2\, x_1\, x_2 \left[(T_c)_{11}\, (T_c)_{22}\right]^{\frac{1}{2}} + x_2^2(T_c)_{22}$$

$$= 494.17\ ^\circ\text{R}$$

From Equation (6-10)

$$P'_c = \frac{T'_c\ Z'_c}{x_1^2(W_{11}) + 2x_1x_2\left[1/2(W_{11})^{1/3} + 1/2(W_{22})^{1/3}\right]^3 + x_2^2(W_{22})}$$

$$= 964.15 \text{ psia}$$

$$P'_r = \frac{P}{P'_c} = 6.223 \qquad T'_r = \frac{T}{T'_c} = 1.254$$

From the compressibility charts (Figures 11 and 12)

$$Z^o = 0.837 \qquad Z^1 = -0.037$$

$$Z = Z^o - \omega'\ Z^1 = 0.835$$

Method 3:

	Comp. 1	Comp. 2
$\frac{T_c}{P_c}$	0.5100	0.5147
$\left(\frac{T_c}{P_c}\right)^{\frac{1}{2}}$	0.7141	0.7174
$\frac{T_c}{(P_c)^{\frac{1}{2}}}$	13.2277	18.6025

From Equation (2-94)

$$J = 1/3\left[x_1\left(\frac{T_c}{P_c}\right)_1 + x_2\left(\frac{T_c}{P_c}\right)_2\right] + 2/3\left[x_1\left(\frac{T_c}{P_c}\right)_1^{\frac{1}{2}} + x_2\left(\frac{T_c}{P_c}\right)_2^{\frac{1}{2}}\right]^2$$

$$= 0.5124$$

From Equation (2-95)

$$K = x_1 \left(\frac{T_c}{P_c^{\frac{1}{2}}} \right)_1 + x_2 \left(\frac{T_c}{P_c^{\frac{1}{2}}} \right)_2 = 15.9151$$

$$T_c' = \frac{K^2}{J} = 494.32\ {}^{o}R \qquad P_c' = \frac{T_c'}{J} = 964.72 \text{ psia}$$

$$\omega' = 0.0565$$

$$T_r' = \frac{T}{T_c'} = 1.254 \qquad P_r' = \frac{P}{P_c'} = 6.219$$

From the compressibility charts (Figures 11 and 12)

$$Z^o = 0.837 \qquad Z^1 = -0.037$$

$$Z = Z^o + \omega' Z^1 = 0.835$$

Method 4:

$$\omega' = 0.0565 \qquad Z_c' = 0.287$$

From Equation (2-92)

$$\alpha = \frac{P\left[x_1(T_c)_1 + x_2(T_c)_2\right]}{T\left[x_1(P_c)_1 + x_2(P_c)_2\right]} = 4.9689 \qquad \therefore\ \Upsilon = 1.0$$

From Equation (6-18)

$$T_c' = \frac{x_1^2(T_c)_{11}(W_{11}) + 2x_1x_2 \left[(T_c)_{11}(T_c)_{22}\right]^{\frac{1}{2}} \left[\frac{1}{2}(W_{11})^{1/3} + \frac{1}{2}(W_{22})^{1/3}\right]^3 + x_2^2(T_c)_{22}(W_{22})}{x_1^2(W_{11}) + 2x_1x_2 \left[\frac{1}{2}(W_{11})^{1/3} + \frac{1}{2}(W_{22})^{1/3}\right]^3 + x_2^2(W_{22})}$$

$$= 493.49$$

From Equation (6-19)

$$P_c' = \frac{T_c' Z_c'}{x_1^2(W_{11}) + 2x_1x_2 \left[\frac{1}{2}(W_{11})^{1/3} + \frac{1}{2}(W_{22})^{1/3}\right]^3 + x_2^2(W_{22})}$$

$$= 962.83$$

$P_r' = \frac{P}{P_c'} = 6.23$ $\qquad$ $T_r' = \frac{T}{T_c'} = 1.256$

From the compressibility charts (Figures 11 and 12)

$Z^o = 0.838$ $\qquad$ $Z^1 = -0.035$

$Z = Z^o + \omega' Z^1 = 0.836$

Method 5:

$\omega' = 0.0565$ $\qquad$ $Z_c' = 0.287$

$(1 + \xi_{12}) = 1.008524$ $\qquad$ $(1 + \xi_{12})^2 = 1.01712$

$(1 + \xi_{12})^{-\frac{1}{2}} = 0.9958$

From Equation (6-24)

$$T_c' = x_1^2(T_c)_{11} + 2x_1x_2 \left[(T_c)_{11}(T_c)_{22} \right]^{\frac{1}{2}} (1+\xi_{12})^2 + x_2^2(T_c)_{22}$$

$$= 498.28\ {}^{o}R$$

From Equation (6-25)

$$P_c' = \frac{T_c' \; Z_c'}{x_1^2(W_{11}) + 2x_1x_2 \left[\frac{1}{2}(W_{11})^{1/3} + \frac{1}{2}(W_{22})^{1/3} \right]^3 (1+\xi_{12})^{-\frac{1}{2}} + x_2^2 W_{22}}$$

$$= 974.16 \text{ psia}$$

$$P_r' = \frac{P}{P_c'} = 6.16 \qquad\qquad T_r' = \frac{T}{T_c'} = 1.244$$

From the compressibility charts (Figures 11 and 12)

$$Z^o = 0.830 \qquad\qquad Z^1 = -0.042$$

$$Z = Z^o + \omega' \; Z^1 = 0.828$$

Method 6:

$$\omega' = 0.0565 \qquad\qquad Z_c' = 0.287$$

$$\Upsilon = 1.0; \quad (1+\xi_{12}) \frac{4^{\Upsilon - 1}}{2} = 1.013$$

$$(1+\xi_{12})^{-\frac{1}{2}} = 0.9958$$

From Equation (6-30)

$$T_c' = \frac{x_1^2(T_c)_{11}(W_{11}) + 2x_1x_2\left[(T_c)_{11}(T_c)_{22}\right]^{\frac{1}{2}}\left[\frac{1}{2}(W_{11})^{1/3} + \frac{1}{2}(W_{22})^{1/3}\right]^3\left[1+\xi_{12}\right]^{3/2} + x_2^2(T_c)_{22}(W_{22})}{x_1^2(W_{11}) + 2x_1x_2\left[\frac{1}{2}(W_{11})^{1/3} + \frac{1}{2}(W_{22})^{1/3}\right]^3\left[1+\xi_{12}\right]^{-\frac{1}{2}} + x_2^2(W_{22})}$$

$= 497.63\ ^{\circ}R$

From Equation (6-31)

$$P_c' = \frac{T_c'\,Z_c'}{x_1^2(W_{11}) + 2x_1x_2\left[\frac{1}{2}(W_{11})^{1/3} + \frac{1}{2}(W_{22})^{1/3}\right]^3\left[1+\xi_{12}\right]^{-\frac{1}{2}} + x_2^2(W_{22})}$$

$= 972.88$ psia

$$P_r' = \frac{P}{P_c'} = 6.17 \qquad T_r' = \frac{T}{T_c'} = 1.245$$

From the compressibility charts (Figures 11 and 12)

$$Z^o = 0.831 \qquad Z^1 = -0.042$$

$$Z = Z^o + \omega' Z^1 = 0.829$$

Method 7:

$\omega' = 0.0565$ $\qquad\qquad$ $Z_c' = 0.287$

$(1 - \xi_{12}) = 0.991476$

$(1 - \xi_{12})^2 = 0.98302$ $\qquad\qquad$ $(1 - \xi_{12})^{-\frac{1}{2}} = 1.0043$

$$T_c' = \sum_{i=1}^{2} \sum_{j=1}^{2} x_i x_j \left[(T_c)_{ii}(T_c)_{jj}\right]^{\frac{1}{2}} \left[1 - \xi_{ij}\right]^2$$

$$= x_1^2 (T_c)_{11} + 2x_1x_2 \left[(T_c)_{11}(T_c)_{22}\right]^{\frac{1}{2}} \left[1 - \xi_{12}\right]^2 + x_2^2 (T_c)_{22}$$

$$= 490.09\ {}^{\circ}\mathrm{R}$$

$$P_c' = \frac{T_c' \sum_{i=1}^{2} x_i (Z_c)_i}{\sum_{i=1}^{2} \sum_{j=1}^{2} x_i x_j \left[\frac{1}{2}\left(\frac{Z_c T_c}{P_c}\right)_{ii}^{1/3} + \frac{1}{2}\left(\frac{Z_c T_c}{P_c}\right)_{jj}^{1/3}\right]^3 \left[1 - \xi_{ij}\right]^{-\frac{1}{2}}}$$

$$= \frac{T_c' \; ; \; Z_c'}{x_1^2 (W_{11}) + 2x_1x_2 \left[\frac{1}{2}(W_{11})^{1/3} + \frac{1}{2}(W_{22})^{1/3}\right]^3 \left[1 - \xi_{12}\right]^{-\frac{1}{2}} + x_2^2 (W_{22})}$$

$$= 954.25 \text{ psia}$$

$P_r' = \dfrac{P}{P_c'} = 6.288$ $\qquad\qquad$ $T_r' = \dfrac{T}{T_c'} = 1.264$

From the compressibility charts (Figures 11 and 12)

$Z^{o} = 0.844$ $\qquad$ $Z^{1} = -0.034$

$Z = Z^{o} + \omega' Z^{1} = 0.842$

Method 8:

$\omega' = 0.0565$ $\qquad$ $Z_c' = 0.287$

$\gamma = 1.0$ $\qquad$ $(1-\xi_{12})^{\frac{(4\gamma-1)}{2}} = 0.9915$

$(1-\xi_{12})^{-\frac{1}{2}} = 1.0043$

$$T_c' = \left[\frac{\sum_{i=1}^{2}\sum_{j=1}^{2} x_i x_j \left[(T_c)_{ii}(T_c)_{jj}\right]^{\gamma/2} \Bigl[\frac{1}{2}\left(\frac{Z_cT_c}{P_c}\right)_{ii}^{1/3}}{\sum_{i=1}^{2}\sum_{j=1}^{2} x_i x_j \left[\frac{1}{2}\left(\frac{Z_cT_c}{P_c}\right)_{ii}^{1/3} + \frac{1}{2}\left(\frac{Z_cT_c}{P_c}\right)_{jj}^{1/3}\right]^{3}} \right.$$

$$\left. \frac{+\frac{1}{2}\left(\frac{Z_cT_c}{P_c}\right)_{jj}^{1/3}\Bigr]^{3} \left[(1-\xi_{ij})^{\frac{4\gamma-1}{2}}\right]}{\left[1-\xi_{ij}\right]^{-\frac{1}{2}}} \right]^{1/\gamma}$$

$$= \frac{x_1^2 (T_c)_{11}(W_{11}) + 2x_1x_2 \left[(T_c)_{11}(T_c)_{22}\right]^{\frac{1}{2}}}{x_1^2(W_{11}) + 2x_1x_2\left[\frac{1}{2}(W_{11})^{1/3} + \frac{1}{2}(W_{22})^{1/3}\right]^{3}}$$

$$\frac{\left[\frac{1}{2}(W_{11})^{1/3} + \frac{1}{2}(W_{22})^{1/3}\right]^3 \left[1-\xi_{12}\right]^{3/2} + x_2^2(T_c)_{22}(W_{22})}{\left[1-\xi_{12}\right]^{-\frac{1}{2}} + x_2^2(W_{22})}$$

$= 490.45\ ^oR$

$$P_c' = \frac{T_c' \sum_{i-1}^{2} x_i\,(Z_c)_i}{\sum_{i=1}^{2}\sum_{i=1}^{2} x_1 x_j \left[\frac{1}{2}\left(\frac{Z_c T_c}{P_c}\right)_{ii}^{1/3} + \frac{1}{2}\left(\frac{Z_c T_c}{P_c}\right)_{jj}^{1/3}\right]^3 \left[1-\xi_{ij}\right]^{-\frac{1}{2}}}$$

$$= \frac{T_c'\,Z_c'}{x_1^2(W_{11}) + 2x_1x_2\left[\frac{1}{2}(W_{11})^{1/3} + \frac{1}{2}(W_{22})^{1/3}\right]^3 \left[1-\xi_{12}\right]^{-\frac{1}{2}}}$$

$$\overline{+\ x_2^2(W_{22})}$$

$= 954.95$ psia

$P_r' = \frac{P}{P_c'} = 6.283$ $\qquad$ $T_r' = \frac{P}{T_c'} = 1.264$

From the Compressibility charts (Figures 11 and 12)

$Z^o = 0.843$ $\qquad$ $Z^1 = -0.034$

$Z = Z^o + \omega' Z^1 = 0.841$

Summary of Calculations:

$$Z_{\text{expt.}} = 0.8485$$

Method	$(Z)_{cal}$	Error (%)
1	0.815	-4.11
2	0.835	-1.62
3	0.835	-1.62
4	0.836	-1.50
5	0.828	-2.48
6	0.829	-2.35
7	0.842	-0.77
8	0.841	-0.89

TABLE D2

SAMPLE CALCULATION FOR PREPARING MIXTURES OF KNOWN COMPOSITION

Mixture B: Methane (1), Ethane (2) and Hydrogen Sulfide (3)

Nominal Composition: $x_1 = 0.85$, $x_2 = 0.10$ and $x_3 = 0.05$

Volume of Mixing Cell, = 400 cc

Temperature of Cell, = 100°F. = 559.69 °R

Pressure of H_2S filling the Cell, P_3 = 90 psig = 104.2 psia

Compressibility of H_2S at P_3 & T (from ref. 80), $Z_3 = 0.9482$

$$(n_g)_3 = \left(\frac{P_3 V}{ZRT}\right) = 2.5859 \times 10^{-4} \text{ lb mole}$$

Mole of Ethane and Methane in the Final mixture:

$$(n_g)_1 = \left(\frac{x_1}{x_3}\right)(n_g)_3 = 21.98015 \times 10^{-4} \text{ lb mole}$$

$$(n_g)_2 = \left(\frac{x_2}{x_3}\right)(n_g)_3 = 1.29295 \times 10^{-4} \text{ lb mole}$$

Mixing of H_2S and C_2H_6:

For Ethane-Hydrogen Sulfide System: $x_3 = 0.3333$ $x_2 = 0.6667$

$$n_g = (n_g)_2 + (n_g)_3 = 3.87885 \times 10^{-4} \text{ lb mole}$$

$$P_c' = \sum x_i (P_c)_i = 1108 \text{ psia}$$

$$T_c' = \sum x_i (T_c)_i = 631 \ {}^{\circ}R$$

$$Z = \left(\frac{V}{n_g RT}\right) P_c' P_r = 6.7180 P_r$$

The method outlined by Sliepcevich, et al (84) is then used to find $Z = 0.92$ and $P_r = 0.14$

$$P = P_c' \cdot P_r = 155 \text{ psia}$$

The final mixing pressure of H_2S, C_2H_6 and CH_4 can be similarly calculated and found to be 982 psia.

TABLE D3

SAMPLE CALCULATION OF COMPRESSIBILITY FACTOR OF GAS FROM EXPERIMENTAL DATA

Methane Sample #3

Gross gas volume (volume of mercury withdrawn from the cell while introducing gas), V_1 = 406.95 cc

Heise gauge pressure = 1000 psig

High pressure cell bath temperature, $T = 101.4\ ^{o}F$

$= 561.09\ ^{o}R$

Room temperature = 74 ^{o}F

Atmospheric pressure 73.35 cm Hg

$$= \begin{array}{c|c|c|c} 73.35 & 13.5381 & & 0.19337 \\ \hline & & 13.5955 & \end{array} = 14.12 \text{ psi}$$

Where 13.5381 and 13.5955 are densities of mercury at 74 ^{o}F and 32 ^{o}F respectively, and 0.19337 is the conversion factor for converting 1 cm Hg at 32 ^{o}F to psi.

Pressure correction due to difference in elevation between Heise gauge and the high pressure cell = +12 psi

Pressure, P = 1000 + 12 = 1012 psig = 1026.12 psia

Correction of Gross Volume

1) Correction due to pressure and temperature difference between cell and mercury pump

$$\Delta V_1 = V_1 \left[\left(1 + \beta_1 P_1\right) \left(\frac{V_2}{V_1}\right) \left(1 - \beta_2 P_2\right) - 1 \right] = 1.31 \text{ cc} \qquad (7\text{-}1)$$

where P_1 = 3000 psig

T_1 = 74 °F

$\beta_1 = 2.762 \times 10^{-7} \frac{cc}{cc\ psi}$ (from Table E2)

v_1 = 1.001413 (from Table E3)

P_2 = 1012 psig

T_2 = 101.40 °F

$\beta_2 = 2.844 \times 10^{-7} \frac{cc}{cc\ psi}$ (from Table E2)

v_2 = 1.004180 (from Table E3)

2) Correction Due to Cell Expansion

$$\Delta V_2 = (\beta_3 - \beta_2) \cdot V_{cell} \cdot P_2 = 0.11\ cc \tag{7-2}$$

where β_3 = the combined correction factor for cell expansion and mercury compression

$= 5.12 \times 10^{-7} \frac{cc}{cc\ psi}$ (from Figure E1)

V_{cell} = volume of cell and the line connecting cell to the pump

= 504 cc

3) Correction Due to Compression of Mercury Remaining in the Cell

$$\Delta V_3 = \beta_2 (V_{cell} - V_1)\ P_2 = 0.03\ cc \tag{7-3}$$

Total correction $\Delta V = \Delta V_1 + \Delta V_2 + \Delta V_3$ = 1.45 cc

Correct volume of gas $V = V_1 + \Delta V$ = 408.40 cc

Pressure, P = 2000 + 12 = 2012 psig = 2026.12 psia

Gross volume of mercury introduced into the cell = 212.53 cc

ΔV_1, ΔV_2 and ΔV_3 are found by using equations (7-1), (7-2) and (7-3) respectively as follows:

$\Delta V_1 = 0.61$ cc $\quad \Delta V_2 = 0.11$ cc $\quad \Delta V_3 = 0.03$ cc

$$\text{Corrected volume} = (408.40) - (212.53 + 0.61 - 0.11 - 0.03)$$
$$= 195.40 \text{ cc}$$

The correct volumes at any other pressures were found similarly.

Compressibility Factor

Mole of gas as determined by the Bean unit

$$n_g = 27.2432 \times 10^{-6} \text{ lb mole}$$

Then by using Equation (7-5) the compressibility factor of methane at $P = 1026.2$ psia, and $T = 101.40\ ^{\circ}F$ was found to be 0.9043.

APPENDIX E

CALIBRATION AND CORRECTION DATA

TABLE E1

CORRECTION FOR CELL EXPANSION AND MERCURY COMPRESSION

Pressure Psia	Correction $x10^7$ vol/vol psi			
	100.6 °F	130.7 °F	160.2 °F	Average
1026	4.59	5.58	5.19	5.12
2026	4.45	5.05	4.85	4.78
3026	4.36	4.82	4.76	4.65
4026	4.41	4.71	4.71	4.61
5026	4.36	4.68	4.64	4.56
6026	4.40	4.63	4.63	4.55
7026	4.39	4.62	4.62	4.54

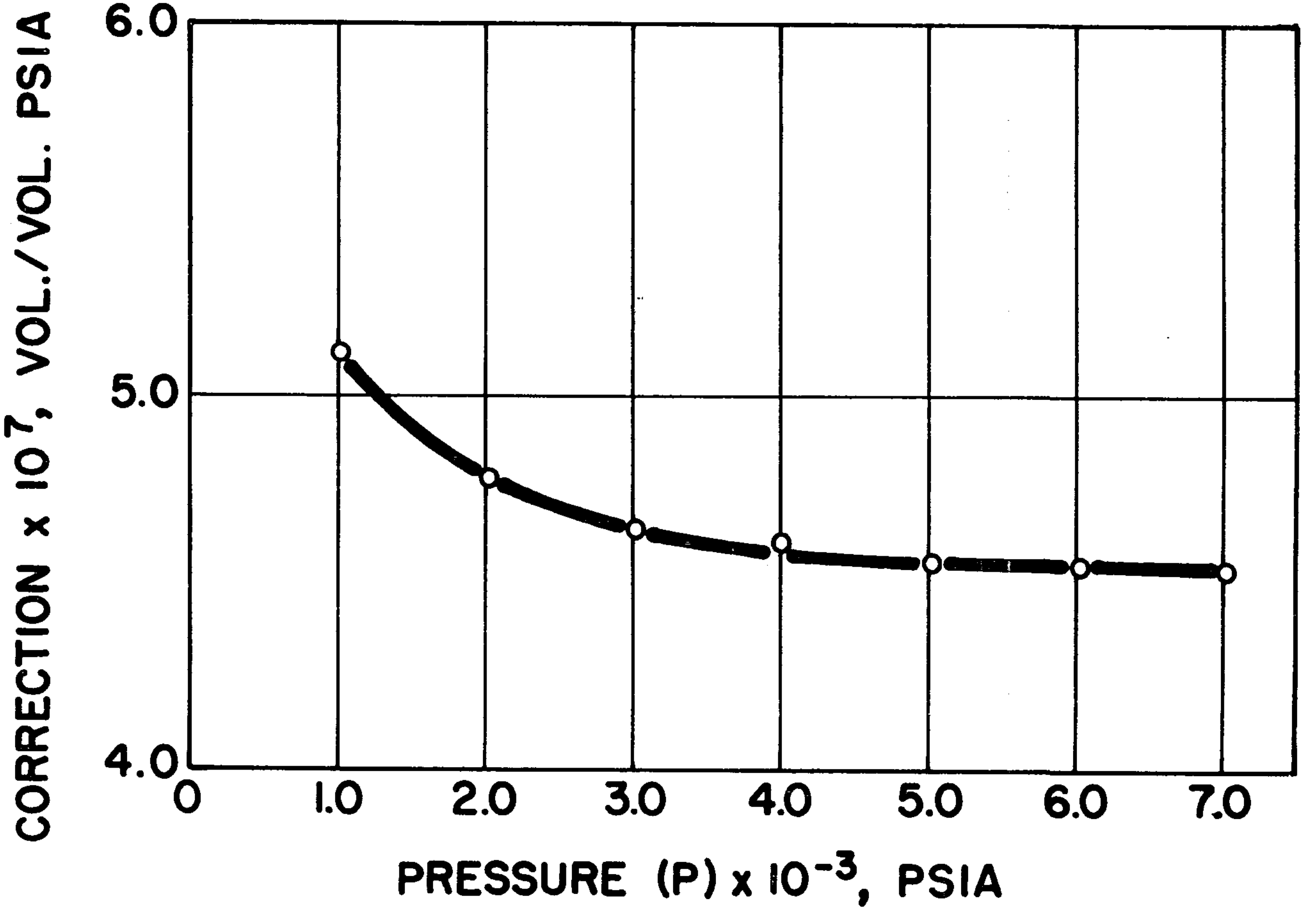

FIGURE E1

CORRECTION FOR CELL EXPANSION AND MERCURY COMPRESSION

TABLE E2

COMPRESSIBILITY OF MERCURY

Temperature $^{\circ}F$	$\beta \times 10^7$ (vol/vol psi)	Temperature $^{\circ}F$	$\beta \times 10^7$ (vol/vol psi)
60	2.72	120	2.90
70	2.75	130	2.93
80	2.78	140	2.96
90	2.81	150	3.00
100	2.84	160	3.03
110	2.87	170	3.06

TABLE E3

VOLUME OF MERCURY AT INDICATED TEMPERATURE RELATIVE TO VOLUME AT 60 °F

Temperature °F	Relative Volume v	Temperature °F	Relative Volume v
60	1.000000	120	1.006060
70	1.001009	130	1.007072
80	1.002018	140	1.008084
90	1.003028	150	1.009097
100	1.004038	160	1.010110
110	1.005049	170	1.011124

TABLE E4

SUMMARY OF CALIBRATION DATA

Volume of burette (1)	994.07 cc
Volume of high pressure cell	501.50 cc
Volume of line connecting mercury pump to the high pressure cell	2.37 cc
Volume of line connecting high pressure cell to the burette (1)	4.83 cc
Estimated pressure difference between the high pressure cell and the Heise gauge	12 psi
Heise gauge pressure correction	none
Thermometer reading correction	none

APPENDIX F

EXPERIMENTAL RESULTS

TABLE F1

COMPARISON OF THE EXPERIMENTAL METHANE COMPRESSIBILITY FACTORS (Z) WITH THOSE OF SAGE, ET AL (79)

Sample A

Pressure Psia	Z at 100.9 °F		Z at 130.2 °F		Z at 159.4 °F	
	This work	Sage, et al	This work	Sage, et al	This work	Sage, et al
1026	0.9051	0.9064	0.9223	0.9247	0.9367	0.9399
2026	0.8576	0.8537	0.8859	0.8852	0.9115	0.9105
3026	0.8641	0.8577	0.8962	0.8899	0.9173	0.9170
4026	0.9149	0.9082	0.9398	0.9330	0.9597	0.9546
5026	0.9917	0.9841	1.0071	0.9990	1.0194	1.0135
6026	1.0785	1.0707	1.0855	1.0783	1.0910	1.0859
7026	1.1700	1.1627	1.1693	1.1636	1.1694	1.1636

TABLE F1--Continued

Sample B

Pressure Psia	Z at 101.4 °F		Z at 130.5 °F		Z at 159.3 °F	
	This work	Sage, et al	This work	Sage, et al	This work	Sage, et al
1026	0.9048	0.9067	0.9224	0.9249	0.9359	0.9398
2026	0.8576	0.8542	0.8858	0.8855	0.9118	0.9104
3026	0.8640	0.8582	0.8894	0.8902	0.9153	0.9168
4026	0.9149	0.9086	0.9308	0.9333	0.9529	0.9545
5026	0.9912	0.9843	0.9953	0.9992	1.0138	1.0134
6026	1.0782	1.0709	1.0721	1.0783	1.0846	1.0858
7026	1.1697	1.1627	1.1548	1.1636	1.1615	1.1636

TABLE F1--Continued

Sample C

Pressure Psia	Z at 101.4 °F		Z at 131.6 °F		Z at 160.1 °F	
	This work	Sage, et al	This work	Sage, et al	This work	Sage, et al
1026	0.9043	0.9067	0.9217	0.9254	0.9346	0.9402
2026	0.8543	0.8542	0.8845	0.8864	0.9096	0.9111
3026	0.8598	0.8582	0.8874	0.8912	0.9139	0.9176
4026	0.9109	0.9086	0.9303	0.9341	0.9508	0.9551
5026	0.9835	0.9843	0.9953	0.9997	1.0106	1.0139
6026	1.0704	1.0709	1.0727	1.0786	1.0797	1.0860
7026	1.1600	1.1627	1.1544	1.1636	1.1556	1.1636

TABLE F1--Continued

Sample D

Pressure Psia	Z at 101.7 °F		Z at 130.5 °F		Z at 161.2 °F	
	This work	Sage, et al	This work	Sage, et al	This work	Sage, et al
1026	0.9069	0.9069	0.9222	0.9248	0.9370	0.9407
2026	0.8573	0.8546	0.8835	0.8854	0.9096	0.9119
3026	0.8631	0.8586	0.8886	0.8901	0.9132	0.9174
4026	0.9135	0.9089	0.9311	0.9332	0.9486	0.9558
5026	0.9889	0.9845	0.9967	0.9991	1.0053	1.0144
6026	1.0761	1.0709	1.0742	1.0783	1.0758	1.0863
7026	1.1671	1.1628	1.1582	1.1636	1.1505	1.1636

TABLE F2

ERROR ANALYSIS OF METHANE COMPRESSIBILITY FACTORS AT THE EXPERIMENTAL PRESSURES

T °F	Root Mean Square Deviation			
	Sample A	Sample B	Sample C	Sample D
100.9	0.0063			
130.2	0.0059			
159.4	0.0043			
All Temperatures	0.0056			
101.4		0.0058		
130.5		0.0045		
159.3		0.0020		
All Temperatures		0.0044		
101.4			0.0017	
131.6			0.0051	
160.1			0.0051	
All Temperatures			0.0043	
101.7				0.0040
130.5				0.0030
161.2				0.0080
All Temperatures				0.0055

Root Mean Square Deviation of Compressibility Factors of All 4 Samples at the Experimental Pressures and Temperatures = 0.0050

TABLE F3

RESULTS OF CHROMATOGRAPHIC COMPOSITION ANALYSIS

(ALL COMPOSITIONS ARE IN MOLE FRACTION)

Components	Mixture A	Mixture B	Mixture C	Mixture D	Mixture E
CH_4	0.871	0.831	0.836	0.800	0.713
C_2H_6	0.064	0.071	0.117	0.107	0.090
H_2S	0.065	0.098	0.047	0.093	0.197

TABLE F4

THE EXPERIMENTAL COMPRESSIBILITY FACTORS OF THE METHANE--ETHANE--HYDROGEN SULFIDE SYSTEM

	Mixture A			Mixture B		
Pressure Psia	Z					
	101.5 °F	130.9 °F	160.0 °F	101.8 °F	131.7 °F	161.1 °F
1026	0.886	0.907	0.920	0.872	0.897	0.915
2026	0.811	0.852	0.883	0.790	0.833	0.863
3026	0.813	0.851	0.880	0.791	0.827	0.860
4026	0.869	0.898	0.918	0.851	0.874	0.898
5026	0.951	0.969	0.982	0.937	0.947	0.961
6026	1.044	1.053	1.056	1.032	1.032	1.037
7026	1.141	1.141	1.138	1.130	1.122	1.120

TABLE F4--Continued

	Mixture C			Mixture D		
Pressure Psia	Z					
	101.0 °F	129.7 °F	160.2 °F	101.7 °F	130.6 °F	160.3 °F
1026	0.865	0.887*	0.911*	0.851	0.874	0.896
2026	0.785	0.825	0.861	0.761	0.804	0.840
3026	0.789	0.825	0.859	0.766	0.803	0.837
4026	0.853	0.876	0.900	0.833	0.855	0.880
5026	0.942	0.954	0.967	0.923	0.934	0.948
6026	1.039	1.042	1.047	1.022	1.023	1.029
7026	1.141	1.134	1.131	1.124	1.116	1.113

*at this point P = 1036 psia

Mixture E

Z		
101.8 °F	130.5 °F	161.0 °F
0.830	0.856	0.880
0.714	0.762	0.807
0.717	0.754	0.794
0.786	0.808	0.835
0.882	0.889	0.905
0.982	0.979	0.985
1.085	1.072	1.071

APPENDIX G

SUMMARY OF CORRELATED DATA

TABLE G1

SUMMARY OF CALCULATED COMPRESSIBILITY FACTORS FOR VARIOUS SYSTEMS

System	Mole Frac. 1st Component	Mole Frac. 2nd Component	Mole Frac. 3rd Component
CH_4 - C_2H_6 (79)	0.800	0.200	
	0.500	0.500	
	0.200	0.800	
CH_4 - C_3H_8 (79)	0.800	0.200	
	0.500	0.500	
	0.200	0.800	
CH_4 - nC_4H_{10} (79)	0.800	0.200	
	0.500	0.500	
	0.200	0.800	
CH_4 - nC_5H_{12} (79)	0.800	0.200	
	0.500	0.500	
	0.200	0.800	
C_2H_6 - CO_2 (80)	0.800	0.200	
	0.500	0.500	
	0.200	0.800	
C_3H_8 - CO_2 (80)	0.800	0.200	
	0.500	0.500	
	0.200	0.800	
n-C_4H_{10} - CO_2 (80)	0.800	0.200	
	0.500	0.500	
	0.200	0.800	
CH_4 - H_2S (80)	0.800	0.200	
	0.500	0.500	
	0.200	0.800	
nC_5H_{12} - H_2S (80)	0.800	0.200	
	0.500	0.500	
	0.200	0.800	
CH_4 - C_2H_6 - H_2S*	0.871	0.064	0.065
	0.831	0.071	0.098
	0.836	0.117	0.047
	0.800	0.107	0.093
	0.713	0.090	0.197

*This work

TABLE G1--Continued

Temperature Range °F	Pressure Range Psia	Number of Points Observed	Method #1		Method #2	
			Deviation, Percent			
			Abs.**	Std.***	Abs.	Std.
70-250	400-3000	28	2.28	2.74	2.94	3.48
70-250	400-3000	27	2.78	3.07	4.30	4.78
70-250	400-3000	28	2.38	4.64	3.13	4.43
100-280	400-8000	44	1.94	2.10	3.00	3.33
100-280	400-8000	42	2.82	3.22	4.94	6.01
100-280	800-8000	42	1.92	2.53	3.27	4.60
100-280	400-7000	32	3.73	4.20	5.99	6.50
100-280	1500-7000	25	3.08	4.34	6.83	8.56
100-280	800-7000	32	1.32	1.84	2.91	3.63
100-280	400-5000	22	2.84	3.21	6.00	6.41
100-280	400-5000	17	2.14	3.13	7.55	8.58
160-280	800-5000	19	1.01	1.32	3.38	4.03
100-280	400-9000	48	4.48	6.13	3.73	5.88
100-280	400-9000	48	6.93	8.68	6.05	8.81
100-280	400-9000	48	4.86	5.86	4.31	5.48
100-280	400-7000	39	7.10	7.97	3.56	4.40
100-280	400-7000	40	10.38	12.45	7.90	10.47
100-280	400-8000	44	8.05	11.00	6.83	10.59
160-340	400-6000	34	8.54	8.87	2.85	3.33
160-340	400-7000	36	11.56	13.00	5.10	5.73
160-340	400-8000	44	7.19	9.28	4.86	6.16
100-280	400-10000	52	2.05	2.28	0.86	0.97
100-280	400-10000	51	4.02	4.83	1.66	2.02
100-280	400-10000	48	2.17	3.01	1.18	1.73
220-340	800-7000	28	14.27	14.32	2.07	2.22
160-340	400-7000	36	21.04	21.48	4.64	5.17
160-340	400-7000	36	11.89	13.76	3.66	4.61
100-160	1026-7026	21	1.72	1.82	0.94	1.03
100-160	1026-7026	21	2.00	2.13	0.90	1.00
100-160	1026-7026	21	0.37	0.47	0.52	0.59
100-160	1026-7026	21	0.85	0.98	0.45	0.53
100-160	1026-7026	21	3.02	3.31	0.97	1.22

**Absolute
***Standard

TABLE G1--Continued

Method #3		Method #4		Method #5		Method #6	
Deviation, Percent							
Abs.	Std.	Abs.	Std.	Abs.	Std.	Abs.	Std.
1.99	2.36	1.69	2.12				
2.05	2.29	1.53	1.82				
2.59	5.12	2.77	5.76				
0.71	0.81	0.20	0.28				
0.79	1.12	0.92	1.14				
0.79	1.13	0.89	1.10				
1.49	2.23	1.47	1.63				
0.55	0.72	1.77	1.83				
0.87	1.37	0.99	1.33				
0.83	0.93	2.53	2.79				
1.03	1.43	3.06	3.29				
0.77	1.16	1.40	1.64				
3.53	5.54	3.74	5.90				
5.69	8.19	6.08	8.84				
4.06	5.18	4.33	5.50				
4.20	5.24	5.04	6.37				
8.83	11.68	10.78	14.39				
7.37	11.06	8.70	12.38				
4.79	6.23	6.09	7.93				
7.71	8.50	10.20	11.33				
6.85	8.52	9.56	11.84				
0.89	1.00	1.13	1.00	1.25	1.38	1.38	1.51
1.72	2.10	1.98	2.29	2.44	2.91	2.76	3.17
1.20	1.75	1.13	1.70	1.50	2.10	1.52	2.17
1.93	2.20	3.51	3.83	2.45	2.70	3.85	4.18
4.29	4.79	7.41	8.85	5.34	5.84	8.26	9.62
3.43	4.40	6.69	8.63	4.21	5.40	7.63	9.70
1.32	1.40	1.42	1.50	1.15	1.23	1.61	1.68
1.30	1.41	1.42	1.51	1.20	1.30	1.71	1.80
0.29	0.35	0.39	0.45	0.37	0.45	0.48	0.57
0.41	0.49	0.42	0.51	0.35	0.42	0.65	0.77
1.40	1.67	1.57	1.78	1.55	1.81	2.17	2.37

TABLE G1--Continued

Method #7		Method #8	
Deviation, Percent			
Abs.	Std.	Abs.	Std.
0.51	0.59	0.66	0.80
0.93	1.19	1.22	1.48
1.01	1.53	0.85	1.35
1.65	1.78	3.14	3.45
4.09	4.52	6.68	8.06
3.22	3.88	5.92	7.80
0.74	0.85	1.23	1.31
0.62	0.72	1.13	1.23
0.67	0.73	0.32	0.36
0.69	0.76	0.26	0.33
0.56	0.74	0.98	1.22

TABLE G1--Continued

Method #1			Method #2		
Maximum Deviation, %	P. M. D.****		Maximum Deviation, %	P. M. D.	
	P_r	T_r		P_r	T_r
+5.75	3.6765	1.3771	+7.24	3.6767	1.3911
+5.50	2.8965	1.3205	+8.19	2.8962	1.2024
-21.59	1.4265	1.0417	-14.42	1.4263	1.0496
+4.30	3.0221	1.3722	+7.39	3.0552	1.4013
+9.68	2.3256	1.2280	+16.65	2.3588	1.2611
+7.59	1.5918	1.1302	+14.13	1.6042	1.1464
+8.04	3.0836	1.4487	+12.34	3.1757	1.4954
+13.55	2.4510	1.2261	+23.45	2.5451	1.2750
-4.97	6.9517	0.8219	+10.12	1.7740	1.0181
+6.08	3.1437	1.5315	+10.12	4.9759	1.4546
+8.52	3.4423	1.2442	+18.74	3.6846	1.3053
-3.61	7.6075	0.8315	+9.84	1.9740	1.0169
-28.48	1.2811	1.0188	-28.17	1.3135	1.0188
-33.22	1.1242	1.0200	-43.60	1.1680	1.0200
-18.07	1.5024	1.0211	-16.90	1.5392	1.0211
-21.71	1.1303	0.9649	-15.70	1.4890	1.0598
-37.51	1.1848	1.0213	-43.37	1.2860	1.0237
-48.67	1.0202	0.9796	-51.22	1.0767	0.9812
-12.85	1.5267	1.0247	-9.38	1.3244	1.0289
-20.64	1.2330	0.9439	-11.08	2.1024	1.0425
-22.25	1.5512	1.0481	-19.74	1.6920	1.0533
-5.21	3.7519	1.3677	-2.06	3.8294	1.3977
-17.16	2.0212	1.1018	-6.90	2.0740	1.1323
-11.15	1.6958	1.0213	-7.21	1.7192	1.0363
-16.23	7.6640	0.8380	-5.56	7.1182	0.8396
-33.34	1.1142	0.9744	-11.09	1.1117	0.8983
-17.55	1.3128	0.9611	-15.41	1.5164	1.0483
-2.71	2.8281	1.4848	-1.65	4.2638	1.5813
-3.62	2.7470	1.4387	-1.85	2.7842	1.4609
-1.26	2.8663	1.4640	0.98	5.7382	1.5575
-1.92	2.7542	1.4176	0.98	1.4135	1.5141
-6.16	3.7785	1.3156	-2.86	3.8667	1.3451

****Point at which maximum deviation occurs

TABLE Gl--Continued

Method #3			Method #4		
Maximum Deviation, %	P. M. D.		Maximum Deviation, %	P. M. D.	
	P_r	T_r		P_r	T_r
+4.82	3.6241	1.3700	+4.47	3.6132	1.3670
+4.38	2.8403	1.3112	+3.94	2.8297	1.3079
-24.18	1.4108	1.0375	-26.70	1.4040	1.0332
+2.01	1.4759	1.3481	+0.67	2.9180	1.3384
+3.61	2.2600	1.2014	-3.74	2.2314	1.0775
+3.02	0.6274	1.0186	-3.12	1.5536	1.0122
+5.01	1.2011	1.4034	+3.06	0.5635	1.3268
+1.93	2.3836	1.1821	-3.12	3.1090	1.0641
+5.56	6.8649	0.8935	+4.97	6.7959	0.8889
+1.76	1.5394	1.4623	-5.04	4.4583	1.1771
+3.58	0.6779	1.1831	-5.87	3.2811	1.0680
+3.53	7.5801	0.8901	+3.61	7.4712	0.8841
-26.36	1.3141	1.0208	-28.28	1.3133	1.0187
-40.01	1.1691	1.0234	-43.73	1.1677	1.0197
-16.30	1.5404	1.0237	-16.94	1.5390	1.0210
-18.90	1.4821	1.0554	-23.64	1.4738	1.0490
-49.25	1.2764	1.0169	-52.91	1.2616	1.0043
-51.88	1.0716	0.9771	-53.38	1.0605	0.9665
-24.22	1.3092	1.0167	-29.21	1.2956	1.0065
-18.93	2.0607	1.1113	-26.79	2.0185	1.0892
-25.76	1.6684	1.0380	-35.98	1.0868	1.0148
-2.15	3.8274	1.3969	-2.35	1.8996	1.3867
-7.20	2.0725	1.1315	-7.22	2.0723	1.1314
-7.36	1.7185	1.0358	-8.05	1.7150	1.0338
-6.22	7.1262	0.8360	-9.37	7.0055	0.8264
-10.18	1.1180	0.8938	-23.61	1.0752	1.0222
-15.65	1.5301	1.0482	-28.37	1.4746	1.0194
-2.11	4.2421	1.5727	-2.16	4.2386	1.5719
-2.48	2.7698	1.4529	-2.53	2.7674	1.4521
-0.91	2.8625	1.4680	-1.01	2.8584	1.4666
-0.90	2.7711	1.4289	-0.97	2.7680	1.4280
-3.63	3.8483	1.3382	-3.67	3.8459	1.3379

TABLE G1--Continued

Method #5			Method #6		
Maximum Deviation, %	P. M. D.		Maximum Deviation, %	P. M. D.	
	P_r	T_r		P_r	T_r
-3.04	3.7992	1.3886	-2.90	3.8030	1.3900
-10.09	2.0526	1.1230	-10.42	2.0508	1.1220
-8.74	1.7093	1.0318	-9.47	1.7050	1.0292
-6.82	7.0837	0.8362	-9.71	6.9800	0.8240
-11.85	1.1023	0.8922	-25.26	1.0669	1.0159
-18.85	1.5070	1.0434	-30.44	1.4631	1.0130
-1.88	4.2502	1.5770	-2.38	4.2260	1.5680
-2.27	2.7715	1.4553	-2.93	2.7556	1.4470
+0.80	5.7248	1.5544	-1.21	2.8523	1.4640
+0.83	1.4075	1.5087	-1.37	2.7570	1.4233
-3.83	3.8373	1.3366	-4.58	3.8182	1.3300

TABLE G1--Continued

Method #7			Method #8		
Maximum Deviation, %	P. M. D.		Maximum Deviation, %	P. M. D.	
	P_r	T_r		P_r	T_r
-1.21	2.5732	1.4069	-1.86	1.2675	1.3860
-3.84	2.0958	1.1418	-4.12	2.0942	1.1409
-5.58	1.7291	1.0409	-6.43	1.7250	1.0384
-4.23	7.1528	0.8431	-8.78	7.0313	0.8287
-10.41	1.1211	0.9044	-21.11	1.0836	1.0285
-12.13	1.5258	1.0532	-26.75	1.4862	1.0259
-1.41	4.2774	1.5855	-1.94	4.2513	1.5758
-1.43	2.7968	1.4665	-2.14	2.7792	1.4572
1.16	5.7516	1.5605	-0.80	2.8645	1.4692
1.18	5.5705	1.5196	-0.61	5.5211	1.4324
-1.88	3.8962	1.3536	-2.75	3.8739	1.3459

TABLE G2

COMPARISON OF STANDARD DEVIATIONS OF PREDICTED COMPRESSIBILITY FACTORS OF DIFFERENT SYSTEMS FROM THE EXPERIMENTAL VALUES

Systems	Number of Points Observed	Standard Deviation, Per Cent		
		PREDICTION METHOD		
		#1	#2	#3
Binary Mixtures of Hydrocarbons	359	3.14	5.41	2.03
	(358)*	2.93	5.34	1.58
Binary Mixtures of Hydrocarbons and Carbon Dioxide	381	9.39	7.27	8.11
		7.97 (355)*	4.68 (353)*	5.50 (350)*
Binary Mixtures of Hydrocarbons and Hydrogen Sulfide	251	11.13	3.00	2.88
Ternary Mixtures of Hydrocarbons and Hydrogen Sulfide	105	2.00	0.92	1.19

Total Number of Points Observed 1096

*The number in the parenthesis is used to calculate revised standard deviation.

TABLE G2--Continued

Standard Deviation, Per Cent					
PREDICTION METHOD					Recommended Method
#4	#5	#6	#7	#8	
2.29 1.81					#3
9.78 6.83 (347)*					$\#2^{**}$ $\#3^{***}$
4.74	3.58	5.37	2.50	4.24	#7 $\#3^{***}$
1.28	1.17	1.59	0.76	0.95	#7 $\#3^{***}$

*The number in the parenthesis is used to calculate revised standard deviation.

**May be used excluding the region $0.9 \leqslant T_r \leqslant 1.15$ and $0.8 \leqslant P_r \leqslant 2.0$ for the best result.

***Simpler method giving nearly equal accuracy. This method may be used for routine calculation.

TABLE G3

EXPERIMENTAL AND PREDICTED (BY METHOD #7) COMPRESSIBILITY FACTORS (Z) OF MIXTURE E OF THE METHANE-ETHANE-HYDROGEN SULFIDE SYSTEM

Pressure Psia	Z at 101.8 °F	
	Experimental	Predicted
1026	0.8300	0.8285
2026	0.7140	0.7048
3026	0.7170	0.7035
4026	0.7860	0.7757
5026	0.8820	0.8726
6026	0.9820	0.9729
7026	1.0850	1.0746

TABLE G3--Continued

Z at 130.5 °F		Z at 161.0 °F	
Experimental	Predicted	Experimental	Predicted
0.8560	0.8600	0.8800	0.8851
0.7620	0.7584	0.8070	0.8057
0.7540	0.7508	0.7940	0.7942
0.8080	0.8058	0.8350	0.8393
0.8890	0.8873	0.9050	0.9068
0.9790	0.9790	0.9850	0.9867
1.0720	1.0741	1.0710	1.0758