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FOR LEAN NATURAL GAS - CARBON DIOXIDE
MIXTURES AT HIGH PRESSURE

A DISSERTATION
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THOMAS S. BUXTON
Norman, Oklahoma

1965

THE PREDICTION OF THE COMPRESSIBILITY FACTOR
FOR LEAN NATURAL GAS - CARBON DIOXIDE
MIXTURES AT HIGH PRESSURE

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THE PREDICTION OF THE COMPRESSIBILITY FACTOR
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MIXTURES AT HIGH PRESSURE

CHAPTER I

INTRODUCTION

The prediction of the pressure-volume-temperature behavior of fluids has occupied the attention of many scientists and engineers during the past century. As a consequence, many methods of making these predictions have been proposed. These include:

1. Equations relating pressure, volume, and temperature which contain one or more empirical constants for which numerical values have been developed for specific systems.
2. Equations expressed in terms of the known microscopic parameters affecting gas behavior. These are relatively rigorous for simple gases consisting of substantially spherical molecules.
3. Correlations for pure gases that utilize some form of the principle of "corresponding states." More recent advances in this area have included

additional parameters to differentiate between the molecular characteristics (size, shape, and polarity). These additional parameters have been expressed in terms of both the macroscopic and microscopic properties of the gas.

4. Various combinations of the above, plus the use of the "pseudocritical concept," in an attempt to extend pure gas methods to gas mixtures.

A careful study of past work has shown that practically all of the microscopic parameters capable of characterizing a pure gas have been included in one form or another. What has evolved, therefore, is at least a semi-quantitative understanding of the relationships which govern pure gas behavior.

Improvements in predicting the behavior of mixtures roughly parallel that for pure gases. Unfortunately, it has been proven impractical to quantitatively characterize gas mixtures entirely by the use of microscopic factors even though they contribute to our knowledge of such systems. Since mixtures occur in an almost infinite number of forms, characterization necessarily becomes semi-empirical at some point. It has been shown that a macroscopic approach is more desirable for complex mixtures, providing that the macroscopic parameter is actually characteristic of the molecular system.

Systems of the type investigated in this study represent a particularly difficult problem for they consist of molecules with widely varying characteristics. All attempts

to predict the properties of such systems assume that the total mixture behavior can be characterized from that of the individual constituents through the use of various "combination rules" in conjunction with some form of the principle of corresponding states.

It has been shown in early studies that the gas compressibility factor, Z , a correlation constant, could be simply related to the molal average system properties of natural gas mixtures provided that the mixtures consisted almost entirely of relatively simple molecules of a single homologous series. As problems developed with this method, additional correlating parameters were added which have been commonly called "third parameters." These have developed from both theoretical and empirical origins. Many of these parameters are related and are actually equivalent.

In recent years combination rules have been developed which are based on the formal use of the microscopic parameters. These are significant and of importance. Unfortunately, the final form of the rules all depend on simplifying assumptions. These assumptions were usually made so that they were compatible with the system being studied. As a result, the final form of the rules differed even though all were working from the same theoretical premise. The only way one can truly ascertain how good (or bad) a given rule is for a given type of mixture is by testing it against available data.

At the present time, no "proven" correlation exists for the natural gas-carbon dioxide system under study even though one of the above, or some combination thereof, must certainly have utility. Therefore, the primary purpose of this study has been to develop a prediction method for this system that has proven reliance, is compatible with our theoretical knowledge of gas behavior, and is practical enough to have widespread application. A necessary part of this study has been a careful appraisal of existing combination rules to determine their utility to the system in question.

CHAPTER II

THEORETICAL BACKGROUND - PURE GASES

While the purpose of this study was to provide a means for predicting the relationship between pressure, volume, and temperature for natural gas mixtures, a review of the developments that have been made for pure gases was deemed necessary. This necessity arises from the fact that prediction techniques for mixtures are all based on methods devised for pure gases. The assumptions and limitations of the single component gas methods are also present in those methods extended to mixtures. The purpose of this chapter is not to consider all of the work on pure gases but only that which has been utilized in the prediction techniques for mixtures.

A. Equations of State

Many attempts have been made to express the relation between pressure, volume, and temperature as a single equation of state. One of the earliest and most notable is the equation of van der Waals (68). To allow for the finite size of the molecules and to correct the pressure term to represent the influence of the forces of attraction between molecules, van der Waals modified the ideal gas equation and arrived at

$$(P + a/\underline{V}^2)(\underline{V} - b) = RT \quad (2-1)$$

where the $a/\underline{V}^2$ is the correction for the attractive forces and b is the correction for the finite size of the molecules. The pressure, volume, and temperature are represented by P , $\underline{V}$, and T respectively, and R is the universal gas constant.

The empirical equation of state which was originally proposed by Kammerlingh-Onnes and has become known as the virial equation of state may be written

$$P\underline{V}/RT = 1 + B(T)/\underline{V} + C(T)/\underline{V}^2 + \dots \quad (2-2)$$

where $B(T)$, $C(T)$, etc. are temperature dependent coefficients (21). This expression, although it has an empirical origin, has been used extensively to increase our knowledge of gas behavior. This has been possible since it may be related to the theoretical expressions deduced for the equation of state.

Based on the theorem of the virial, Fowler (12) has shown that the real gas law for moderate pressures is given in a general form by the equation

$$P\underline{V}/RT = 1 - \frac{2\pi N_0}{V} \int_0^\infty r^2 (e^{-\phi(r)/kT} - 1) dr \quad (2-3)$$

in which $\phi(r)$ is defined as the potential energy of the molecules at a distance r . The integral in this expression comes from the second virial in the deduction of the gas law.

For moderate pressures, the terms in the virial equation beyond $B(T)$ may be neglected. When the abbreviated form of the virial equation is compared with the expression derived

by Fowler, $B(T)$ may be related to the integral which was derived from the second virial. Hence, $B(T)$ has become known as the second virial coefficient, $C(T)$ the third virial coefficient, etc. By relating empirically determined second virial coefficients to the expression for the second virial, much has been learned about the microscopic behavior of gases. Unfortunately, our present knowledge of the microscopic properties can only be used for the prediction of the second virial for a limited number of simple gases.

Many more equations of state have been proposed. In general, the ability of such equations to represent the volumetric behavior of gases is usually dependent on the number of adjustable constants. While these equations are useful for representing observed data, they are of little use in predicting the properties of uninvestigated gases.

In engineering application, the usual method of expressing the deviation from ideal gas behavior is through the use of the compressibility factor given by

$$Z = PV/RT, \quad (2-4)$$

Generalized charts represent the most practical method of predicting the volumetric behavior of gases. These charts are constructed from known data for one or more substances by plotting the compressibility factor as a function of reduced temperatures and pressures. The basis for plotting such generalized charts rests on the principle of corresponding states.

B. The Principle of Corresponding States

The principle of corresponding states forms the basis for all of the generalized compressibility factor charts in use today. The principle asserts that when the reduced temperatures and reduced pressures of two gases are the same, the reduced volumes will also be the same. The reduced quantities are defined as follows:

$$\text{reduced temperature, } T_r = T/T_c \quad (2-5)$$

$$\text{reduced pressure, } P_r = P/P_c \quad (2-6)$$

$$\text{reduced volume, } V_r = V/V_c \quad (2-7)$$

where T , P , and V refer to temperature, pressure, and volume respectively and the subscript c denotes the critical state.

For brevity, the expression "Principle of Corresponding States" will hereafter be referred to as PCS.

The original derivation of the PCS as made by van der Waals begins with his form of the equation of state

$$(P + a/\underline{V}^2)(\underline{V} - b) = RT. \quad (2-8)$$

By applying the conditions at the critical point that

$$dP/dV = 0 \quad (2-9)$$

$$d^2P/dV^2 = 0 \quad (2-10)$$

the equation can be put into the reduced form

$$(P_r + 3/V_r^2)(V_r - 1/3) = 8/3 T_r. \quad (2-11)$$

This equation is now the same for all gases since the quantities a and b , which vary from one gas to another, have

entirely disappeared. Assuming that van der Waals' equation is true for all gases, it appears that when any two of the quantities T_R , P_R , or V_R are given, the third is also given. In equation form, this may be written

$$V_R = f(T_R, P_R) \quad (2-12)$$

where f denotes a universal function. Equation (2-12) represents the original PCS as developed by van der Waals.

While this principle was developed from van der Waals' equation, it is not limited to those gases for which that equation of state is valid. The principle may also be developed from a more general equation of state if it depends on only two quantities which determine the particular structure of the gas in question.

In 1939, Pitzer was able to derive this PCS by using classical statistical mechanics (39). To make the derivation, it was necessary to make simplifying assumptions. These were:

1. classical statistical mechanics is applicable,
2. the gas molecules are spherically symmetrical, either actually or by virtue of rapid and free rotation,
3. the nature of any intramolecular vibrations is the same whether the molecules are in the liquid or gaseous states,
4. the potential energy of an assemblage of molecules is a function only of the various intermolecular distances,

5. the potential energy for a pair of molecules can be written

$$\phi(r) = \epsilon f(r/\sigma) \quad (2-13)$$

where f is a universal function, r is the inter-molecular distance, and ϵ and σ are constants to be specified for each substance.

Guggenheim in 1945 (13) and Hirschfelder, Curtiss, and Bird in 1954 (16), also presented statistical mechanical derivation of the PCS. The assumptions made by these investigators were essentially the same as those used by Pitzer. All three derivations required that the potential between a pair of molecules be of the form of Equation (2-13).

In the Hirschfelder, Curtiss, and Bird derivation, it is assumed that the equation of state of a gas may be written in the form

$$P = kT \frac{\partial}{\partial V} \ln \int e^{-\phi(\mathbf{r}^N)/kT} d\mathbf{r}^N. \quad (2-14)$$

In Equation (2-14) the pressure, P , depends only on kT , the volume, V , and on the two scale factors ϵ and σ and the form of the universal function, f .

The quantities ϵ and σ may be used to define the reduced variables

$$P^* = P \sigma^3 / \epsilon \quad (2-15)$$

$$V^* = V / \sigma^3 \quad (2-16)$$

$$T^* = kT / \epsilon \quad (2-17)$$

From the considerations discussed above and from dimensional

analysis, it is possible to write the reduced pressure as a universal function of the reduced volume and temperature

$$P^* = f(V^*, T^*). \quad (2-18)$$

From this form of the PCS and the definition of the critical point, it follows that the critical temperature and pressure reduced in terms of the molecular constants are universal constants. Hirschfelder, Curtiss, and Bird presented values for the constants for several gases. For those gases for which quantum deviations can be neglected, the values of $(P^*)_c$, $(V^*)_c$, $(T^*)_c$ are approximately the same. Assuming them to be the same, the PCS may be written

$$V_r = f(T_r, P_r). \quad (2-19)$$

This is identical with the original PCS proposed by van der Waals.

Since the reduced volume may be written

$$V_r = \underline{v}/v_c = Z/Z_c \cdot T_r/P_r \quad (2-20)$$

the principle may be written

$$Z/Z_c = f(T_r, P_r). \quad (2-21)$$

If the assumption is made that Z_c is a constant for all gases, the PCS can be written

$$Z = f(T_r, P_r). \quad (2-22)$$

This is the form of the principle that has been used to prepare the many generalized correlations of Z as a function of P_r and T_r .

At the critical point where T_r and $P_r = 1.0$, Equation (2-22) becomes

$$Z_c = f(1,1). \quad (2-23)$$

The value of the compressibility factor at the critical point should then be a universal constant.

Simple molecules which are essentially spherical and nonpolar have values of the critical compressibility factor approximately equal to 0.292, but the hydrocarbon molecules (excluding methane which falls into the first group) have values of Z_c approximately equal to 0.267. These hydrocarbon molecules, while nonpolar, have a nearly ellipsoidal shape. Values of Z_c for polar molecules vary from 0.269 down to 0.181.¹

The PCS derived from classical statistics and given in Equation (2-19) was based on the assumption that the potential energy of a pair of molecules may be written

$$\phi(r) = \epsilon f(r/\sigma). \quad (2-24)$$

A potential function satisfying Pitzer's assumptions and of the form of Equation (2-24) is the Lennard-Jones potential function (30) which may be written

$$\phi(r) = 4\epsilon \left[(\sigma/r)^{12} - (\sigma/r)^6 \right] \quad (2-25)$$

¹The discussion presented in this paragraph is a summary of a similar discussion presented by Hirschfelder, Curtiss, and Bird (16). The discussion is based on values of Z_c presented by these authors. Other authors have presented slightly higher values of Z_c for the hydrocarbons.

where ϵ is the maximum depth of the potential, σ is the collision diameter or distance at which $\phi(r)$ is zero. This potential function is shown in Figure II-1.

In a discussion of the Lennard-Jones potential, Rowlinson (52) has stated that this potential function might suffice for spherical nonpolar molecules, but for more complex molecules, several modifications are needed. These are:

1. the addition of direct and induced electrostatic terms to account for attractive forces arising from multipole interactions,
2. the addition of a means for representing the shape of the molecules since for a nonspherical shape, the repulsive forces in the potential change with orientation of the molecules,
3. an alteration of the exponents of the potential for the case of globular molecules since for globular molecules, the origins of the attractive and repulsive forces are not the geometrical centers of the molecules but are the atoms or groups that are disposed symmetrically about the center.

When the molecular model or the potential function are modified to account for other than spherical nonpolar molecules, the PCS is no longer given by Equation (2-19). The reduced volume is no longer just a function of the reduced temperature and pressure but a function of a third parameter in addition to the critical temperature and pressure.

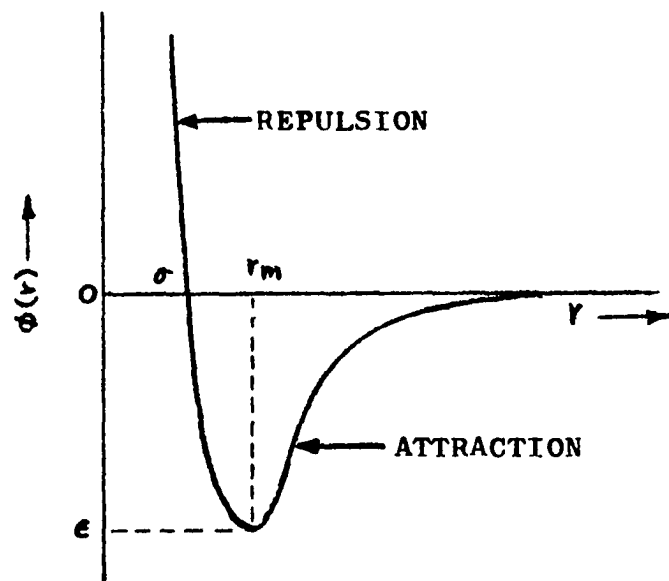


FIGURE II-1. LENNARD-JONES POTENTIAL ENERGY OF MOLECULAR INTERACTION AS A FUNCTION OF DISTANCE r BETWEEN THE TWO MOLECULES

C. Third Parameters

The failure of the original PCS to predict the compressibility factor for all gases, regardless of their mass, shape, or polar moment, has led to the introduction of an additional parameter into the PCS so that it has the form

$$Z = f(T_r, P_r, X) \quad (2-26)$$

where X represents the additional parameter. The need for these third parameters is apparent not only from the failure of the original principle to predict the compressibility factors of certain gases but also from the realization that only a few gases obey the assumptions which were necessary in the derivation of the principle.

Although many of the third parameters are interrelated and, indeed, do in certain cases show a functional relationship to one another, they have been divided into groups depending on the particular deviation they were intended to correct. The parameters were grouped as follows:

1. quantum deviation parameters,
2. parameters for nonspherical or globular molecules,
3. polar moment correction parameters,
4. general parameters intended to correct for one or more of the above.

1. A Parameter to Account for Quantum Effects

The first assumption of Pitzer (39) in the derivation of the PCS was that classical statistical mechanics is

applicable. This required that quantum effects be negligible.

In 1921, Byk (7) published a discussion on the influence of the introduction of the classical quantum theory on the PCS. He stated that the volume of the unit cell in phase space, h^3 , must be expressed in a unit derived from the critical constants of the gas. This unit was determined to be $m^{3/2} (V_c/n)(kT_c)^{3/2}$. From this, he concluded that the deviations from the principle, as far as they result from quantum theory, should be a function of the parameter

$$\Lambda_r = h / \left\{ m^{1/2} (V_c/n)^{1/3} (kT_c)^{1/2} \right\}. \quad (2-27)$$

With this parameter, the PCS would be

$$V_r = F(T_r, P_r, \Lambda_r). \quad (2-28)$$

De Boer and Michels (7), in 1938, showed that the reduced second virial coefficient is not a function of the reduced temperature alone as in the classical expression, but depends also on the value of Λ/σ where $\Lambda = h/\sqrt{m\epsilon}$. The principle of corresponding states would then have the form

$$V_r = F(T_r, P_r, \Lambda^*) \quad (2-29)$$

$$\text{where } \Lambda^* = \Lambda/\sigma$$

Hirschfelder, Curtiss, and Bird arrived at this form of the PCS by assuming that the equation of state may be written in the form

$$P = F(V/N, kT, h, m, \sigma, \epsilon) \quad (2-30)$$

and by using the molecular parameters σ and ϵ for the

reduction of variables. They arrived at

$$P^* = F(V^*, T^*, \Lambda^*) \quad (2-31)$$

by dimensional analysis and concluded that the dimensionless quantities in Equation (2-31) are the only dimensionless quantities which could be arrived at from Equation (2-30).

It is generally considered that Λ^* is better suited for the study of quantum effects than Λ_r since Λ_r is itself influenced by the quantum effects through the quantities V_c and T_c . De Boer and Michels have shown that when the effect on the critical constants is small

$$\Lambda_r \approx 0.61 \Lambda^* \quad (2-32)$$

Leland, Kobayashi, and Mueller (29), in working with the second virial coefficient for quantum gases arrived at the parameter

$$Q' = \frac{59.0}{(\phi V_c^{1/3}) \sqrt{M \theta T_c}} \quad (2-33)$$

as a means of evaluating $h/\sigma \sqrt{m \epsilon}$, from the critical constants. The values of ϕ and θ were calculated from

$$\phi = (\sigma_q / \sigma_{cl})^3 \quad (2-34)$$

$$\theta = (\epsilon_q / \epsilon_{cl}) \quad (2-35)$$

where σ and ϵ are the Lennard-Jones constants and the subscripts q and cl denote quantum and classical. At high molecular weights, the values of θ and ϕ become unity.

Satter (61) arrived at a third parameter by assuming

an equation of state of the form

$$P = f(V/N, kT, h, m, P_c, V_c/N, kT_c) \quad (2-36)$$

and utilizing dimensional analysis. The parameter that Satter obtained is

$$F = \frac{h P_c^{1/3}}{(kT_c)^{5/6} (m)^{1/2}} \quad (2-37)$$

or

$$F = 5.665 \frac{P_c^{1/3}}{T_c^{5/6} M^{1/2}} \quad (2-38)$$

If one substitutes

$$P_c^{1/3} = \left(\frac{RT_c Z_c}{V_c} \right)^{1/3} \quad (2-39)$$

then

$$F = 5.665 (RZ_c^{1/3}) \frac{1}{V_c^{1/3} \sqrt{MT_c}} \quad (2-40)$$

Satter also used a fourth parameter, Z_c , and arrived at a PCS of the form

$$Z = f(P_r, T_r, F, Z_c) \quad (2-41)$$

Satter evaluated the applicability of

$$Z = f(P_r, T_r, F/Z) \quad (2-42)$$

as a possible PCS for the components of natural gas. He found that this particular combination of F/Z_c was suitable but not a particularly convenient parameter. Satter's work has been included in this section on quantum parameters because of the similarity of F to the quantum correction parameters.

For natural gas, there is no need for a parameter to correct for quantum deviations. Only at very low temperatures and high pressures does methane, the lightest of the hydrocarbons, show any quantum effects. At the temperatures and pressures with which the natural gas engineer is concerned, quantum deviations are negligible.

2. Parameters for Nonspherically Shaped and Globular Molecules

The second assumption which was necessary in the statistical mechanical derivation of the PCS was that the gas molecules were spherical. Of the hydrocarbon constituents of natural gas, only methane, by virtue of its rapid and relatively free rotation, may be considered as spherical. The other hydrocarbon constituents have a nearly ellipsoidal shape.

Kihara (26), in arriving at an expression for the second virial coefficient, utilized a potential function of the form of the Lennard-Jones potential but replaced the point center model by an impenetrable core whose dimensions are suggested by the geometry and inter-nuclear distances of the molecule. The potential function was then written not as a function of the distance between molecular centers but rather as a function of the minimum distance between molecular cores. This potential function has the form

$$U = U_0 \left[(\rho_0/\rho)^{12} - 2 (\rho_0/\rho)^6 \right] \quad (2-43)$$

where:

U = potential energy

U_0 = maximum (negative) potential energy

ρ = shortest distance between molecular cores

ρ_0 = shortest distance between molecular cores
at the energy minimum.

Kihara, in his final formula for his core models, gives the second virial coefficient as a function not only of temperature but also a function of M_0 , the mean curvature, S_0 , the surface area, and V_0 , the volume of the core. Pitzer (40) has shown that for molecules approaching the shape of a thin rod of length L_0

$$M_0 = \pi L_0, S_0 = V_0 = 0 \quad (2-44)$$

and for a sphere of radius a_0

$$M_0 = 4\pi a_0, S_0 = 4\pi a_0^2, V_0 = 4\pi a_0^3/3. \quad (2-45)$$

The work of Kihara illustrates the need for a factor to account for molecular shape.

Corner (4), to account for a cylindrical molecular shape, assumed that long molecules could be represented by four centers of force arranged rigidly along a line. He further assumed that the total intermolecular force is given by the sum of the interactions between force centers, each interaction being of the form of Equation (2-24). From these considerations, the resulting PCS has the form

$$P_r = f(V_r, T_r, L_r) \quad (2-46)$$

where $L_r = L/\sigma$ and L is the distance between force centers.

Similarly, for globular molecules, Corner's model would lead to a PCS of the form

$$P_r = f(V_r, T_r, a_r, n_o) \quad (2-47)$$

where $a_r = a_o/\sigma$, a_o is the distance from the center of the molecule to the force centers, and n_o is the number of force centers.

To correct for a nonspherical shape, Lyderson, Greenkorn, and Hougen (33) suggested the use of dimensionless molecular bond-length factor as a third parameter. This parameter was given as

$$L'/^3 \sqrt{RT_c/P_c}$$

where L' = sum of the bond lengths in the longest molecular chain.

Since methane is the only hydrocarbon molecule in natural gas which can be considered as being spherical, a shape factor parameter should be considered as a possible third parameter.

3. Polar Moment Parameters

Rowlinson (52), in his discussion of a two parameter potential function stated that a potential function of this type fails to include direct and induced electrostatic terms. By assuming a potential function

$$\phi(r) = \epsilon f(r/\sigma) - (\mu^2/r^3)g(\phi_1, \phi_2, \phi_2 - \phi_1) \quad (2-48)$$

in which $f(r/\sigma)$ is a universal function of the reduced distance, r/σ , and $g(\theta_1, \theta_2, \phi_2 - \phi_1)$ describes the angle dependence of the interaction of two dipoles, a corresponding states relation

$$V(r) = f(P_r, T_r, \mu_r) \quad (2-49)$$

is obtained. The reduced dipole moment, μ_r , is given by

$$\mu_r = \mu / \sqrt{\epsilon \sigma^3} \quad (2-50)$$

where μ is the molecular dipole moment.

Various investigators have used third parameters closely related to the reduced dipole moment. Lyderson, Greenkorn, and Hougen (33) investigated the use of

$$\mu_r = \frac{\mu \sqrt{P_c}}{RT_c} \quad (2-51)$$

Pitzer (40) has shown that the second virial coefficient is dependent upon $\mu^4/\epsilon_0^2 r_0^6$ and Hall and Ibele (15) have proposed the use of the third parameter

$$\mu_r = \mu^2 / (kT_c)(V_c/N) \quad (2-52)$$

in the determination of the compressibility factor of polar gases.

The work of Pople (44) on the statistical mechanics of assemblies of axially symmetric molecules suggests the use of a third parameter to account for a quadrupole moment. He showed that for a gas such as carbon dioxide, which has a strong quadrupole interaction between molecules, the second

virial coefficient is dependent upon $Q^2/\epsilon_0 \sigma^5$ where Q is the quadrupole moment.

$$Q_r = Q^2/\epsilon_0 \sigma^5 \quad (2-53)$$

is a possible third parameter for gases with quadrupole moments.

While parameters such as the reduced dipole or quadrupole moment would not apply to any of the hydrocarbon constituents, they would apply to the three principle diluents of natural gas. These are hydrogen sulfide, which has a polar moment, and carbon dioxide and nitrogen, which have quadrupole moments.

4. General Parameters

This last group of third parameters consists of those parameters intended to correct for one or more deviations from the conditions necessary for the statistical mechanical derivation of the PCS. These parameters are more empirical in nature and are not as directly related to the potential function.

The form of the principle of corresponding states derived from van der Waals' equation and from statistical mechanics is

$$V_r = f(T_r, P_r) \quad (2-54)$$

Since

$$V_r = Z/Z_c \cdot T_r/P_r \quad (2-55)$$

the principle may be written

$$Z/Z_c = f(T_r, P_r). \quad (2-56)$$

For most of the generalized charts, Z_c was assumed to be constant so that

$$Z = f(T_r, P_r) . \quad (2-57)$$

Meissner and Sefferian (34) have used Z_c as a third parameter so that

$$Z = f(T_r, P_r, Z_c) . \quad (2-58)$$

To account for the deviation in Z_c between gases, they have prepared a Z versus P_r and T_r correlation for a gas with $Z = 0.27$. To use this chart for gases with Z_c not equal to 0.27, they have prepared a set of correction charts with $Z/Z(0.27)$ plotted versus Z_c for various values of T_r .

Lydersen, Greenkorn, and Hougen (33) have also used Z_c as a third parameter. They have prepared different tables of compressibility factors for values of Z_c , of 0.23, 0.25, 0.27, and 0.29 and suggested using the table for a value of Z_c nearest to the Z_c of the gas in question.

Nelson and Obert (38) have stated that the compressibility factors of gases with the same value of Z_c usually correlate closely, but this happens only when the gases have similar molecular structures. When the structures or molecular laws of force are different, gases will not correlate well whether the Z_c values are equal or not.

Sarem (60) proposed the use of the molecular refraction

of a substance as a third parameter for characterizing the gas because it is related to refractive index, molecular weight, and density. He reasoned that light dispersion, which is manifested in the refractive index, is intimately related to the London dispersion forces. The molecular refraction in terms of the refractive index, n_r , as measured by the sodium D line, density d , and molecular weight may be expressed as follows:

$$R_d = \frac{n_r^2 - 1}{n_r^2 + 2} M / d . \quad (2-59)$$

Pitzer (40) has stated that the effect of nonspherical, globular, or polar molecules on the potential function is a narrowing of the potential well. While the effect of each of these is not exactly the same, it is in each case manifested in the slope of the vapor pressure versus temperature curve. For this reason, Pitzer used the increase in slope over that of a simple fluid (the inert gases, krypton or xenon) to obtain a third parameter, ω , which he called the acentric factor. The acentric factor may be calculated from

$$\omega = - \log P_r^0 - 1.00 \quad (2-60)$$

where P_r^0 is the reduced vapor pressure at a reduced temperature of 0.7. A reduced temperature of 0.7 was chosen since at this point the acentric factor for the simple fluids is zero.

Cook and Rowlinson (3) developed a parameter to account

for elliptical nonpolar molecules, The parameter was also developed to account for slightly polar molecules. This parameter was intended to account for the orientation effects that are present in the intermolecular potential for these types of molecules.

This parameter, δ^c , was evaluated from the reduced vapor pressure or from the rectilinear diameter. To evaluate it from the vapor pressure, they used for elliptic molecules

$$\ln P_r^0 = -c(1-T_r)/T_r - \delta^c \left[(1-T_r)(2c-3T_r)/T_r^2 \right] \quad (2-61)$$

and for polar molecules

$$\ln P_r^0 = -c(1-T_r)/T_r - \delta^c \left[(1-T_r)(4c-5T_r)/T_r^2 \right]. \quad (2-62)$$

In these expressions P_r^0 is the reduced vapor pressure, δ^c is the correction parameter, and c is a positive constant.

The first term on the right of these expressions is the value of $\ln P_r^0$ predicted by the original PCS. The value of δ^c has also been evaluated from the rectilinear diameter with reasonable agreement with the value obtained from the vapor pressure.

Rowlinson's work further indicates that the effects caused by nonspherical, globular, or slightly polar molecules not obeying the required assumptions for the statistical mechanical derivation of the PCS are manifested in the vapor pressure curve.

Riedel (50) has proposed a third parameter which is

also obtained from the vapor pressure curve. This parameter, α_k , is the temperature derivative of the vapor pressure curve at the critical point and is given by the following:

$$\alpha_k = \frac{T_c}{P_c} \left(\frac{\partial P^o}{\partial T} \right). \quad (2-63)$$

Again, it was realized that the deviation from the simple fluid behavior was present in the difference between vapor pressure curves,

Third parameters for the constituents of natural gas are tabulated along with the critical properties in Table 2, Appendix B.

Inasmuch as Pitzer's acentric factor will be relied upon quite heavily in the remainder of this study, a more detailed discussion of the acentric factor follows.

In a 1955 paper, Pitzer (40) discussed the need for a third parameter to measure the deviation of the intermolecular potential from that of a simple fluid. He discussed the effect that globular molecules, nonspherical molecules, and slightly polar molecules have on the potential function and in turn on the vapor pressure curve.

In a second paper by Pitzer et al. (42), the acentric factor was introduced to account for the deviation arising in the intermolecular potential due to the fact that the sum of the inverse sixth power terms applying to the various portions of a pair of complex molecules cannot be replaced by a single inverse sixth power term in the distance between

molecular centers. The fact that the forces between the non-central portions of the molecules must be considered, suggested the term acentric factor.

The empirical quantity selected as indicative of the deviation was the reduced vapor pressure at a point well removed from the critical point. Since the reduced vapor pressure of Pitzer's "simple fluid" is almost precisely 0.1 at a reduced temperature of 0.7, this was the point used. The acentric factor was then defined as

$$\omega = -\log P_r^0 - 1.00 \quad (2-64)$$

where P_r^0 is the reduced vapor pressure at $T_r = 0.7$.

With the acentric factor as a third parameter, the PCS may be written

$$\frac{PV}{RT} = Z(T_r, P_r, \omega) \quad (2-65)$$

and the compressibility factor may be expanded as a power series in the acentric factor

$$Z = Z^0 + \omega Z' + \dots \quad (2-66)$$

where Z^0 , Z' etc. are each functions of T_r and P_r . Pitzer found that in almost all regions, the first two terms of the expansion were sufficient and that the third terms when obtainable showed considerable doubt as to their validity. Consequently, no values of the third term were reported or utilized. Due to the omission of the quadratic term, Pitzer indicated that compressibility factors calculated in the

region $T_r = 1.05 - 1.10$ and $P_r = 1.4 - 2.0$ might be less precise.

To arrive at the values of Z^0 and Z' , the compressibility factors for many fluids were interpolated graphically to even values of T_r and P_r . The region T_r from 0.8 to 4.0 and P_r from 0 to 9.0 were studied. For each value of P_r , a plot such as Figure II - 2 was prepared in which the compressibility factor was plotted as a function of the acentric factor with the reduced temperature as a parameter. In plots such as these, Z^0 represents the intercept at $\omega = 0$ and Z' represents the slope of the T_r lines. From many plots such as these, the values of Z^0 and Z' were read and tabulated as functions of T_r and P_r .

Satter (61) later expanded the tables for values of $T_r = 1.0$ to 2.0 from the termination of Pitzer's tables at $P_r = 9.0$ to a P_r of 14.0. The tabulations of Pitzer plus the extended region of Satter were plotted by Satter and are shown in Figures II - 3 and II - 4. To utilize these figures, it is necessary to calculate reduced temperature and reduced pressure utilizing the critical temperature and pressure of the gas. Values for Z^0 and Z' are then read from the figures and the compressibility is calculated from

$$Z = Z^0 + \omega Z' \quad (2-67)$$

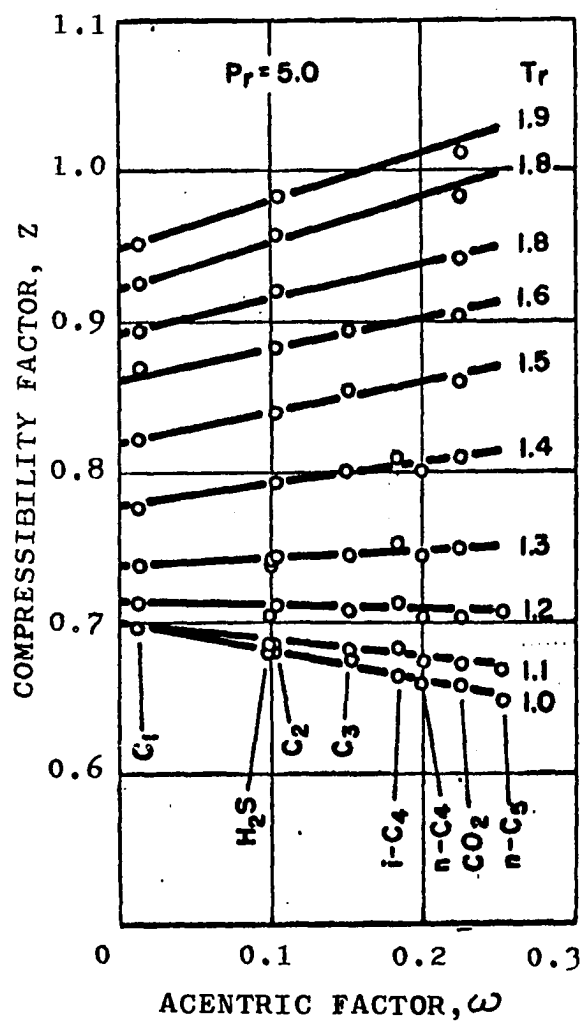


FIGURE II-2. THE COMPRESSIBILITY FACTOR AS A FUNCTION OF ACENTRIC FACTOR AT $P_r = 5.0$ AND THE VALUES OF T_r INDICATED (REF. NO. 61)

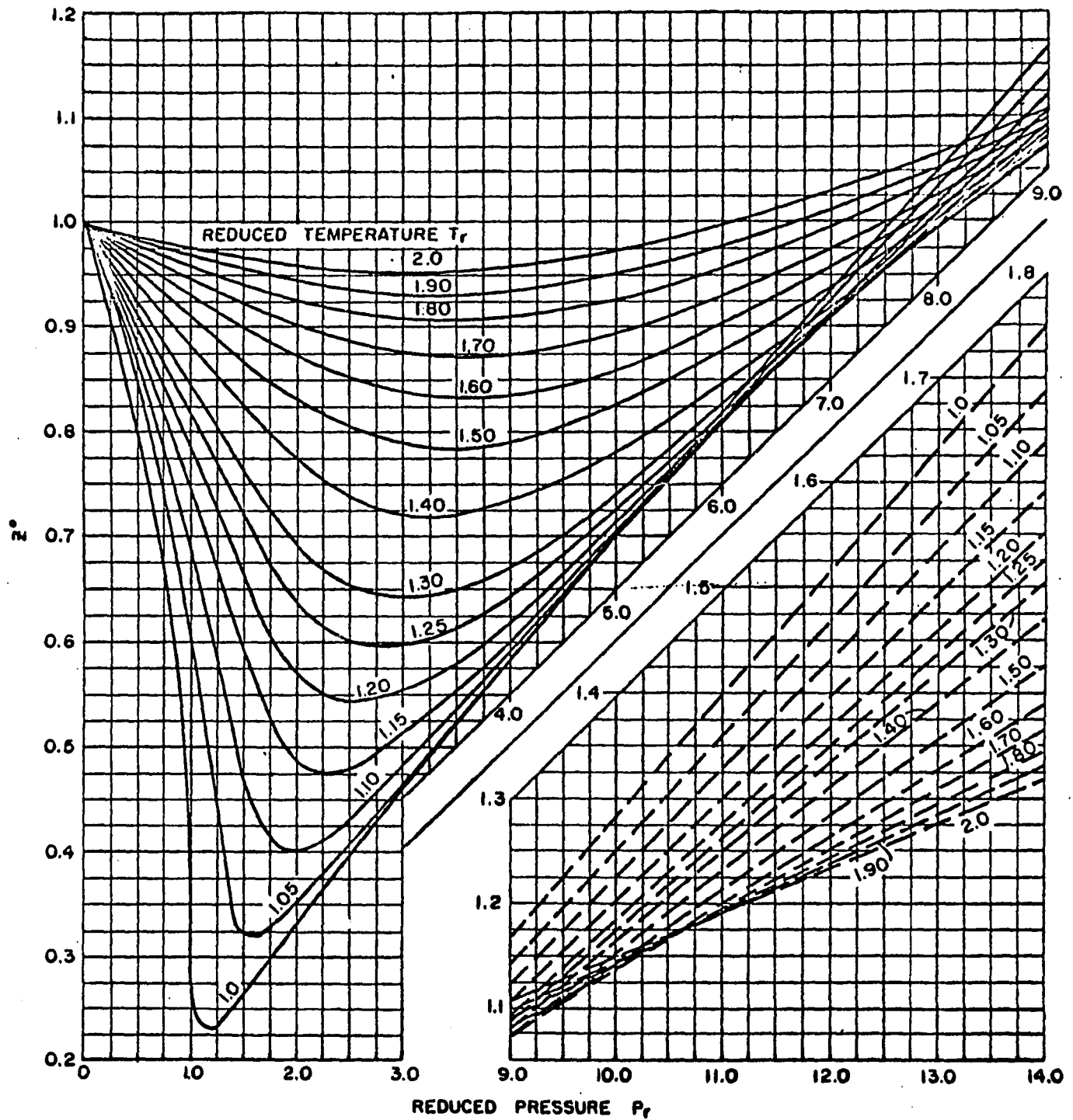


FIGURE II-3. GENERALIZED COMPRESSIBILITY FACTORS Z° AT REDUCED TEMPERATURES AND PRESSURES (REF. NO. 61)

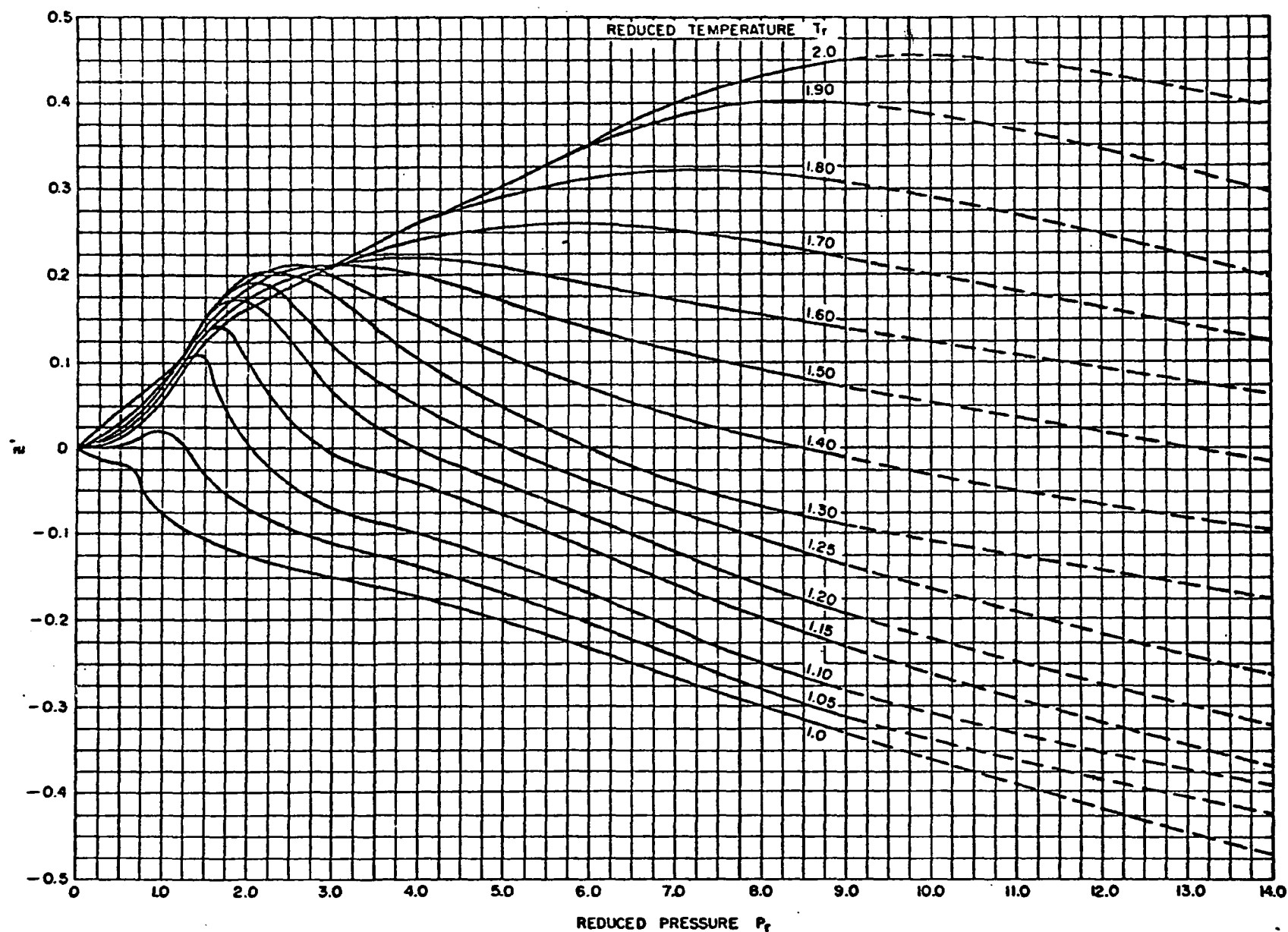


FIGURE II-4. GENERALIZED COMPRESSIBILITY FACTORS Z^1 AT REDUCED TEMPERATURES AND PRESSURES (REF. NO. 61)

CHAPTER III

CHARACTERIZATION OF GAS MIXTURES

For gas mixtures, P-V-T prediction techniques become all the more difficult since one must not only be concerned with the deviation from simple fluid behavior of each constituent but also with the complex problem of the interaction between the dissimilar molecules in the system. The general approach to mixtures has been to combine pure component properties through some combination rule to arrive at properties characteristic of the mixtures. These mixture properties are then used in the pure component relationships to predict the volumetric behavior for the mixture.

Several different methods have been proposed for estimating the P-V-T behavior of mixtures. These may be briefly summarized as follows:

1. A possible method of dealing with mixtures is by using average constants in the equations of state that were discussed in Chapter II. For example, the constants a' and b' in van der Waals' equation could be calculated from

$$a' = [y_1 a_1^{\frac{1}{2}} + y_2 a_2^{\frac{1}{2}}]^2 \quad (3-1)$$

$$b' = y_1 b_1 + y_2 b_2 \quad (3-2)$$

2. A second method would be to use a mean compressibility factor. Edminster (10) has shown that if one assumes that Dalton's law of additive pressures is applicable, then

$$Z_{\text{mix}} = y_1 Z_1 + y_2 Z_2 + \dots \sum_i y_i Z_i \quad (3-3)$$

where Z_1 , Z_2 etc. are evaluated at the T and V of the system. If one assumes that Amagat's law of additive volumes is applicable, then

$$Z_{\text{mix}} = y_1 Z_1 + y_2 Z_2 + \dots \sum_i y_i Z_i \quad (3-4)$$

where Z_1 , Z_2 etc. are evaluated at the T and P of the system.

3. A third method is by using generalized charts where the reduced temperatures and pressures are no longer calculated from the critical properties but from the pseudocritical properties of the system.

The last method which was proposed by Kay (25) has received the widest engineering application.

In attempting to use the pure component generalized compressibility charts for gaseous mixtures, Kay realized that there was considerable deviation, particularly in the critical region. By comparing the P-V-T data of a single component gas with that of a mixture, he concluded that the

deviation results from an improper selection of the critical point used to reduce the temperature and pressure.

If one plots the constant density lines for a pure component on a pressure-temperature diagram, the lines will intersect the vapor pressure line which terminates at the critical point. For a mixture, the vapor pressure line on a pressure-temperature diagram is replaced by a two phase envelope. If a similar plot is made for a mixture and the constant density lines are extrapolated inside the two phase envelope, the lines will intercept some hypothetical line terminating not at the critical point of the mixture but at some point inside the two phase envelope. This plot for a methane-butane system is shown in Figure III - 1. From this, Kay concluded that if the data in the superheated region of a mixture are to be compared with the superheated region of a single component gas by the PCS, the point for calculating the reduced properties is not the actual critical point but some hypothetical point inside the two phase envelope. Kay referred to this point as the pseudocritical point and the temperature and pressure at this point as the pseudocritical temperature and pseudocritical pressure of the mixture.

Kay postulated that, if the chemical composition of the mixture were known, the pseudocritical temperature and pressure could be calculated by a mixture rule from the composition expressed in mole fraction and the critical constants of the constituents in the mixture. The mixture rules used

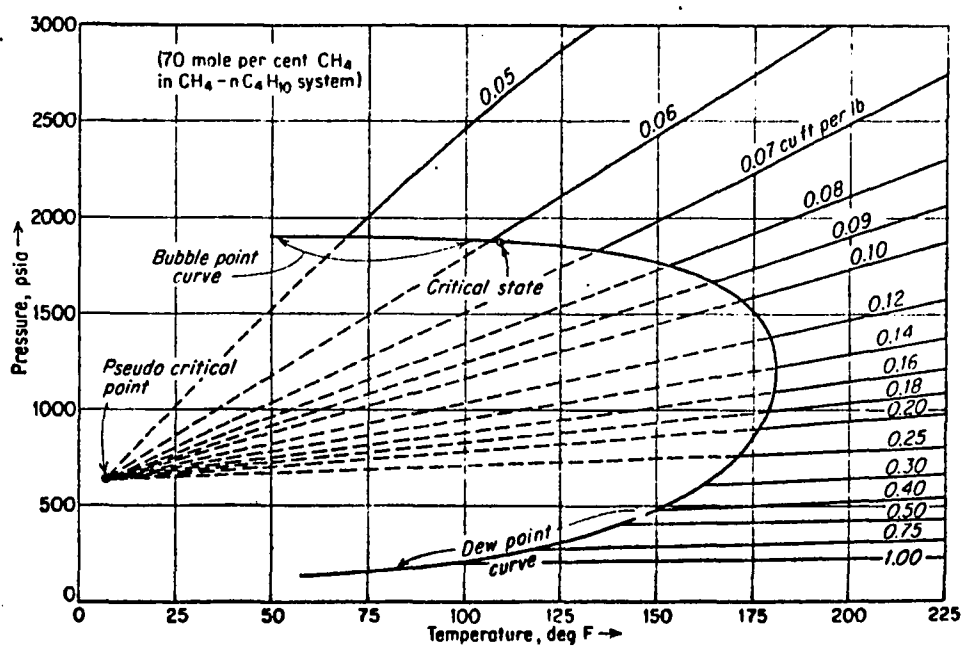


FIGURE III-1. PRESSURE-TEMPERATURE DIAGRAM ILLUSTRATING PSEUDOCRITICAL POINT FOR A CH_4 - C_4H_{10} SYSTEM (REF. NO. 24)

by Kay are

$$T_c' = \sum_i y_i T_{ci} \quad (3-5)$$

$$P_c' = \sum_i y_i P_{ci} \quad (3-6)$$

where T_c' and P_c' denote the pseudocritical temperature and pressure, respectively.

To provide a comparison for these rules, Kay graphically determined the pseudocritical constants for several mixtures by the following method:

1. A general plot was prepared of the compressibility factor versus the logarithm of reduced pressure for various reduced temperatures of isopentane.
2. The mixture data was then plotted on a separate sheet of semi-transparent paper with the temperature and pressure expressed in degrees Rankine and pounds per square inch absolute.
3. By laying the second plot over the first and shifting it along the pressure axis each isotherm could be matched with a corresponding reduced isotherm and the pseudocritical temperatures and pressure could be calculated.

By comparing the pseudocritical constants calculated by his mixture rule with those graphically determined, Kay concluded that values of the pseudocritical constants evaluated by these rules for the light hydrocarbons are sufficiently accurate for most engineering calculations. Kay

warned that for mixtures whose constituents differ greatly in molecular weight as well as chemical nature, values of the pseudocritical constants calculated in a similar manner are likely to be in error by amounts greater than that allowable.

In graphically determining the pseudocritical constants, Kay used predominantly isopentane data along with the mixture data. For a methane-propane mixture, he used pure methane data. Kay never mentioned the fact, but if his method for graphically determining the pseudocritical constants is used for the same mixture with two different sets of pure component data, the pseudocritical constants will differ unless both of these pure gases have identical Z versus T_r and P_r plots. The two pure gases will not have identical plots unless they obey the PCS equally well. While the difference may not be very great, empirically determined pseudocritical constants are dependent upon the general plot that was used to obtain them. In other words, the pseudocritical constants that are the most applicable depend upon the generalized correlation one uses. This establishes the need for third parameters in dealing with mixtures. If the mixture can be characterized by a third parameter, then the general plot for a gas with the same characteristic third parameter could be used to determine the behavior of the mixture.

Based on the work done on pure gases and the findings presented by Kay, two avenues of approach, to improved

prediction of the volumetric behavior of mixtures are:

1. The use of combination rules to combine pure component third parameters to obtain a mixture parameter which characterizes the mixture.
2. The development of combination rules for predicting the pseudocritical constants which do not suffer from the limitations of the molal average rules of Kay.

A. Third Parameters for Mixtures

Of the third parameters discussed in Chapter II, three have been used in the prediction of the compressibility factor of hydrocarbon binaries. The molecular refraction, R_d , was proposed and utilized by Sarem (60). To obtain the molecular refraction for a mixture, Sarem used

$$R_d' = \sum_i y_i R_{di}. \quad (3-7)$$

Stewart, Burkhardt, and Voo (64), as well as Leland and Mueller (28), have used a pseudocritical compressibility factor

$$Z_c' = \sum_i y_i Z_{ci}. \quad (3-8)$$

Prausnitz and Gunn (45), and Satter (61), have made use of a mixture acentric factor

$$\omega' = \sum_i y_i \omega_i. \quad (3-9)$$

In using Z_c as a third parameter, Leland and Mueller calculated Z_c' by equation (3-8) and then chose a reference

substance from among the normal paraffins between CH_4 and C_7H_{16} . The compressibility factor chart for the normal paraffin having a value of Z_c nearest to the value of Z_c' of the mixture was then used. Steward, Burkhardt, and Voo also calculated Z_c' by equation (3-8) but for a reference substance, they made use of the charts of Lydersen, Greenkorn, and Hougen.

One of the main disadvantages in the use of Z_c' lies in the difficulty in obtaining the right reference substance. The differences in the value of Z_c of the reference substances is small. Only a small error in the determination of Z_c' could cause the selection of the wrong reference substance.

Sarem avoided part of the difficulty of choosing the reference substance by utilizing molecular refraction. The molecular refraction has the advantage that the difference in R_d between components is significant.

Sarem utilized the molecular refraction in the same manner in which Leland and Mueller used Z_c' . The compressibility chart for the substances having a value of R_d nearest to the R_d' of the mixture was used. The problem that arises here is what reference substance one uses if the R_d' of the mixture lies between the R_d of two reference substances. Sarem has suggested that, in this case, a binary mixture with an R_d' equal to the R_d' of the mixture in question could be used. This presents a judgement decision since there are several conceivable binary mixtures which have the same value

of R_d' . If one is working with the normal paraffins, perhaps the logical choice is a binary consisting of the two normal paraffins with molecular refractions lying on opposite sides of the mixture R_d' .

One of the main arguments in favor of using the molecular refraction lies in the fact that the molecular refraction of the heptanes plus fraction of a natural gas is a measurable quantity. It may be difficult in natural systems because of the opaque color, but if it can be measured, it would avoid the necessity of separating the C_7+ fraction into individual components.

In using the mixture acentric factor as calculated with Equation (3-9), the difficulty of choosing the proper reference substance is avoided. To use the acentric factor for mixtures requires only the charts given in Figure II - 3 and II - 4. These same two charts are used for all mixtures.

In all of the instances where a mixture third parameter was employed, it was realized that it is necessary to further characterize the mixture by the use of combination rules to obtain pseudocritical constants. It is difficult to evaluate how successful the above mixture third parameters were because of the different combination rules used to obtain the pseudocritical constants. In the following sections, some of the combination rules that have been proposed are discussed.

B. Pseudocritical Constants from Two
Parameter Equations of State

The most notable pseudocritical constant prediction methods developed since the molal average rule proposed by Kay have been based on either a two constant equation of state or on the virial approach to mixtures. This section is concerned with those predicted from two constant equations of state.

The development of pseudocritical combination rules based on two parameter equations of state depends upon the combining rules used to obtain the constants in the mixture equation of state. This is evident from the work of Joffe (22,23). He developed two different sets of combining rules from the van der Waals' equation of state.

To compute the constant a for a binary mixture, he used the expression

$$(a')^{\frac{1}{2}} = y_1 a_1^{\frac{1}{2}} + y_2 a_2^{\frac{1}{2}} \quad (3-10)$$

For the constant b , he used two different expressions. The first was the one suggested by van der Waals,

$$b' = y_1 b_1 + y_2 b_2 \quad (3-11)$$

and the second was an expression suggested by Lorentz

$$b' = y_1^2 b_1 + y_2^2 b_2 + \frac{1}{4} y_1 y_2 (b_1^{1/3} + b_2^{1/3})^3 \quad (3-12)$$

Van der Waals' constants for the individual components may be expressed in terms of the critical constants by

$$a_i = 27 R^2 T_i^2 / 64 P_i \quad (3-13)$$

$$b_i = R T_i / 8 P_i \quad (3-14)$$

and by analogy, the constants for the mixture may be expressed by

$$a' = 27 R^2 (T_c')^2 / 64 P_c' \quad (3-15)$$

$$b' = R T_c' / 8 P_c' \quad (3-16)$$

Equations (3-15) and (3-16) define the pseudocritical constants of the gaseous mixture

On substituting Equations (3-13), (3-14), (3-15) and (3-16) into Equations (3-10) and (3-11), the following expressions are obtained

$$T_c' / (P_c')^{1/2} = y_1 T_1 / P_1^{1/2} + y_2 T_2 / P_2^{1/2} \quad (3-17)$$

$$T_c' / P_c' = y_1 T_1 / P_1 + y_2 T_2 / P_2 \quad (3-18)$$

If one substitutes Equations (3-13), (3-14), (3-15) and (3-16) into Equations (3-10) and (3-12), the following are obtained

$$T_c' / (P_c')^{1/2} = y_1 T_1 / P_1^{1/2} + y_2 T_2 / P_2^{1/2} \quad (3-19)$$

$$T_c' / P_c' = y_1^2 T_1 / P_1 + y_2^2 T_2 / P_2 + \frac{1}{4} y_1 y_2 \left[(T_1 / P_1)^{1/3} + (T_2 / P_2)^{1/3} \right]^3 \quad (3-20)$$

For n components, Equations (3-17) and (3-18) would be written

$$T_c' / (P_c')^{1/2} = \sum_i y_i T_i / P_i^{1/2} \quad (3-21)$$

$$T_c' / P_c' = \sum_i y_i T_i / P_i \quad (3-22)$$

and Equations (3-19) and (3-20) would be written

$$T_c' / (P_c')^{\frac{1}{2}} = \sum_i y_i T_{ci} / (P_{ci})^{\frac{1}{2}} \quad (3-23)$$

$$T_c' / P_c' = 1/8 \sum_i \sum_j y_i y_j \left[\left(\frac{T_i}{P_i} \right)^{1/3} + \left(\frac{T_j}{P_j} \right)^{1/3} \right]^3 \quad (3-24)$$

If the procedure employed by Joffe is applied to the Dieterici equation of state (21) given by

$$P = \frac{RT}{V-b} e^{-a/RTV} \quad (3-25)$$

the pseudocritical constant combination rules will be the same as those obtained from van der Waals' equation of state since a and b expressed in terms of the critical constants only differ from those of van der Waals' equation by a constant multiplying factor.

Applying the procedure to the Redlich and Kwong equation of state (48) given by

$$P = \frac{RT}{V-b} - \frac{a}{T^{\frac{1}{2}} V(V+b)} \quad (3-26)$$

results in different pseudocritical rules dependent upon the combination rules used to obtain a and b for the mixture. If Equations (3-10) and (3-11) are used, the resulting equations are

$$(T_c')^{5/4} / (P_c')^{\frac{1}{2}} = \sum_i y_i T_{ci}^{5/4} / P_{ci}^{\frac{1}{2}} \quad (3-27)$$

and

$$T_c'/P_c' = \sum_i y_i T_{ci}/P_{ci} \quad (3-28)$$

If Equations (3-10) and (3-12) are used, then

$$(T_c')^{5/4}/(P_c')^{1/2} = \sum_i y_i (T_{ci}^{5/4}/P_{ci}^{1/2}) \quad (3-29)$$

and

$$T_c'/P_c' = \sum_i \sum_j y_i y_j \left[\frac{1}{2} (T_c/P_c)_i^{1/3} + \frac{1}{2} (T_c/P_c)_j^{1/3} \right]^3. \quad (3-30)$$

The only difference between these equations and those obtained from van der Waals' equation is that the exponents on T_{ci} and T_c' in Equations (3-21) and (3-23) have been changed from 1.0 to 1.25.

The rules that Redlich and Kwong recommended for obtaining the mixture a' and b' are

$$b' = \sum_i y_i b_i \quad (3-31)$$

and

$$a' = \sum_i \sum_j y_i y_j a_{ij} \quad (3-32)$$

with a_{ij} given by

$$a_{ij} = \sqrt{a_i a_j}. \quad (3-33)$$

When these combination rules are used, the resulting equations for the pseudocritical constants are

$$(T_c')^{2.5}/P_c' = \sum_i \sum_j y_i y_j \left[\frac{(T_{ci} T_{cj})^{2.5}}{P_{ci} P_{cj}} \right]^{1/2} \quad (3-34)$$

and

$$T_c'/P_c' = \sum_i y_i (T_{ci}/P_{ci}). \quad (3-35)$$

The basic difference between the pseudocritical combination rules obtained from two parameter equations of state lies in the different assumptions used to combine the pure component a and b to obtain the a' and b' of the mixture. From theoretical considerations alone, the choice of one rule over another would be strictly arbitrary. The choice must be determined by actually testing the rules with experimentally determined data. Joffe made a comparison for his two sets of rules and concluded that those given by Equations (3-23) and (3-24) represented the best rules for predicting the pseudocritical constants.

C. The Virial Approach to Mixtures

1. The Basis for the Virial Approach to Mixtures

One of the primary contributions showing that the PCS could be applied to mixtures was the work of Guggenheim and McGlashan (14). In an earlier work, Guggenheim (13) showed that, based on the PCS for pure substances

$$B/V^* = \phi (T/T^*) \quad (3-36)$$

where B is the second virial coefficient, V^* and T^* are a volume and temperature that are characteristic for the substance, T is the absolute temperature, and ϕ denotes a universal function.

For a two component system, the dependence of the second virial coefficient on the composition at a fixed

temperature is of the form

$$B = (1-y)^2 B_{11} + 2y(1-y) B_{12} + y^2 B_{22} \quad (3-37)$$

where y is the mole fraction of the second component, B_{11} and B_{22} are the values of B for the pure gases 1 and 2 respectively, and B_{12} is the second virial coefficient characteristic of the mixture. Just as B_{11} and B_{22} are related to the interaction between similar molecules, B_{12} is related to the interaction between the dissimilar molecules.

For substance 1 Equation (3-36) is

$$B_{11}/V_{11}^* = \phi(T/T_{11}^*) \quad (3-38)$$

and for substance 2

$$B_{22}/V_{22}^* = \phi(T/T_{22}^*) \quad (3-39)$$

These equations result from the assumption of an interaction energy, ϵ , whose dependence on the distance is of the form

$$\epsilon/\epsilon^* = \phi_1(r/r^*) \quad (3-40)$$

where ϵ^* is an energy and r^* is a length bond characteristic of the molecule. The symbol ϕ_1 denotes a universal function.

Guggenheim and McGlashan then made the assumption that

$$\epsilon_{12}/\epsilon_{12}^* = \phi_1(r_{12}/r_{12}^*) \quad (3-41)$$

where ϵ_{12} is the interaction energy between the dissimilar molecules and r_{12} is their distance apart. These authors then define a characteristic temperature, T_{12}^* , and volume

V_{12}^* by

$$T_{12}^*/\epsilon_{12}^* = T_{11}^*/\epsilon_{11}^* = T_{22}^*/\epsilon_{22}^* \quad (3-42)$$

and

$$V_{12}^*/(r_{12}^*)^3 = V_{11}^*/(r_{11}^*)^3 = V_{22}^*/(r_{22}^*)^3. \quad (3-43)$$

By similarity with the second virial for the similar interactions, it follows that

$$B_{12}/V_{12}^* = \phi(T/T_{12}^*). \quad (3-44)$$

This represents Guggenheim and McGlashan's formulation of the PCS for mixtures. The remaining problem is one of relating r_{12}^* to r_{11}^* and r_{22}^* and ϵ_{12}^* to ϵ_{11}^* and ϵ_{22}^* . The combining rules which they suggested as reasonable are

$$r_{12}^* = \frac{1}{2}(r_{11}^* + r_{22}^*) \quad (3-45)$$

$$\epsilon_{12}^* = (\epsilon_{11}^* \epsilon_{22}^*)^{\frac{1}{2}}. \quad (3-46)$$

The exact relationship between the above quantities has not been established. The above relationships have in some instances failed to predict the correct values of ϵ_{12}^* and r_{12}^* .

Combining Equation (3-43) with Equation (3-45), the characteristic volume for the unlike pair becomes

$$(V_{12}^*)^{1/3} = \frac{1}{2}(V_{11}^*)^{1/3} + \frac{1}{2}(V_{22}^*)^{1/3}. \quad (3-47)$$

Combining Equation (3-42) with Equation (3-46), the

characteristic temperature becomes

$$T_{12}^* = (T_{11}^* T_{22}^*)^{\frac{1}{2}}. \quad (3-48)$$

To test the validity of Equation (3-44), Guggenheim and McGlashan plotted B_{12}^*/V_{12}^* for six different mixtures versus T/T_{12}^* and found reasonable agreement between the resulting curve and the curve for pure components.

2. The Pseudocritical Constants of Leland and Mueller

Based on the second virial coefficient, Leland and Mueller (28) developed a set of rules with which the pseudocritical constants for a gaseous mixture may be determined. Their derivation begins with the theoretical expression for the second virial coefficient. This expression

$$B = 2\pi N_0 \int_0^\infty r^2 (1 - e^{-u(r)/kT}) dr \quad (3-49)$$

was integrated by Lennard-Jones (30) for a potential term given by

$$u(r) = \epsilon f(\sigma/r). \quad (3-50)$$

The resulting expression for the second virial was

$$B = 2/3\pi N_0 \sigma^3 (4\epsilon/kT)^{\frac{1}{4}} \sum_{\nu=0}^{\infty} f(\nu) (4\epsilon/kT)^{\nu/2} \quad (3-51)$$

where

$$f(\nu) = - \frac{\Gamma(-\frac{1}{4} + \nu/2)}{4}.$$

Leland and Mueller rewrote equation (3-51) as

$$B = \sum_{\nu=0}^{\infty} f_{\nu}(T) \sigma^3 \epsilon^{\frac{2\nu+1}{4}} \quad (3-52)$$

The second virial coefficient for a mixture is given by

$$B_m = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} y_i y_j B_{ij} \quad (3-53)$$

If Equation (3-52) is substituted into Equation (3-53), the second virial coefficient for a mixture becomes

$$B_m = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} y_i y_j \sum_{\nu=0}^{\infty} f_{\nu}(T) \sigma_{ij}^3 \epsilon_{ij}^{2\frac{\nu+1}{4}} \quad (3-54)$$

If the pseudocritical concept of Kay is valid, there should exist a hypothetical pure substance with critical properties, T_c' , P_c' , and V_c' , such that the P-V-T properties of this hypothetical substance are identical with those for the mixture. The second virial coefficient for this hypothetical mixture would be given by

$$B = \sum_{\nu=0}^{\infty} f_{\nu}(T) \sigma^3 \bar{\epsilon}^{2\frac{\nu+1}{4}} \quad (3-55)$$

where σ and $\bar{\epsilon}$ represent the Lennard-Jones potential parameters for the hypothetical substance.

If the right sides of Equations (3-54) and (3-55) are equated, the following expression results:

$$\sum_{\nu=0}^{\infty} f_{\nu}(T) \sigma^3 \bar{\epsilon}^{2\frac{\nu+1}{4}} = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} y_i y_j \sum_{\nu=0}^{\infty} f_{\nu}(T) \sigma_{ij}^3 \epsilon_{ij}^{2\frac{\nu+1}{4}} \quad (3-56)$$

By equating coefficients of like values of $f_{\nu}(T)$, there results a set of equations of the form

$$\sigma^3 \bar{\epsilon}^{2\frac{\nu+1}{4}} - \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} y_i y_j \epsilon_{ij}^{2\frac{\nu+1}{4}} \sigma_{ij}^3 = 0 \quad (3-57)$$

where

$$\nu = 0, 1, 2, 3, \dots$$

There are more equations in the set than are necessary to evaluate $\bar{\sigma}$ and $\bar{\epsilon}$. No value of $\bar{\sigma}$ and $\bar{\epsilon}$ will satisfy all of them. Leland and Mueller stated that two values of ν should be selected so that the remaining equations in the set will as nearly as possible equal zero. For one of the values of ν , these authors selected zero and for the second value, they chose a parameter, α , which they evaluated empirically. The following two equations were obtained as a result of this selection:

$$\bar{\epsilon} = \left[\frac{\sum_{i=1}^n \sum_{j=1}^n y_i y_j (\epsilon^\alpha \sigma^3)_{ij}}{\sum_{i=1}^n \sum_{j=1}^n y_i y_j \sigma_{ij}^3} \right]^{1/\alpha} \quad (3-58)$$

$$\bar{\sigma}^3 = \sum_{i=1}^n \sum_{j=1}^n y_i y_j \sigma_{ij}^3. \quad (3-59)$$

If the assumptions that

$$\epsilon \propto T_c \quad (3-60)$$

$$\sigma^3 \propto v_c \propto \frac{Z_c T_c}{P_c} \quad (3-61)$$

$$(\epsilon^\alpha \sigma^3)_{ij} = \sqrt{(\epsilon^\alpha \sigma^3)_i (\epsilon^\alpha \sigma^3)_j} \quad (3-62)$$

$$\sigma_{ij} = \left[\frac{1}{2}(\sigma_i^3)^{1/3} + \frac{1}{2}(\sigma_j^3)^{1/3} \right]^3 \quad (3-63)$$

and

$$Z_c' = \sum_{i=1}^m y_i (Z_c)_i \quad (3-64)$$

are made, then the following rules for the pseudocritical constants are obtained:

$$T_c' = \left[\frac{\sum_{i=1} \sum_{j=1} y_i y_j \left(\frac{Z_c T_c}{P_c} \right)_i^{\alpha+1} \left(\frac{Z_c T_c}{P_c} \right)_j^{\alpha+1}}{\sum_{i=1} \sum_{j=1} y_i y_j \left[\frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_i^{1/3} + \frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_j^{1/3} \right]^3} \right]^{1/\alpha} \quad (3-65)$$

$$P_c' = \frac{T_c' \sum_{i=1} y_i Z_{ci}}{\sum_{i=1} \sum_{j=1} y_i y_j \left[\frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_i^{1/3} + \frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_j^{1/3} \right]^3} \quad (3-66)$$

Leland, Mueller, and Kobayashi (29) gave the following method for calculating the empirical exponent, α

$$\alpha = -0.75 \left(\frac{P \sum y_i T_{ci}}{T \sum y_i P_{ci}} \right) + 2.44 \quad (3-67)$$

For values of $P \sum y_i T_{ci} / T \sum y_i P_{ci} \geq 2.0$, α may be set equal to 1.0 and for values ≤ 0.4 , α may be set equal to 2.2.

Several alternate rules based on the derivation of Leland and Mueller are possible by varying the assumptions made in equations (3-60) through (3-64).

Satter (61) has shown that if equation (3-62) is replaced by

$$\epsilon_{ij} = (\epsilon_i \epsilon_j)^{\frac{1}{2}}$$

the resulting equations are

$$T_c' = \left[\frac{\sum_{i=1} \sum_{j=1} y_i y_j [T_{cii} T_{cjj}]^{\alpha/2} \left[\frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_{ii}^{1/3} + \frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_{jj}^{1/3} \right]^3}{\sum_{i=1} \sum_{j=1} y_i y_j \left[\frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_i^{1/3} + \frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_j^{1/3} \right]^3} \right]^{1/\alpha} \quad (3-68)$$

$$P_c' = \frac{T_c' \sum_{i=1} y_i Z_{ci}}{\sum_{i=1} \sum_{j=1} y_i y_j \left[\frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_i^{1/3} + \frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_j^{1/3} \right]^3} \quad (3-69)$$

The form for ϵ_{12} that Satter used is identical with the form that was used in the work of Guggenheim and McGlashan that was discussed in the previous section.

Sarem (60) also assumed alternate forms of the interaction parameter and in so doing arrived at pseudocritical constant rules somewhat different than those of Leland and Mueller. In one set of rules, he assumed that the parameters were given by a geometric mean

$$\sigma_{ij} = \sqrt{\sigma_i \sigma_j} \quad (3-70)$$

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \quad (3-71)$$

and in another, he assumed a harmonic mean given by

$$\sigma_{ij} = \frac{2\sigma_i \sigma_j}{\sigma_i + \sigma_j} \quad (3-72)$$

$$\epsilon_{ij} = \frac{2\epsilon_i \epsilon_j}{\epsilon_i + \epsilon_j} \quad (3-73)$$

In his work, Sarem concluded that the geometric means

provided the most applicable pseudocritical constants for his prediction technique.

It is interesting to note that in the derivation of the Leland and Mueller rules, if the assumptions are made that $\alpha = 1$ and Z_c is a constant, then

$$\frac{T_c'}{P_c'} = 1/8 \sum_i \sum_j y_i y_j \left[\left(\frac{T_c}{P_c} \right)_i^{1/3} + \left(\frac{T_c}{P_c} \right)_j^{1/3} \right]^3. \quad (3-74)$$

This is identical with the form of this ratio that Joffe obtained.

It is apparent from the above discussion that, just as in the case of Joffe's rules, several alternate forms of Leland and Mueller's rules may be arrived at by alternate forms of the equations used to obtain the mixture constants.

3. The Pseudocritical Constants of Stewart, Burkhardt, and Voo

Stewart, Burkhardt, and Voo (64) developed several different pseudocritical constant rules from the second virial approach. They used the expression for the mixture second virial coefficient

$$B = \sum_i \sum_j y_i y_j B_{ij} \quad (3-75)$$

and assumed that the interaction second virial coefficient may be represented by

$$B_{ij} = \sum_{k=1}^m f_k(P_{cij}, T_{cij}, Z_{cij}) T^{\theta_k}. \quad (3-76)$$

In this equation T_{cij} , P_{cij} and Z_{cij} are the critical parameters for the interaction of species i and j . When $j=i$, these parameters are the true critical properties of species i . The exponent θK was assigned various integral and fractional values in their work.

It was further assumed that the second virial coefficient is given by an expression analogous to Equation (3-76). That is,

$$B = \sum_{k=1}^m f_k(T_c', P_c', Z_c') T^{\theta K}. \quad (3-77)$$

By combining Equations (3-75), (3-76), and (3-77) there results

$$\sum_{k=1} T^{\theta K} \left[f_k(P_c', T_c', Z_c') - \sum_i \sum_j y_i y_j (T_{cij}, P_{cij}, Z_{cij}) \right] = 0. \quad (3-78)$$

As in the derivation presented by Leland and Mueller, each bracketed term must vanish independently for each power of T . This gives a set of n equations of the form

$$f_k(T_c', P_c', Z_c') = \sum_i \sum_j y_i y_j f_k(T_{cij}, P_{cij}, Z_{cij}) \quad (3-79)$$

$$k = 1, 2, \dots, n.$$

Equation (3-79) gives a set of n equations in the three unknowns, P_c' , T_c' and Z_c' . To obtain a rigorous solution for the three unknowns, the number of equations must equal the number of unknowns. For three unknowns, the second virial

coefficient would have to be expressed by an equation containing only three powers of T .

In order to use Equation (3-79), it is necessary to specify the form of the function f_k in Equation (3-76). These authors chose several different forms of f_k and evaluated the resulting pseudocritical constants. One form that they assumed for Equation (3-76) is

$$B_{ij} = c_1 \left(\frac{T_c}{P_c} \right)_{ij} + c_2 \left(\frac{T_c^2}{P_{cij}} \right) T^{-1} \quad (3-80)$$

with

$$\left(\frac{T_c}{P_c} \right)_{ij} = \left[\frac{1}{2} \left(\frac{T_{ci}}{P_{ci}} \right)^{1/3} + \frac{1}{2} \left(\frac{T_{cj}}{P_{cj}} \right)^{1/3} \right]^3 \quad (3-81)$$

and

$$(T_c^2/P_c)_{ij} = (T_{ci}^2/P_{ci} T_{cj}/P_{cj})^{1/2} . \quad (3-82)$$

Application to Equation (3-79) gives Joffe's rules for T_c' and P_c' . The value of Z_c' has to be found by other means, in this case, since B_{ij} was assumed independent of Z_{cij} . These authors stated that the numerical values of c_1 and c_2 do not enter into the calculation except that they must be non-zero and independent of temperature.

A variety of other forms of Equation (3-76) was assumed and corresponding sets of pseudocritical constant rules were obtained. In all, Stewart, Burkhardt, and Voo tested a total of twenty one different rules. Some of these were simple rules not derived from this virial approach. The rule that they deemed most applicable was one based on a slight

modification of the mixing rule of Joffe.

The rules which they recommended are given by the following:

$$T_c' / P_c' = 1/3 \sum_i y_i T_{ci} / P_{ci} + 2/3 \left[\sum_i y_i (T_{ci} / P_{ci})^{1/2} \right]^2 \quad (3-83)$$

$$T_c' / (P_c')^{1/2} = \sum_i y_i T_{ci} / (P_{ci})^{1/2} . \quad (3-84)$$

4. The Pseudocritical Constants of Prausnitz and Gunn

Prausnitz and Gunn (45) developed a set of pseudocritical constant rules based on the virial approach. Their derivation is quite similar to the two virial derivations previously discussed, but differs in that they assume that the second virial coefficient is also a function of Pitzer's acentric factor. These authors recommend the following procedure for calculating the pseudocritical constants:

- a. Calculate all possible values of T_{cij} and V_{cij} from

$$T_{cij} = (T_{ci} T_{cj})^{1/2} - \Delta T_{cij} \quad (3-85)$$

$$V_{cij} = \frac{1}{2}(V_{ci} + V_{cj}) - \Delta V_{cij} \quad (3-86)$$

ΔT_{cij} and ΔV_{cij} , are correction terms which can be read from curves prepared from binary data.

- b. Compute the pseudocritical volume and the acentric factor from

$$V_c' = \sum_{ij} y_i y_j V_{cij} \quad (3-87)$$

$$\omega' = \sum_i y_i \omega_i \quad (3-88)$$

c. Compute the quantities β' and γ from

$$\beta' = \sum_{ij} y_i y_j (V_c T_c)_{ij} \quad (3-89)$$

$$\gamma = \sum_{ij} y_i y_j (V_c T_c^2)_{ij} . \quad (3-90)$$

d. Calculate the pseudocritical temperature from

$$T_c' = \frac{\beta' + \sqrt{\beta'^2 + r' V_c' \gamma}}{2s V_c'} \quad (3-91)$$

and the pseudocritical pressure from

$$P_c' = RT_c' / V_c' \sum_i y_i Z_{ci} . \quad (3-92)$$

The constants r' and s may be read from tables that Prausnitz and Gunn presented. In these tables, r' and s are tabulated as functions of the reduced temperature and Pitzer's acentric factor. This requires that the pseudocritical temperature be estimated before the table may be used.

Because of the complexity of the proposed method, Prausnitz and Gunn presented a simplified method which they felt would be sufficiently accurate for most chemical engineering purposes. The pseudocritical constants are calculated in the simplified method from

$$T_c' = \sum_i y_i T_{ci} \quad (3-93)$$

$$P_c' = RT_c' / \sum_i y_i V_{ci} \sum_i y_i Z_{ci} . \quad (3-94)$$

Reid and Leland (49) have shown that, aside from the empirical factors introduced to obtain a better fit with experimental data, the basic differences in the pseudocritical rules obtained from the second virial coefficient lie in the different assumptions employed to obtain the interaction terms from those of the pure components. This being true, as in the case of the pseudocritical rules obtained from two parameter equations of state where the final form depended upon the combination rules used to obtain the mixture a' and b' , it is impossible to choose one of these sets of rules over another on a theoretical basis. Again the choice must be based on a comparison with experimental data. No such comparisons have established pseudocritical rules for hydrocarbon - carbon dioxide mixtures.

CHAPTER IV

THE EXPERIMENTAL DETERMINATION OF COMPRESSIBILITY FACTORS

While experimental compressibility factors are available for binaries of a hydrocarbon plus carbon dioxide, no such data were available for systems containing more than one hydrocarbon and carbon dioxide.

The experimental phase of this study was to provide data on mixtures of hydrocarbons and carbon dioxide. Compressibility factors were determined for five mixtures of methane, carbon dioxide, and ethane or propane at 100, 130, and 160° F, and pressures up to 7,026 psia. A comparison of determined compressibility factors with published data and an analysis of the error involved have shown that the equipment that was employed might not be sufficiently accurate for a basic study of molecular interactions, but it is sufficiently accurate for the determination of usable volumetric data. The accuracy of the experimental data is sufficient for the purpose of this study.

A. Experimental Equipment

The experimental equipment used in this study was

originally assembled at the University of Oklahoma by Nassiri (37). The technique for utilizing this equipment was later perfected by Satter (61). Slight modifications in the experimental set-up of these investigators were made in this study when it was felt that either safety, accuracy, or ease of operation could be improved.

Based on the phase of the experiment in which they are employed, the equipment may be conveniently divided into three groups: the high pressure equipment which is utilized to determine the pressure, volume, and temperature relationship for a gas sample; the low pressure equipment which is employed to determine the number of moles of gas present in the sample; and the auxiliary equipment.

1. The High Pressure Equipment

A high pressure cell and a mercury pump were the two principle components of the high pressure equipment. Both were made by the Ruska Instrument Corporation of Houston, Texas. They are shown schematically in Figure IV-1.

The 500 cc. cell has a maximum working pressure of 12,000 psia. It is equipped with two stainless steel valves which serve as inlet and outlet for the cell and an internal paddle mechanism which stirs the contained fluid when the cell is rocked. The cell was mounted in a constant temperature water bath in such a manner that it could be manually rocked when desired. Constant temperature was maintained in

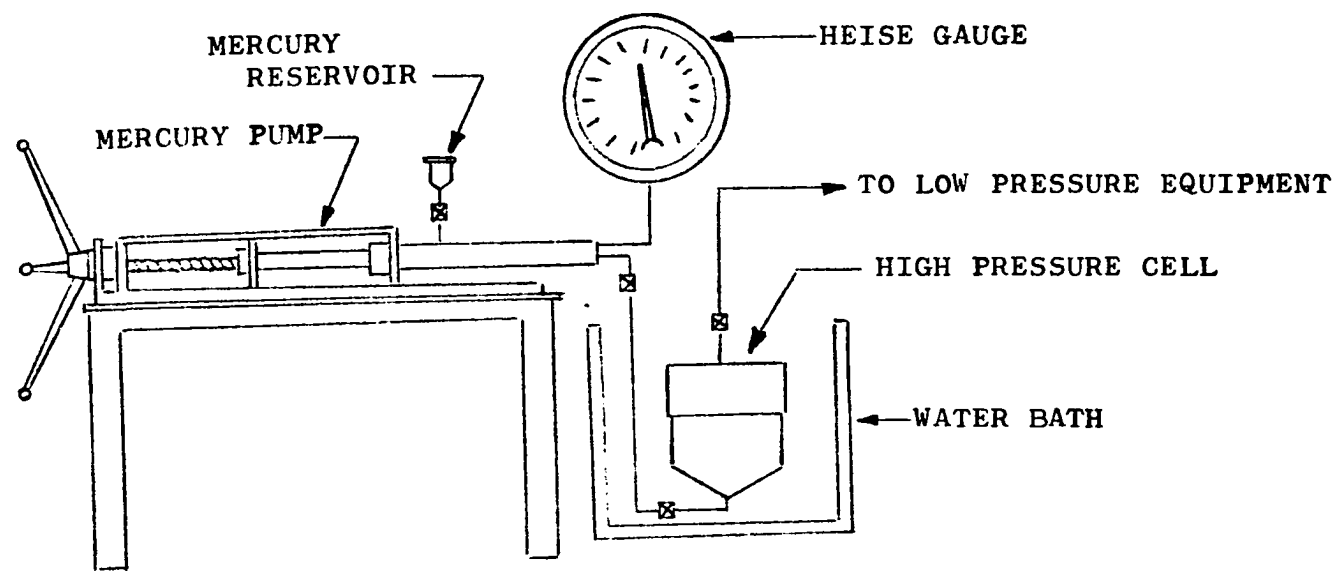


FIGURE IV-1. HIGH PRESSURE EQUIPMENT

the bath with a circulating pump and a thermostatically controlled 3,000 watt electric heater.

The 250 cc. mercury pump has a maximum working pressure of 8,000 psia. The smallest scale division on the pump for measuring the volumes of mercury injected is 0.01 cc. Since the cell volume is twice the volume capacity of the mercury pump, a means of adding mercury to the system was necessary. This was done through the mercury reservoir located on top of the pump.

Coiled stainless steel tubing was used to connect the pump to the high pressure cell. The pump was also connected to a 10,000 psig Heise gauge with scale divisions of 10 psig.

2. The Low Pressure Equipment

For determining the number of moles present in a gas sample, components of a standard Bean unit manufactured by the Refinery Supply Company of Tulsa, Oklahoma were used. These components were a 1,000 psig stainless steel cell, a glass expansion burette, a glass mercury reservoir, a manometer tube, and a constant temperature bath. The unit as employed in this study is depicted in Figure IV-2.

As used in this study, the stainless steel cell's sole purpose was to avoid expanding from the variable volume cell (in the high pressure part of the equipment) directly into the glass expansion burette. With this stainless steel expansion cell, it was possible to expand in steps and thus

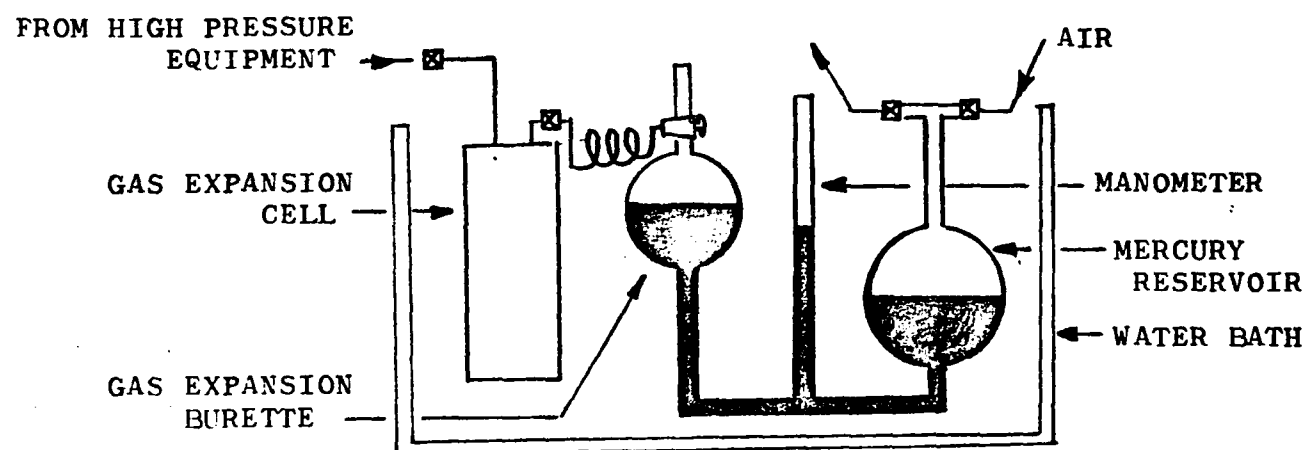


FIGURE IV-2. LOW PRESSURE EQUIPMENT

avoid the danger of applying excessive pressures to the glass expansion burette.

The approximately 1,000 cc. glass expansion burette is equipped with a three way stopcock on the top and an etch mark on its lower stem. When this burette is filled with gas from the stopcock to the etch mark, one has a known volume of gas at the temperature of the bath and the pressure which is read on the manometer tube.

Through a tee and valve arrangement atop the glass mercury reservoir, the reservoir may be subjected to either atmospheric or some higher pressure. The purpose of the reservoir is to alternately inject and remove mercury from the glass expansion burette. This is done by controlling the pressure on the mercury in the reservoir.

The stainless steel constant temperature water bath is equipped with glass windows to allow visual observations of the burettes and the manometer. It is also equipped with an electric stirrer, a 700 watt electric heater for bringing the bath to a desired temperature, and a 200 watt thermostatically controlled heater for maintaining the desired temperature,

Coiled stainless steel tubing was used to connect the stainless steel cell to the glass expansion burette. It was used to inhibit the cooling that takes place when gas is expanded from the cell to the burette and thus shorten the time required to bring the gas up to the bath temperature.

3. Auxiliary Equipment and Accessories

Satter stated that one possible source of error in utilizing this equipment was the fluctuation in room temperature. For this reason, the room temperature was thermostatically controlled. Thermostatic controls were used to turn on an air conditioning system or a steam heating system whenever they were necessary to maintain the room temperature. It was possible to maintain the room at $77 \pm 1^{\circ}$ F. throughout the experiments. This not only provided a fairly constant base temperature for reading pressures and volumes on the mercury pump but also made it easier to maintain a constant temperature in the two water baths.

For preparing gas mixtures, an auxiliary 100 cc. mercury pump equipped with an 8,000 psig Heise gauge and a 500 cc. high pressure cell were used. This equipment was assembled similarly to that shown in Figure IV-1 with the exception that the cell was not placed in a constant temperature bath. This system was used only to prepare approximate mixtures to be analysed later.

Some of the accessories that were used are a dead weight tester, mercury in glass thermometers, a vacuum pump, a barometer, balances, and graduated cylinders.

B. Calibration of Equipment

Before proceeding with the experimental work, it was necessary to check the calibration of several components. It

was also necessary to accurately determine volumes of cells, burettes, and lines.

1. The Heise Gauge

The 10,000 psig Heise gauge was checked with a dead weight tester from 50 to 8,000 psig. Only in the high pressure range from 6,000 to 8,000 psig was there any appreciable difference between the gauge reading and those of the tester. This difference never exceeded the 10 psig scale division of the gauge.

In the experimental assemblage of the equipment, the distance from the center of the Heise gauge to the center of the high pressure cell amounts to a pressure difference of 12 psi. This is the only correction that was applied to the gauge reading to obtain gauge pressure in the cell.

2. The High Pressure Cell

Before determining the volume of the high pressure cell, the cell was disassembled and thoroughly cleaned with acetone. It was then reassembled and checked for leaks.

The volume of the high pressure cell and the line from the mercury pump to the cell were determined as a function of temperature and pressure. This was done by evacuating the cell from the valve on top of the cell to the discharge valve of the pump. The discharge valve of the pump was then opened and the cell filled with mercury. By varying the temperature

and pressure of the mercury in the cell, the cell volume as a function of temperature and pressure could be calculated from

$$V_2 = V_1 \left[(1 + \beta_1 P_1) v_2 / v_1 (1 - \beta_2 P_2) \right] \quad (4-1)$$

where β is the compressibility of mercury, v is the volume of mercury relative to the volume at 60° F., V denotes volume, and P denotes gauge pressure. The subscript 1 denotes the base temperature and pressure for making volume measurements on the mercury pump. A pressure of 3,000 psi and 77° F. were used for base conditions. V_1 is the volume the cell would have if the mercury it contained were at 3,000 psi and 77° F. The subscript 2 denotes the temperature and pressure of the cell. V_2 is the volume of the cell at the pressure P_2 . Values of β and v were taken from the literature (35) and are presented in Table 1 of Appendix C.

The procedure discussed above was performed several times at temperatures of 100, 130, and 160° F. and the pressure range of 1,000 to 7,000 psig. It was found that the cell volume varied linearly with pressure at a given temperature and nearly linearly with temperature at a given pressure. At any one temperature and pressure, subsequent determinations of the cell volume never differed by more than 0.05 cc. The volumes as a function of temperature and pressure are shown in Figure 1 of Appendix C.

3. Expansion Cells

The volume of the stainless steel expansion cell and

the lines connecting it to the high pressure cell and the gas expansion burette were determined by evacuating them and measuring the volume of gas necessary to fill them to atmospheric pressure. The volume of gas was measured with a gas expansion bottle. The average of several volumetric determinations was 250.0 cc.

The volume of the glass expansion burette is far more critical than the volume of the steel expansion cell since this volume is multiplied by the number of expansions necessary to go from the pressure of the high pressure cell down to atmospheric pressure. Prior to determining the volume of this burette, it was cleaned with dilute hydrochloric acid, acetone, and distilled water. It was then thoroughly dried and filled with mercury from the stopcock to the etch mark on the lower stem. The mercury was then removed and weighed. Its volume was determined by dividing the weight by the density at the temperature of the determination. Several determinations of the burette's volume were made. The values obtained from different determinations never differed by as much as 0.1 cc. and had an average value of 997.34 cc.

4. Thermometers

Two different thermometers manufactured by the Central Scientific Company were used in this study. Both of these had scale divisions of 0.2° F. The boiling point of pure pentane at atmospheric pressure was measured to within

0.1° F with both of the thermometers. No correction was applied to temperatures measured as this difference in terms of absolute temperature is insignificant.

C. Experimental Procedure

A standard sequence was set up for performing the experiments. The sequence consisted of a preliminary checking and preparing of the equipment, making the gas mixtures, determining the P-V-T relationship for the mixture in the high pressure equipment, and finally determining the number of moles in the mixture with the low pressure equipment.

1. Preliminary Preparations

Prior to and throughout each of the experimental runs, checks were made to be sure the system was leakproof. The checks before the run were either made by establishing a components ability to hold a vacuum or by its ability to hold mercury at a pressure of 7,000 psig. Visual observations for leaks were also made throughout the experiments.

The high pressure part of the equipment was prepared by evacuating the high pressure cell from the valve on top of the cell to the discharge valve of the mercury pump. With the discharge valve on the mercury pump closed, the pump was brought to 3,000 psig and a base pump reading was then made at this pressure and a room temperature of 77° F. (Subsequent pump readings were all made at these conditions.) The evacuated cell was then filled with mercury to 3,000 psig

and its water bath was brought to 100° F. Following a sufficient amount of time to allow the cell to come to equilibrium the cells volume was checked at 3,000 psig and 100° F, with the calibration curve given in Figure 1 of Appendix C.

Since the volume of the cell exceeds that of the pump, it was necessary to add mercury to the pump during the filling of the cell. Following a complete stroke of the pump, the discharge valve on the cell was closed and a pump reading was made at the base conditions. The pump pressure was reduced to zero and the valve connecting the pump to the mercury reservoir was opened. The pump's plunger was withdrawn allowing mercury to enter the pump. Care was taken to maintain the mercury level in the reservoir and thus prevent air from entering the system. When the pump's plunger was completely withdrawn, the valve to the reservoir was closed and the pump was brought to 3,000 psig and a reading of the pump was recorded. This procedure was always used to add mercury to the system. The procedure in reverse was employed whenever it was necessary to remove mercury from the system.

The low pressure equipment was prepared by filling the burettes of the modified Bean unit so that the mercury was on the plane of the etched mark of the gas expansion burette and the zero of the manometer tube when the system was exposed to atmospheric pressure and the bath was at 100° F. (A bath temperature of 100° F. was always used in

the low pressure phase of the experiment.) The air pressure available for moving mercury from the reservoir to the gas expansion burette was adjusted so that the mercury would rise to the stopcock of the gas expansion burette when this burette was opened to atmospheric pressure.

2. Preparation of Mixtures

The pure hydrocarbon gases used to prepare the mixtures were obtained from the Phillips Petroleum Company. The methane and propane were pure grade with a minimum purity of 99.0 mole per cent. The ethane was research grade with a purity of 99.9 per cent. The carbon dioxide obtained from the Matheson Company was bone dry grade with a minimum purity of 99.8 per cent.

Following the preparation of the high pressure equipment, the cell was at 3,000 psig and 100° F. The cell was then connected through stainless steel tubing to a methane bottle. This line was evacuated and purged several times with methane. The pressure in the cell was then reduced to just below the pressure in the gas bottle and the valve between the two containers was opened. Approximately 400 cc. of methane at 1,000 psig were taken into the cell by withdrawing mercury. The valve on top of the cell was then closed and the volume of methane in the cell was determined at 1,000, 2,000, and 3,000 psig and 100° F. By knowing the pressure, volume, and temperature, literature values of the methane compressibility factor could then be used to determine

the moles of methane in the system.

By knowing the number of moles of methane and the desired composition of the mixture, the number of moles of additional components in the mixture could be calculated. Once the number of moles of additional components were determined, they were added to the system by using the auxiliary pump and cell. The auxiliary cell was connected to the high pressure P-V-T cell through stainless steel tubing. The cell and tubing were evacuated, purged, and filled with the component to be added. They were then pressured to 2,000 psig. Since the moles, pressure, room temperature, and literature compressibility factors were known, the volume of this component that should be injected at 2,000 psig could be calculated. This volume of mercury was then injected into the auxiliary cell raising the cell's pressure to above 2,000 psig. The auxiliary equipment was then opened to the P-V-T cell and bled down to 2,000 psig. This allowed the required volume to enter the P-V-T cell. All additional components were added in this manner.

A procedure such as the one employed in this study will not give exactly the desired mixture but it was found that it worked very well for approximating the desired mixture. An example calculation for a mixture preparation is given in Appendix D.

The mixtures prepared in this study were chromatographically analyzed by the Phillips Petroleum Company

Research Center at Bartlesville, Oklahoma. Table 1 of Appendix F shows the results of their analysis.

3. P-V-T Measurement

Following the preparation of the desired mixture, the high pressure part of the experimental equipment was used to determine the pressure, volume, and temperature relationship of the mixture. With the gas mixture contained in the P-V-T cell, the bath temperature was controlled at 100° F. and the pressure in the cell was adjusted to 1,000 psig.

After a sufficient amount of time to allow equilibrium to be reached (approximately 30 minutes), the discharge valve of the mercury pump was closed and the pump pressure was brought to 3,000 psig. A pump reading at 3,000 psig and 77° F. was then made. From the preliminary preparation of the equipment, a base pump reading at these same conditions was available. With these two numbers, the volume of mercury in the cell could be calculated. This volume was corrected to 1,000 psig and 100° F. By knowing the cell's volume at 1,000 psig and 100° F. and the mercury's volume at these conditions, the volume of gas in the cell could be calculated.

With the determination of the gas volume at 1,000 psig and 100° F. completed, the pump pressure was reduced from 3,000 to 1,000 psig and the discharge valve of the pump was opened to the cell. The cell pressure was then increased from 1,000 psig to 1,500 psig and the above procedure was repeated. Subsequent readings were taken in 500 psi

increments to 5,000 psig and then in 1,000 psi increments to 7,000 psig. After the determination of the volume at 7,000 psig and 100° F, the entire pressure range from 1,000 to 7,000 psig was covered at 130° F. and then at 160° F.

For this phase of the experimental work, as large a gas volume as possible was always employed. This required that mercury be added to the pump system before the 2,000 psig reading and that the mercury be removed from the system after the 7,000 psig reading. This was performed as outlined in the equipment preparation section. While this could have been avoided by starting with a smaller gas volume, it was not difficult enough to warrant the loss in accuracy which would be caused by using the smaller volume.

4. The Determination of the Moles of Gas

For this phase of the experimentation, the high pressure equipment was connected to the low through stainless steel tubing. Both water baths were set at 100° F and the system from the valve on top of the P-V-T cell to the three way stopcock on the top of the gas expansion burette was evacuated. The gas in the P-V-T cell was then allowed to fill the line to the valve on top of the steel expansion cell. The discharge valve on this cell was closed and the inlet valve opened until a pressure of approximately 95 psig was in the cell. By opening the gas expansion burette to the atmosphere through the three way stopcock and applying

pressure to the top of the mercury reservoir burette, the gas expansion burette was filled with mercury. The air supply on top of the mercury reservoir was then shut off and the gas expansion burette was opened to the line to the gas expansion cell. By careful reduction of the pressure on the mercury reservoir and careful opening of the valve on top of the steel expansion cell, the mercury in the gas expansion burette was replaced with gas down to the etched mark on the lower stem. The gas was allowed to come to equilibrium and the pressure on the mercury reservoir necessary to maintain the mercury level on the etched mark was read from the manometer. With the development of experimental technique, it was possible to keep this pressure at zero psig. Expansions into the stainless steel cell and then into the gas burette were repeated until the pressure in the P-V-T cell was reduced to atmospheric pressure. By knowing the number of expansions into the gas burette and the pressure and temperature of this gas and by knowing the volume of the stainless expansion cell, the tubing to the P-V-T cell and the volume in the P-V-T cell, the total volume of the gas mixture at 100° F and atmospheric pressure could be calculated. By assuming perfect gas behavior, the number of moles in the mixture could then be calculated.

D. Accuracy of the Experimental Method

Before any of the mixtures were studied, it was felt that a comparison should be made between the compressibility

factors obtained with this equipment and some published data. Two sets of methane compressibility factors were determined at 100, 130, and 160° F and pressures up to 7,026 psia. A comparison between these values and compressibility factors obtained by interpolation of the methane data of Sage and Lacey (59) showed no point deviating by more than 0.5 per cent. Following the study of the first three mixtures, two more sets of methane compressibility factors were determined at 100° F, and pressures up to 7,026 psia. In each set, only one point deviated by more than 0.5 per cent. Both of these occurred at 1,026 psia. In the first set, the deviation at 1,026 psia was 0.65 per cent. In the second set, the deviation was 0.55 per cent.

A satisfactory comparison with published data increases one's confidence in experimental equipment, but it does not establish the accuracy which can be expected. To establish the maximum errors which might be introduced by the equipment, an analysis of the errors which could be introduced by each component was made.

The largest source of error in the equipment is the inability to read the 10,000 psig Heise pressure gauge more accurately than to the nearest 10 psi. An error of 10 psi in the pressure reading at 1,026 psia will introduce an error of 0.977 per cent in the subsequently determined Z. The error reduces to 0.142 per cent at 7,026 psia. This accounts for the largest deviations from Sage and Lacey's methane data

occurring at 1,026 psia.

The error introduced by the volume and temperature measurements in the high pressure phase is considerably less than those introduced by the pressure reading. To illustrate this point, the data from the third methane run at 100° F. was considered. The gas volume at 1,026 psia was 388.48 cc. Since the mercury pump can be read to the nearest 0.01 cc., the maximum error involved in this measurement was taken to be the maximum difference of 0.05 cc. that was obtained in the calibration of the P-V-T cells volume. With a gas volume of 388.48 cc., the error in the compressibility factor introduced by a 0.05 cc. error in the gas volume will be 0.011 per cent. At 7.026 psia, the gas volume was reduced to 73.05 cc. and an error of 0.05 cc. would result in an error of 0.068 per cent. The thermometers used were accurate to the nearest 0.2° F. An error of 0.2° F. would introduce a maximum error in the compressibility factor of 0.035 per cent.

In the low pressure equipment, the pressure can be read to the nearest .05 inches of mercury. Taking the maximum error in reading the barometric pressure as 1.5 mm. of mercury, the error in the compressibility factor for a barometric pressure of 730 mm. of mercury would be .206 per cent. No difference as large as 0.1 cc. was obtained in measuring the volume of the gas expansion burette. A gas volume in the P-V-T cell of 380 cc. at 1,000 psig and 100° F. takes about 33 expansions to bring the gas to atmospheric pressure.

Assuming an error of 0.1 cc, per expansion would result in an error of 3.3 cc. in the gas volume at atmospheric pressure and 100° F. Adding to this a 1 cc. error in the volume of the stainless steel expansion cell and lines would give a total error in the volume of 4.3 cc. By beginning with 380 cc. in the high pressure cell at 1,000 psig and 100° F, the volume would be approximately 33,000 cc. at atmospheric pressure. The error in reading the volume would then cause an error of 0.001 per cent in the compressibility factor. As the temperature is again read at 100° F, another temperature error of 0.035 per cent could be introduced.

Assuming that all of the discussed errors are cumulative, a maximum error of 1.265 per cent could be obtained for the compressibility factor at 1,026 psig. The maximum error for all of the rest of the points would be less than 1.0 per cent. Based on the above analysis, the accuracy of the data is considered to be within 1.0 per cent at the pressure points studied above 1,026 psig. This analysis indicates that the equipment as assembled should not be used for pressures below 1,000 psig without providing a more accurate means of measuring the pressure in the P-V-T cell.

E. Mixture Compressibility Factors

Compressibility factors were determined for five mixtures of hydrocarbons and carbon dioxide. The procedure used for calculating the compressibility factors from the

experimental data is illustrated by a sample calculation in Appendix D. The compressibility factors for the five mixtures are tabulated in Table 2 of Appendix F and are plotted in Figures IV-3 through IV-7.

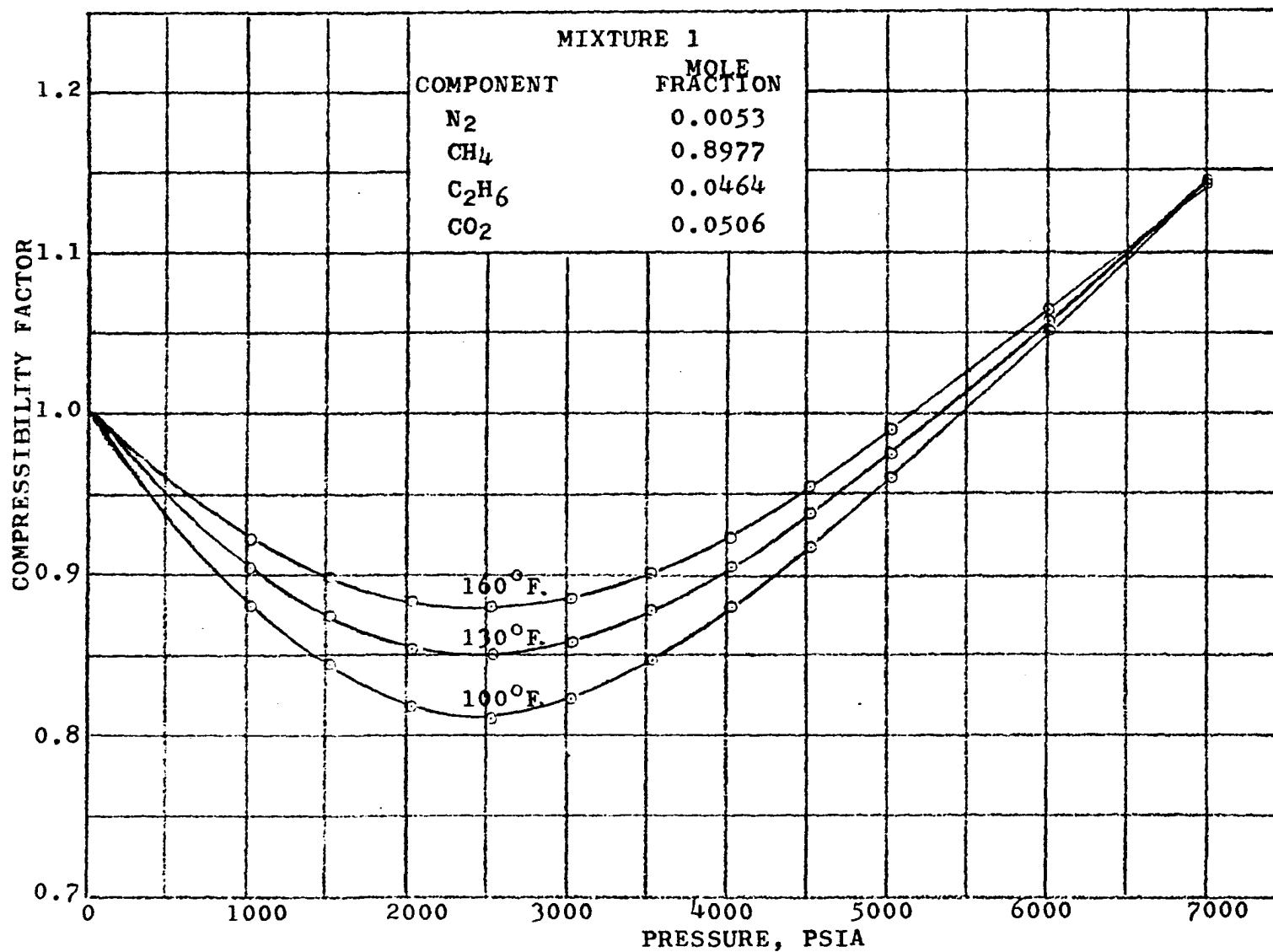


FIGURE IV-3. EXPERIMENTAL COMPRESSIBILITY FACTORS FOR MIXTURE 1

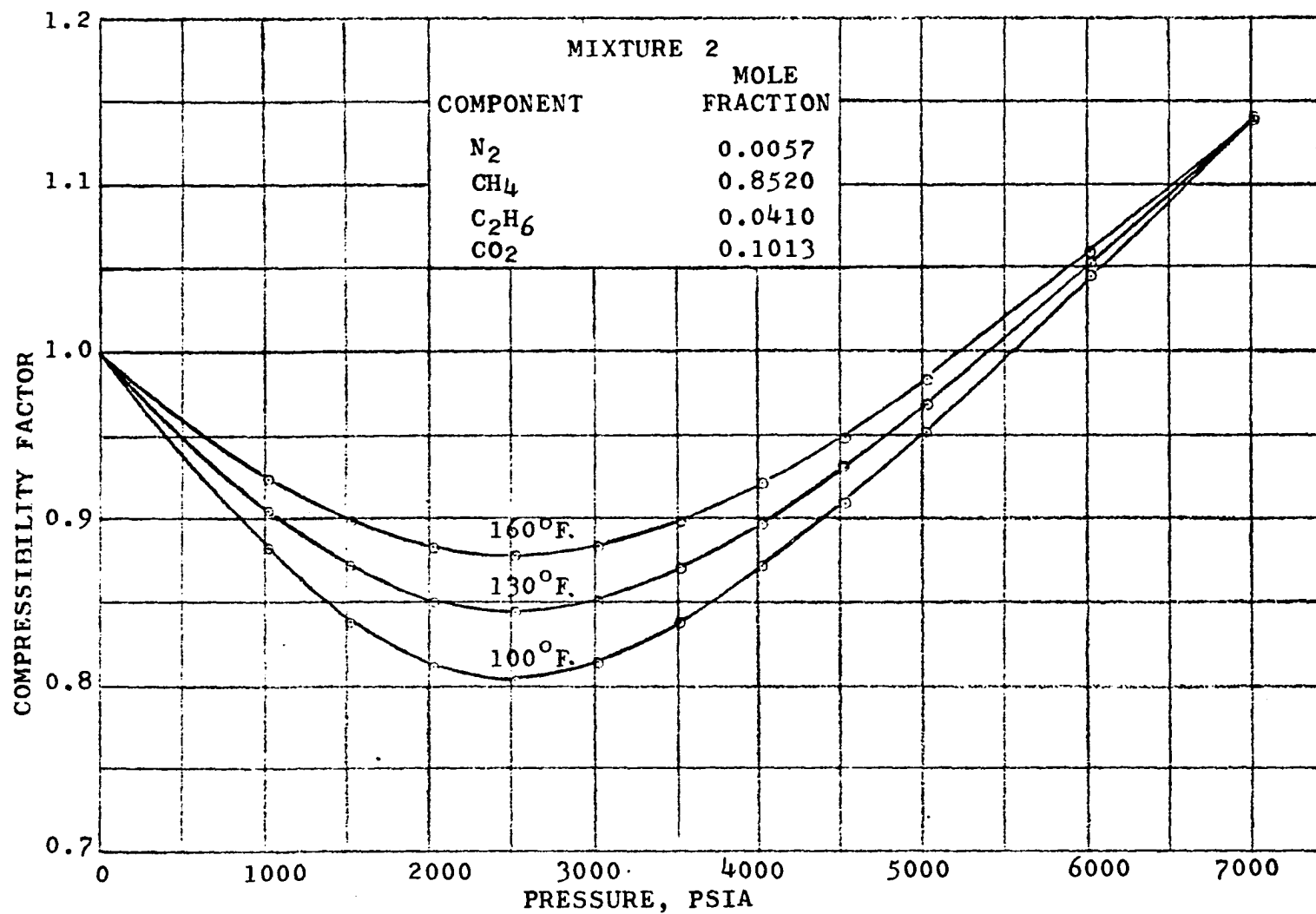


FIGURE IV-4. EXPERIMENTAL COMPRESSIBILITY FACTORS FOR MIXTURE 2

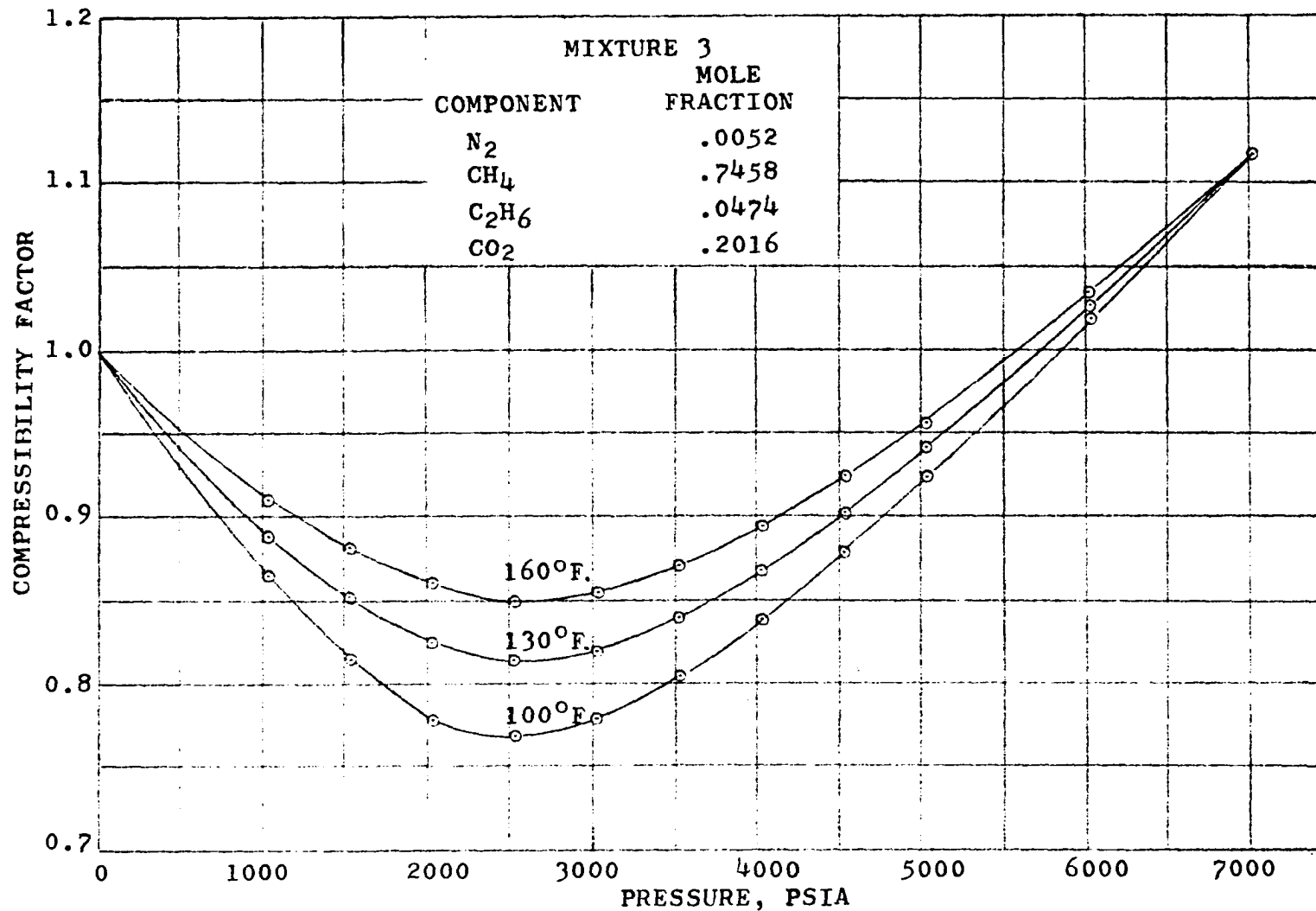


FIGURE IV-5. EXPERIMENTAL COMPRESSIBILITY FACTORS FOR MIXTURE 3

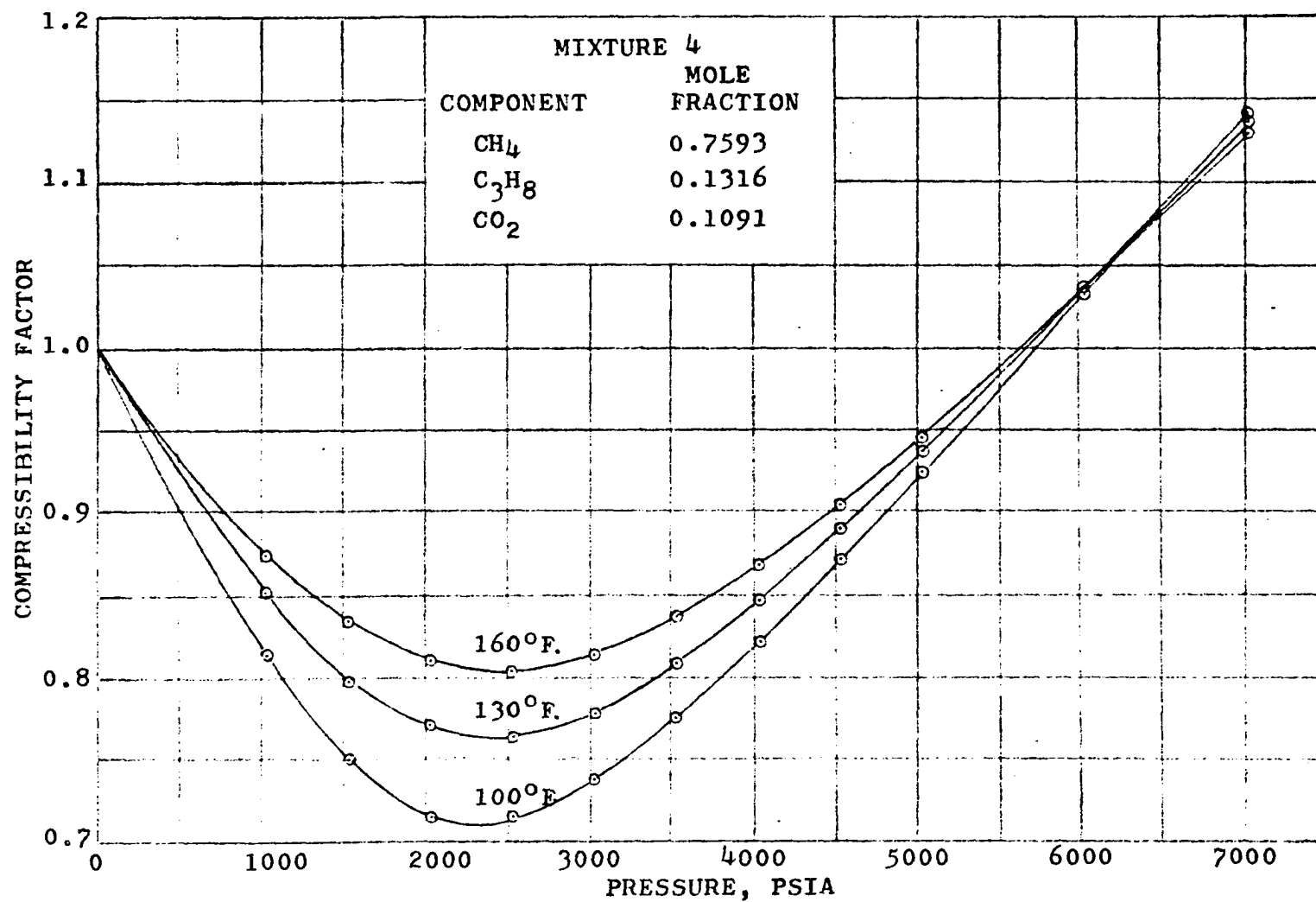


FIGURE IV-6. EXPERIMENTAL COMPRESSIBILITY FACTORS FOR MIXTURE 4

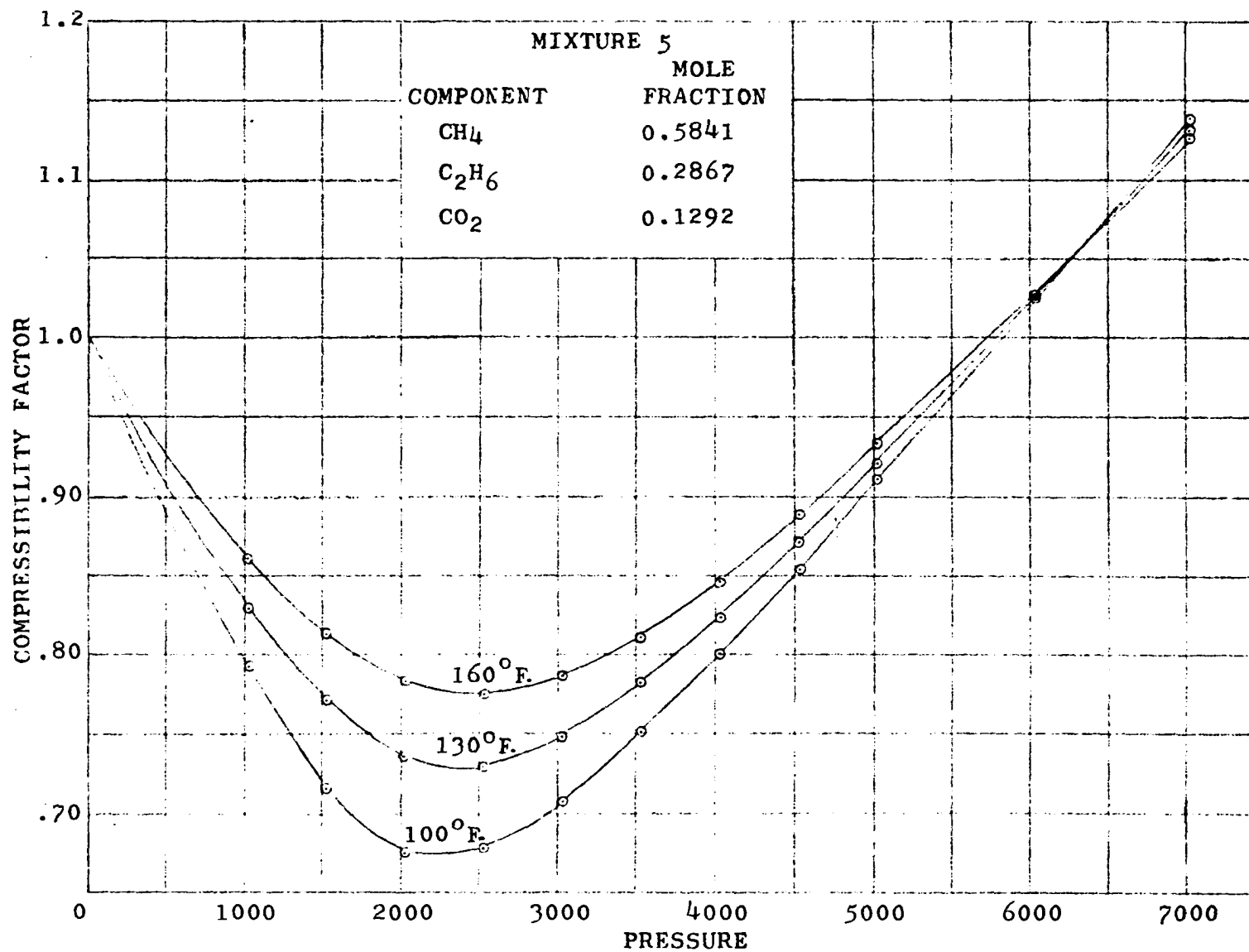


FIGURE IV-7. EXPERIMENTAL COMPRESSIBILITY FACTORS FOR MIXTURE 5

CHAPTER V

THE SELECTION OF A THIRD PARAMETER FOR HYDROCARBON--CARBON DIOXIDE SYSTEMS

The remainder of this study is aimed at the selection of a third parameter and a set of pseudocritical rules which will provide a reliable prediction of the compressibility factors for hydrocarbon - carbon dioxide systems. The selection of the third parameter is the subject of this chapter.

As far as the hydrocarbon constituents of natural gas are concerned, a definite relationship exists between the general third parameters. In Figure V-1 through V-4, Z_c , R_d , δ_c , and α_k are plotted versus ω . In each of these plots, a nearly linear relationship exists between the parameters.

In Figure V-1, where Z_c is plotted versus ω , the straight line drawn may be represented by

$$Z_c = 0.293 - .093 \omega \quad (5-1)$$

In Pitzer's tables, the values of Z^0 and Z' at a reduced temperature and pressure of one are given by 0.291 and -0.080 respectively. The critical compressibility factor should then be related to ω by

$$Z_c = 0.291 - .080 \omega \quad (5-2)$$

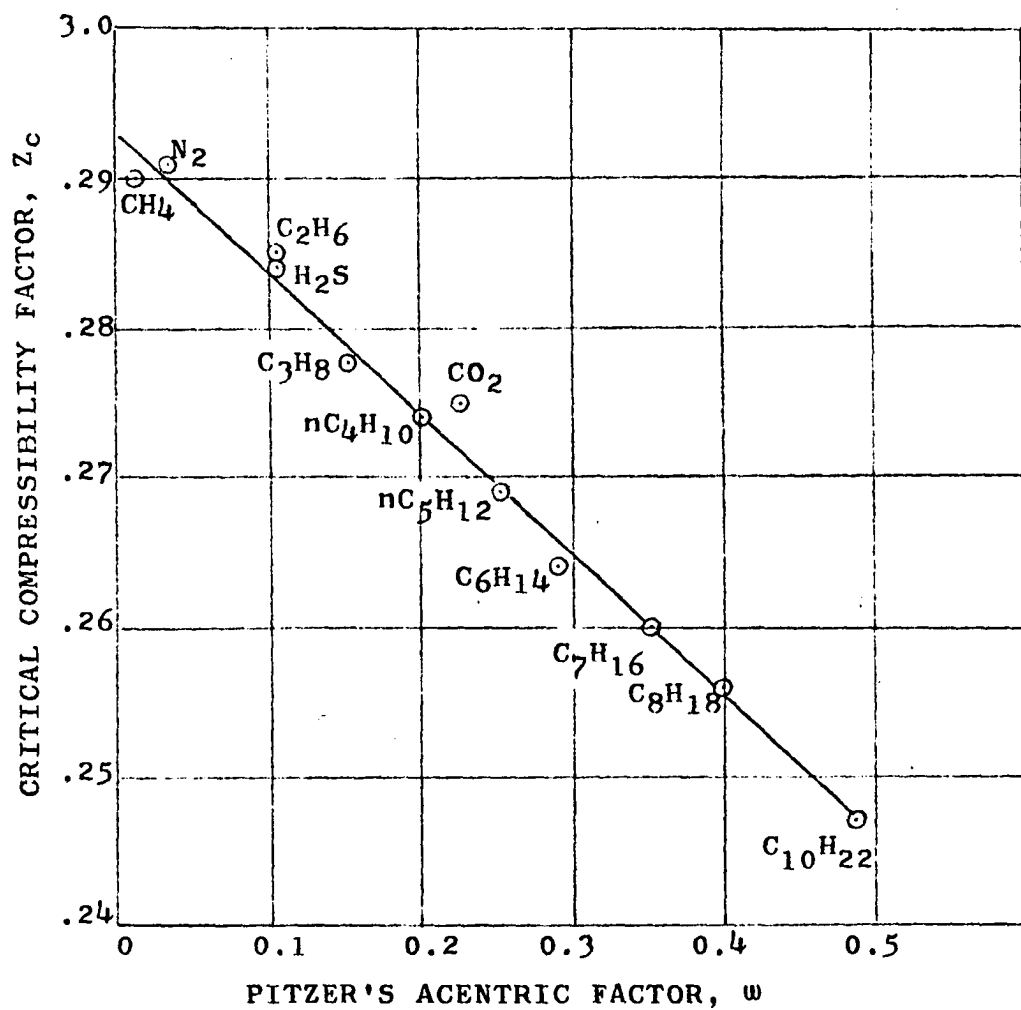


FIGURE V-1. THE CRITICAL COMPRESSIBILITY FACTOR
VERSUS PITZER'S ACENTRIC FACTOR

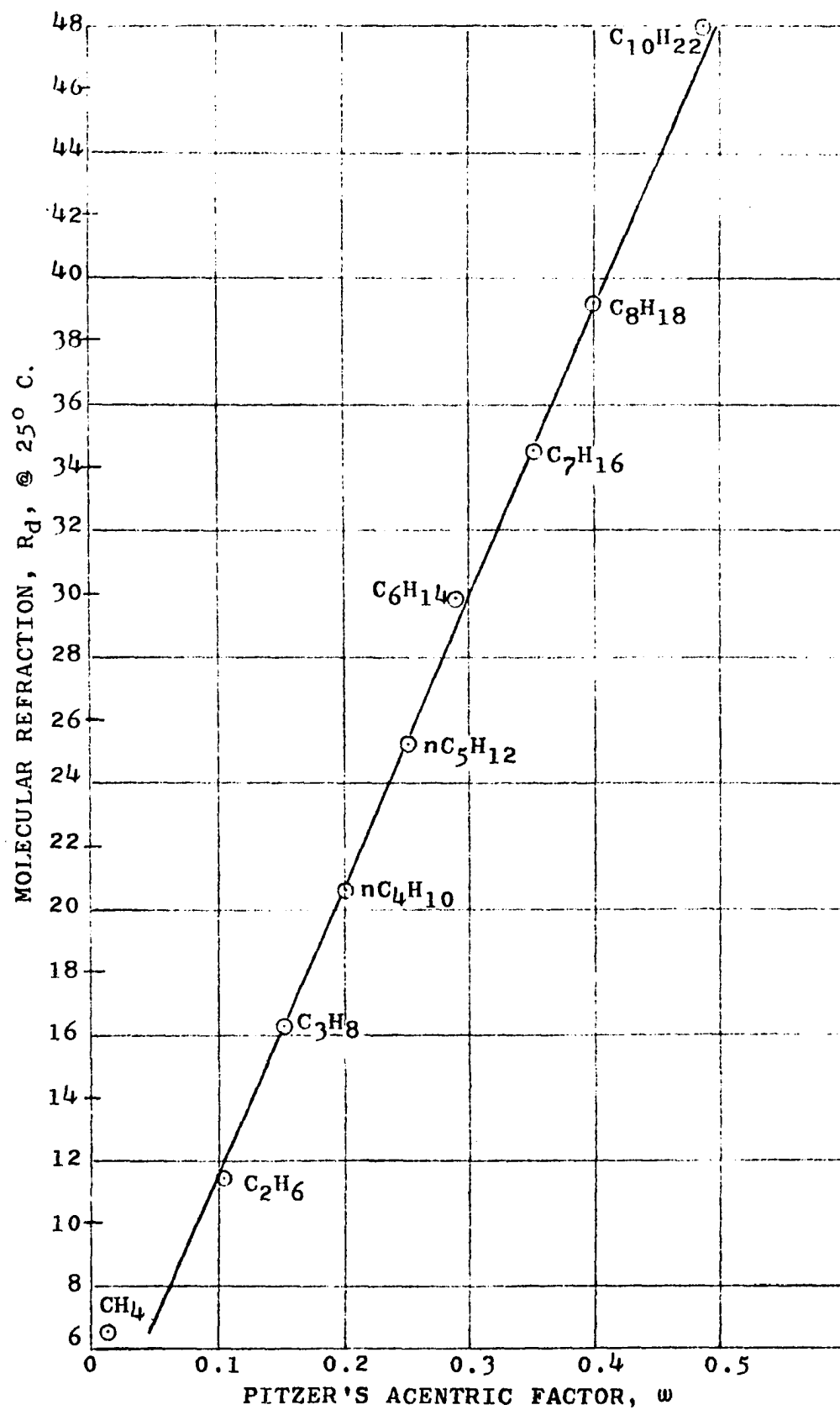


FIGURE V-2. MOLECULAR REFRACTION VERSUS PITZER'S ACENTRIC FACTOR

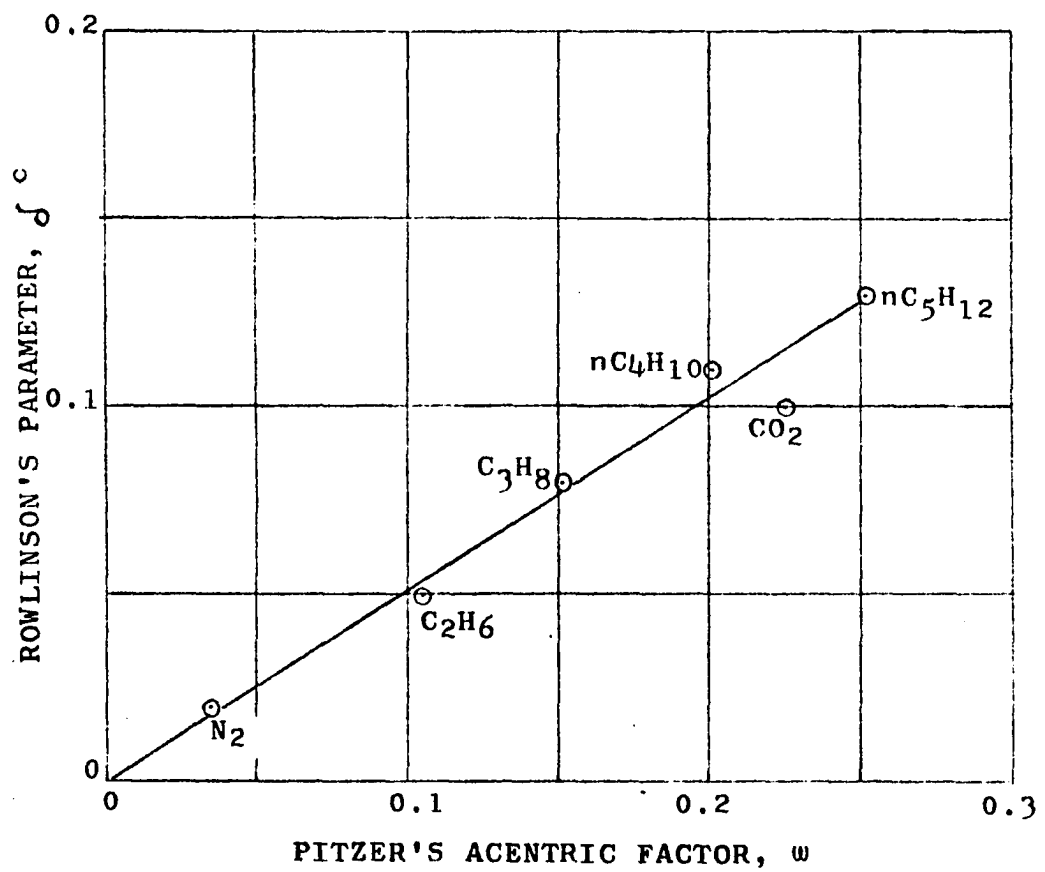


FIGURE V-3. ROWLINSON'S THIRD PARAMETER VERSUS PITZER'S ACENTRIC FACTOR

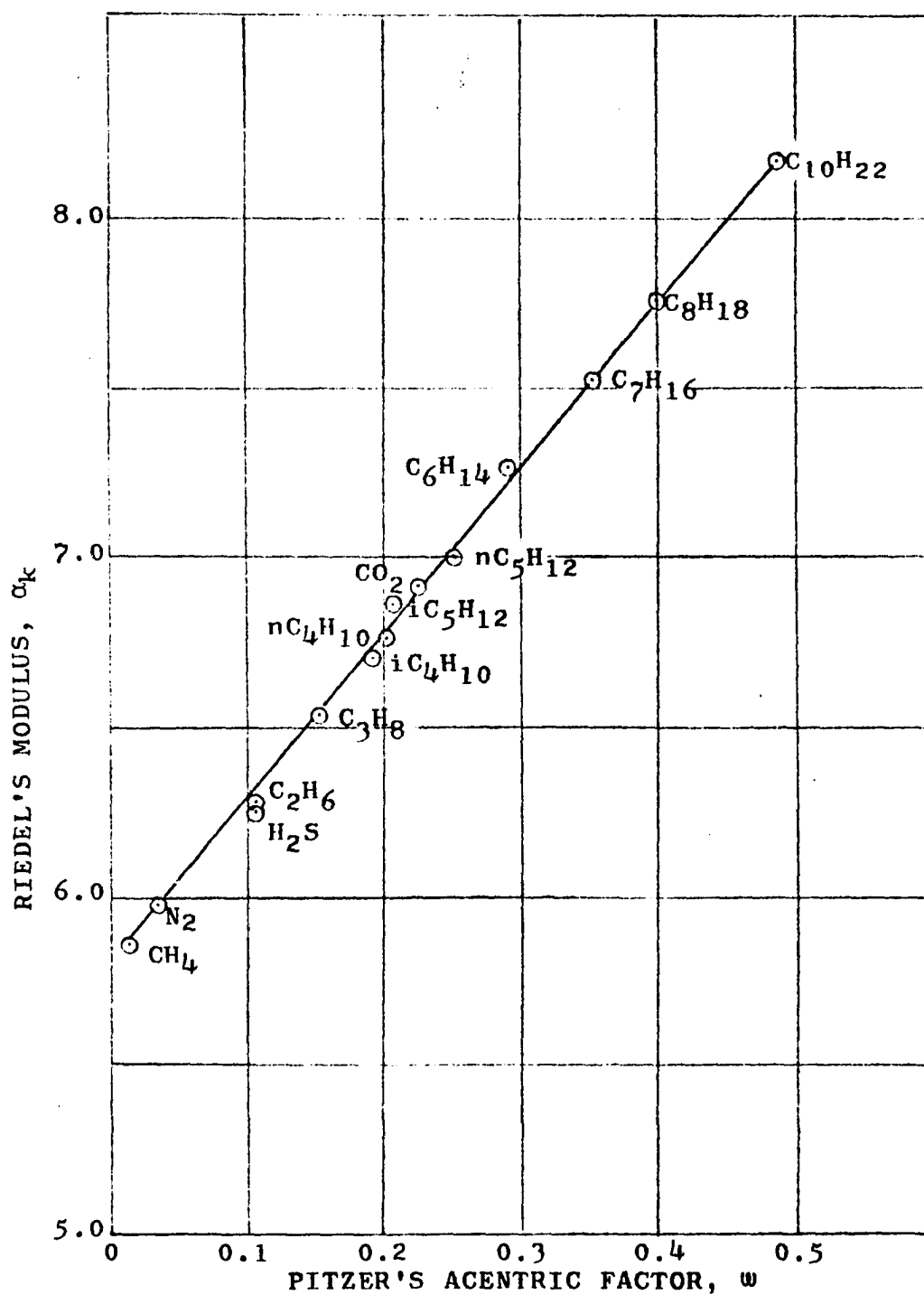


FIGURE V-4. RIEDEL'S MODULUS VERSUS
PITZER'S ACENTRIC FACTOR

The fact that all of the gases do not lie on this line is an indication of a slight inconsistency in Pitzer's tables in the critical region.

The straight line drawn for the plot of R_d versus ω is exceptionally good for the heavier hydrocarbons. The straight line drawn on this figure is

$$R_d = 2.4 + 92.2 \omega \quad (5-3)$$

When Rowlinson's parameter, δ_c , is plotted versus Pitzer's acentric factor, the straight line relationship is

$$\delta_c = 0.51 \omega \quad (5-4)$$

Rowlinson (52) gave the relationship between the two as

$$\delta_c = 0.417 \omega \quad (5-5)$$

but Rowlinson's data included other gases (not present in natural gas) in addition to those shown in Figure V-3 to obtain his correlation.

The general third parameters which have been discussed are assumed to be a measure of the deviation from the PCS caused by the molecules being either globular, non-spherical, or slightly polar.

If only one of these properties of the molecules is causing the deviation, then a microscopic third parameter characterizing this cause of deviation should be expressible as a function of the general third parameter. If the only cause of the normal paraffins' deviation is their non-spherical shape, a microscopic parameter such as Corner's

L/σ ratio for the normal paraffins should be expressible as a function of a general third parameter. In Figure V-5, the L/σ for the first four normal paraffins and for carbon dioxide are plotted versus the acentric factor. For the paraffins, the relationship is nearly a straight line. For carbon dioxide, the acentric factor is affected by its quadrupole moment and consequently, it deviates from the straight line a little more than the hydrocarbons do.

In searching for a third parameter which could be related to the microscopic properties of the molecules, Satter (61) attempted to use F/Z_c as a third parameter. The similarity between F given by

$$F = 5.665 P_c^{1/3} / T_c^{5/6} M^{1/2} \quad (5-6)$$

and the quantum parameters based on microscopic properties was previously pointed out. When F/Z_c was plotted versus the acentric factor, Figure V-6 was obtained. The large deviation between the curve drawn through the hydrocarbon points and the carbon dioxide point is indicative that a property of carbon dioxide which is manifested in ω is not present in the dimensionless group F/Z_c . The large quadrupole moment of carbon dioxide probably causes this deviation.

In attempting to modify the F/Z_c to obtain better agreement between the normal paraffins and carbon dioxide, the author found that if F/Z_c is multiplied by the specific volume at the critical point and the product is plotted versus

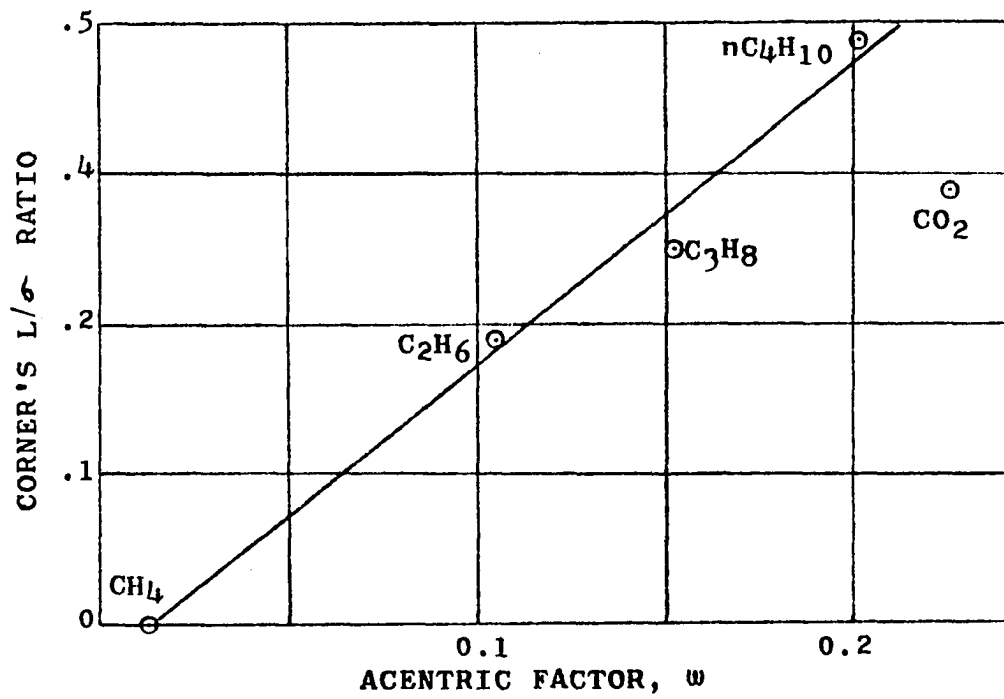


FIGURE V-5. CORNER'S SHAPE FACTOR VERSUS
PITZER'S ACENTRIC FACTOR

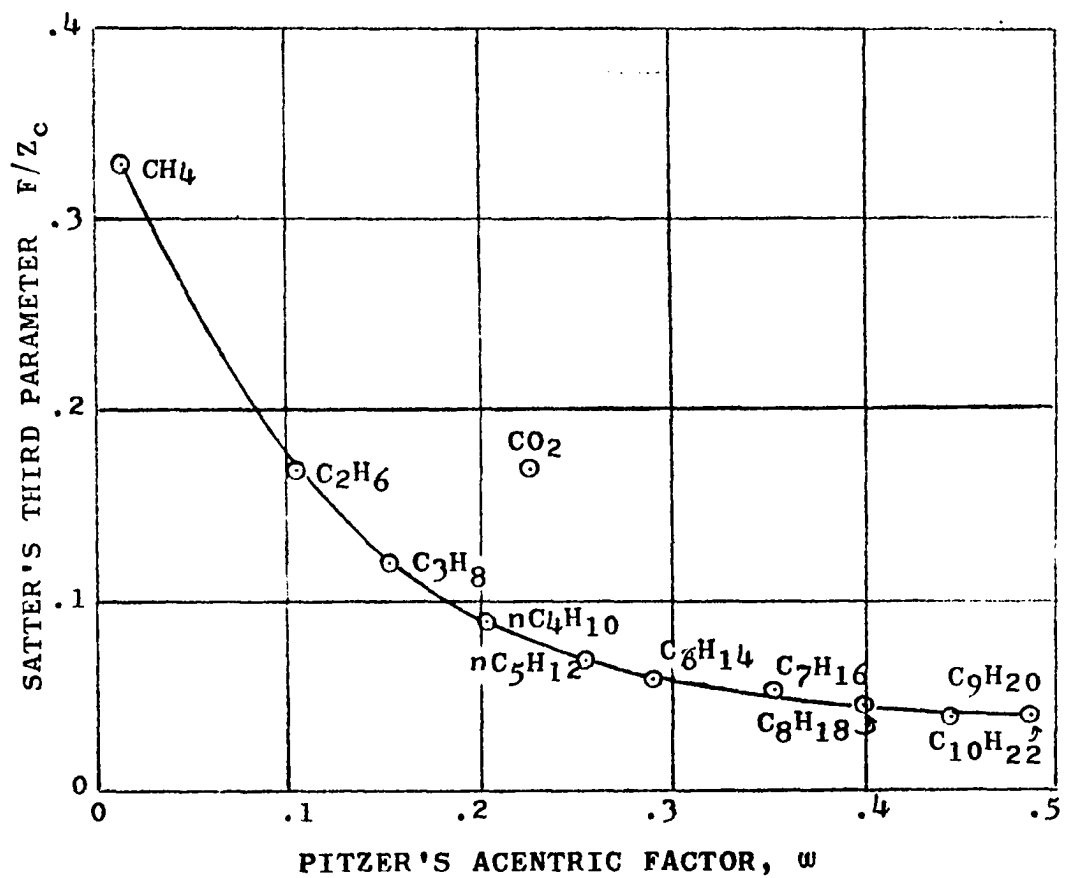


FIGURE V-6. SATTER'S THIRD PARAMETER VERSUS
PITZER'S ACENTRIC FACTOR

the acentric factor, the carbon dioxide point falls very close to the curve drawn through the hydrocarbon points.

To preserve the excellent agreement and still keep dimensionless groups, a reduced critical density was defined as

$$d_c/d_{c_{\text{methane}}} = d_r \quad (5-7)$$

The methane density was chosen to reduce the other densities since, among the constituents of natural gas, methane comes closest to being a simple fluid.

In Figure V-7, the product of $F/Z_c \cdot 1/d_r$ is plotted versus the acentric factor. Carbon dioxide lies very close to the line drawn through the hydrocarbon points. The relationship between these two dimensionless numbers may be approximated by

$$d_r \cdot \frac{1}{F/Z_c} = 34.3 \omega (\omega + 2). \quad (5-8)$$

This relationship suggests that the product of $F/Z_c \cdot 1/d_r$ might be a useful parameter for characterizing the constituents of natural gas. The critical properties making up this group are directly related to the microscopic properties. Figure V-7 further illustrates the relationship of the general parameters, such as the acentric factor, to the microscopic properties.

If one were dealing with a group of gases that deviated from simple fluid behavior because of either quantum effects, globular molecules, non-spherical molecules, or polar

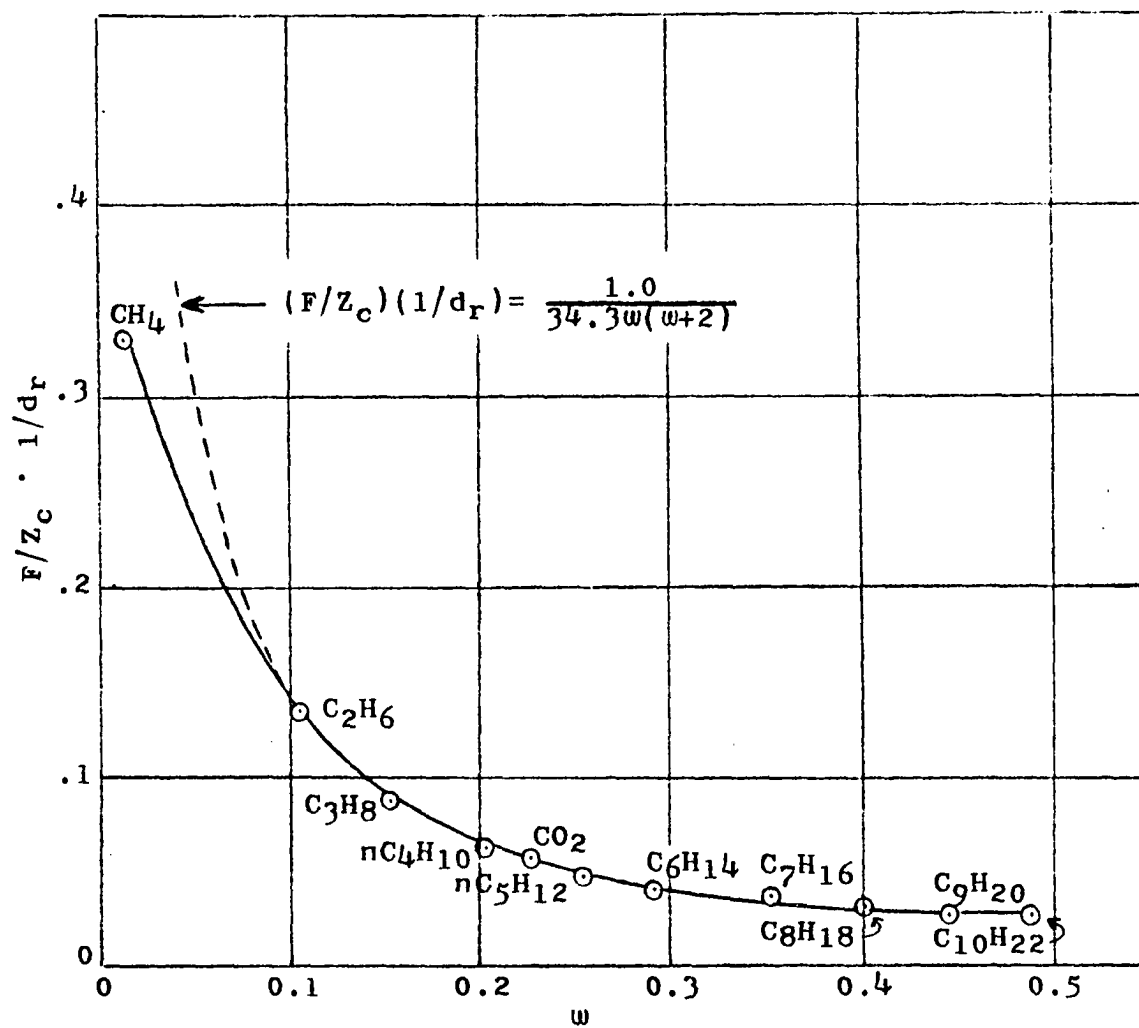


FIGURE V-7. THE PRODUCT OF SATTER'S THIRD PARAMETER TIMES THE REDUCED DENSITY VERSUS THE ACENTRIC FACTOR

molecules, the selection of a microscopic parameter proposed to correct for one of these deviations would be appropriate. To obtain correspondence among the individual constituents of a group of gases where all of these causes of deviation were present would require a rather complex form of the PCS of the general form,

$$Z = F(T_r, P_r, \Lambda_r, L_r, \mu_r, Q_r, \dots) \quad (5-9)$$

To maintain the PCS in as simple a form as possible it is more desirable to have a third parameter which is based on some bulk property influenced by several of the factors causing deviation. For this reason, the general third parameters have been used more frequently by those associated with the natural gas industry.

The fact that all of the general third parameters plot as nearly straight line functions of the acentric factor indicates that they could also be plotted as straight line functions of one another. The fact that this relationship exists between these parameters means that the selection of one over the other would be strictly arbitrary. It should be remembered that the gases used to prepare the figures presented in this section were predominantly the normal paraffin constituents of natural gas. The relationships obtained should not be indiscriminately extended to all gases.

In Chapter III the use of R_d' , Z_c' , and ω' to characterize mixtures was discussed. One of the objections to the

use of Z_c or ω as a third parameter has been that there is no theoretical justification for Equations (3-8) or (3-9). It has been shown for the normal paraffins that molecular refraction is an additive property and Equation (3-7) will hold. If molecular refraction is an additive property and it is linearly related to Z_c and ω , it follows that for the normal paraffins, Z_c and ω must also be additive properties and Equations (3-8) and (3-9) should hold. The extent to which the additive rule is applicable for components such as carbon dioxide or hydrogen sulfide has as yet not been established. Pitzer and Hultgren (41) have been able to predict an empirically determined ω for several carbon dioxide-hydrocarbon binaries by equation (3-9).

Pitzer's acentric factor was arbitrarily chosen as the third parameter to be used in this study. The use of Pitzer's acentric factor avoids the difficulty of selecting a reference substance. The fact that molecular refraction is a linear function of the acentric factor will enable one to convert the molecular refraction of the C_7+ fraction to an acentric factor so the necessity of separating the fraction may still be avoided. The degree of success with which the acentric factor has been utilized in the past affected this decision but the ease with which the compressibility charts of Pitzer can be used also made it attractive. The simplicity and ease with which a generalized correlation such as that of Standing and Katz (63) may be applied, requires that any prediction technique adopted by the engineer be of

comparable simplicity while giving an increased reliability in the prediction of the compressibility factor.

To make use of the acentric factor for the calculation of mixture compressibility factors requires calculation of the mixture acentric factor from

$$\omega' = \sum_i y_i \omega_i \quad (5-10)$$

and calculation of the pseudocritical constants with combination rules such as were discussed in Chapter III. With values of the pseudocritical constants and the temperature and pressure, the reduced temperature and pressure can be calculated so that Z^0 and Z' can be read from Figures II-3 and II-4. The compressibility factor may then be calculated from

$$Z = Z^0 + \omega' Z' \quad (5-11)$$

CHAPTER VI

A TEST OF PSEUDOCRITICAL COMBINATION RULES

With the selection of the mixture acentric factor as the third parameter to be used to characterize mixtures, the remaining problem is to determine which of the combination rules for determining pseudocritical constants is the most applicable for natural gas mixtures. From the discussion of the available pseudocritical constant prediction techniques, it is apparent that a large number of methods are available. Some of these techniques have a stronger theoretical basis than others, but it was necessary to make simplifying assumptions in the derivation of all of them. It is impossible to select one of these rules over the others on a strictly theoretical basis. The selection must be based on the applicability of the combination rule for predicting reliable compressibility factors of mixtures characteristic of the system being studied. The purpose of this chapter is to compare the results obtained when some of these rules are used in conjunction with Pitzer's acentric factor tables on binary mixtures.

A. A Preliminary Investigation
of Binary Mixtures

Nine different binary mixtures made up of components found in natural gas were studied. These binaries along with the source of the experimental compressibility data are listed in the following table:

TABLE 3-1

Binary	SOURCE OF EXPERIMENTAL DATA REFERENCE NUMBER
$\text{CH}_4\text{-CO}_2$	47
$\text{C}_2\text{H}_6\text{-CO}_2$	58
$\text{C}_3\text{H}_8\text{-CO}_2$	58
$\text{nC}_4\text{H}_{10}\text{-CO}_2$	58
$\text{CH}_4\text{-H}_2\text{S}$	58
$\text{CH}_4\text{-C}_2\text{H}_6$	59
$\text{CH}_4\text{-C}_3\text{H}_8$	59
$\text{CH}_4\text{-nC}_4\text{H}_{10}$	59
$\text{CH}_4\text{-nC}_5\text{H}_{12}$	59

The equal molal mixture provides the severest test for any compressibility factor prediction technique. For this reason, equal molal mixtures were used for all but the $\text{CH}_4\text{-CO}_2$ system. For this system, a mixture containing 60.50 mole per cent methane was used since experimental data for the equal molal mixture were not available.

For this comparison of pseudocritical combination

rules, five of the simpler methods were used. It was felt that if a satisfying prediction could be made with one of the simpler rules, the procedure would have a much better chance of widespread use by the natural gas industry. The methods tested are as follows:

METHOD 1. Kay's rule pseudocriticals

$$T_c' = \sum_i y_i T_{ci} \quad (6-1)$$

$$P_c' = \sum_i y_i P_{ci} \quad (6-2)$$

METHOD 2. Joffe's pseudocriticals

$$T_c' / (P_c')^{\frac{1}{2}} = \sum_i y_i T_{ci} / (P_{ci})^{\frac{1}{2}} \quad (6-3)$$

$$T_c' / P_c' = 1/8 \sum_i \sum_j y_i y_j \left[\left(\frac{T_{ci}}{P_{ci}} \right)^{1/3} + \left(\frac{T_{cj}}{P_{cj}} \right)^{1/3} \right]^3 \quad (6-4)$$

METHOD 3. Stewart, Burkhardt, and Voo's pseudocriticals

$$J = T_c' / P_c' = 1/3 \left(\sum_i y_i T_{ci} / P_{ci} \right) + 2/3 \left[\sum_i y_i (T_{ci} / P_{ci})^{\frac{1}{2}} \right]^2 \quad (6-5)$$

$$K = T_c' / (P_c')^{\frac{1}{2}} = \sum_i y_i T_{ci} / (P_{ci})^{\frac{1}{2}} \quad (6-6)$$

$$T_c' = K^2 / J \quad (6-7)$$

$$P_c' = T_c' / J \quad (6-8)$$

METHOD 4. Satter's modified Leland and Muller's
pseudocriticals

$$T_c' = \left[\frac{\sum_{i=1}^n \sum_{j=1}^n y_i y_j \left[(T_{cii} T_{cjj})^{\frac{1}{2}} \right]^{\alpha/2} \left[\frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_{ii}^{1/3} + \frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_{jj}^{1/3} \right]^3}{\sum_{i=1}^n \sum_{j=1}^n y_i y_j \left[\frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_{ii}^{1/3} + \frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_{jj}^{1/3} \right]^3} \right]^{1/\alpha} \quad (6-9)$$

$$P_c' = \frac{T_c' \sum_{i=1}^n y_i Z_{ci}}{\sum_{i=1}^n \sum_{j=1}^n y_i y_j \left[\frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_{ii}^{1/3} + \frac{1}{2} \left(\frac{Z_c T_c}{P_c} \right)_{jj}^{1/3} \right]^3} \quad (6-10)$$

METHOD 5. Prausnitz and Gunn's simplified pseudo-
criticals

$$T_c' = \sum_i y_i T_{ci} \quad (6-11)$$

$$P_c' = \frac{RT_c'}{\sum_i y_i V_{ci}} \sum_i y_i Z_{ci} \quad (6-12)$$

Hereafter, these pseudocritical constant prediction rules will be referred to by the indicated method numbers.

Compressibility factors for some of the mixtures were predicted using methods 1, 3, and 4 along with the acentric factor on an IBM 7090 computer by the Continental Oil Company. The remainder were calculated on the University of Oklahoma's IBM 1620 Model II computer. The program used on the IBM 1620 was tested by comparing results with those calculated on the

IBM 7090 and by comparing calculated pure component compressibilities with actual experimental data.

The average absolute deviation, maximum deviation, and point of maximum deviation that were obtained are tabulated along with the ranges of pressure and temperature in Table 1 of Appendix E.

Examination of the results of this study indicate that when these pseudocritical constant rules were used with the acentric factor charts:

1. Methods 1 and 5 failed to adequately predict the pseudocriticals to be used with the acentric factor for the prediction of the compressibility factor.
2. Methods 2, 3, and 4 allowed prediction of the compressibility factor with comparable accuracy. Methods 2 and 3 were slightly superior.
3. None of the pseudocritical constant prediction techniques satisfactorily predicts pseudocritical constants for the binaries of carbon dioxide with ethane, propane, or n-butane.
4. For each of the pseudocritical constant prediction techniques, the largest deviations usually occur in the region of the pseudocritical pressure and temperature.

The fact that the largest deviations occurred in the critical region might be attributed to the fact that Pitzer's

acentric factor charts are inconsistent in the critical region. The discussion that was presented in Chapter V of the plot of Z_c versus ω tends to support this notion. However, it is highly probable that the largest deviations would occur in this region regardless of what generalized plot is used. For temperatures near the critical temperature, the slope of Z versus P_r is the greatest just to the left of the curve's minimum. To the left of the minimum is the region of the critical pressure. Due to the large slope, missing the experimental curve only slightly will result in a large error in the compressibility factor.

Of the methods used to predict the pseudocritical constants, methods 2 and 3 were found to be the most applicable for predicting the compressibility factor for the hydrocarbon binaries. The average absolute deviation for method 3, the rules of Stewart, Burkhardt, and Voo, was 1.0 per cent. Using method 2, Joffe's rules, the deviation was only slightly larger. Neither of these methods adequately predicted the hydrocarbon carbon dioxide binaries.

Using method 3, compressibility factors were determined for several other hydrocarbon - carbon dioxide binaries. The composition of these mixtures are listed in Figure VI-1 where the per cent deviations are plotted versus the reduced temperatures. Since the reduced pressure ranges at which the points were determined were not the same, the deviations for the propane and n-butane binaries are

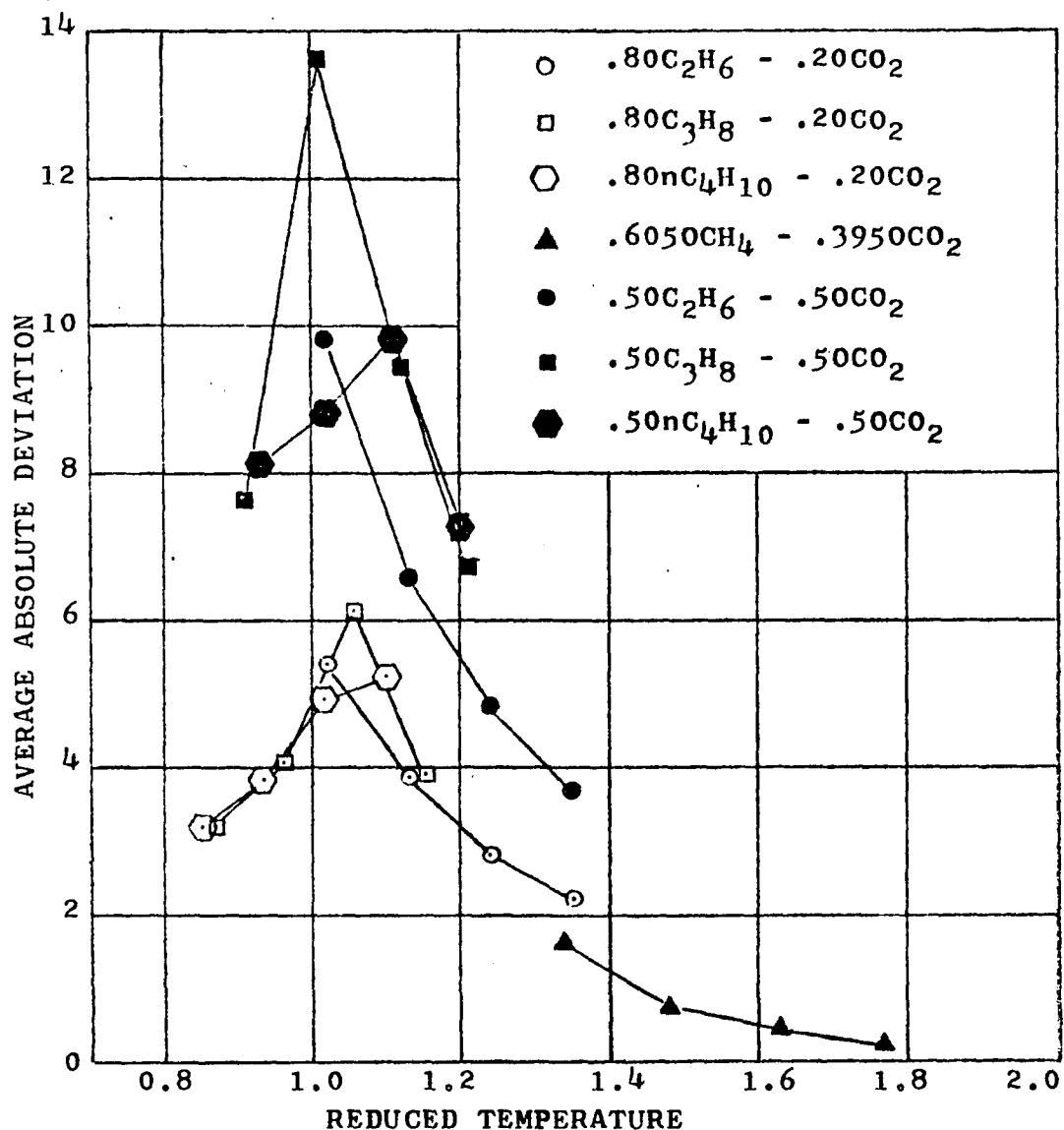


FIGURE VI-1. AVERAGE ABSOLUTE DEVIATION BETWEEN PREDICTED AND EXPERIMENTAL COMPRESSIBILITY FACTORS AS A FUNCTION OF REDUCED TEMPERATURE

relatively lower than they would be if the deviations were compared on an equal reduced pressure basis. This figure indicates that when method 3 is used with Pitzer's tables for hydrocarbon - carbon dioxide mixtures, the deviation that may be expected is a function of both the percentage carbon dioxide and what hydrocarbon is in the mixture.

B. The Graphical Determination of Pseudocritical Constants

To determine what pseudocritical constants should be used for the nine binaries considered in this chapter, an empirical method of determining the pseudocritical constants was devised. The procedure employed was slightly different than that employed by Kay, but the basic idea was the same. The pseudocritical temperature controls the location of an isotherm on a Z versus P_r plot in a vertical direction, and the pseudocritical pressure controls its spread in a horizontal direction. If a pseudocritical temperature can be obtained which allows a predicted minimum Z value to match the experimental minimum Z , for a given isotherm, then the isotherm should be located in a vertical direction. If the high pressure part of the predicted isotherm can be made to match the high pressure part of the experimental data by proper selection of the pseudocritical pressure then the horizontal spread should be established.

Since both the experimental and predicted isotherm must have a value of 1.0 at zero pressure, proper selection

of the pseudocritical constants should give considerable control over the shape of a particular isotherm. In Figure VI-2, both the experimental and predicted curves must begin at a Z value of 1.0, both must be tangent to line B - C, and both curves must coincide with line D - E. If the acentric factor satisfactorily predicts the shape of the dotted portion of the curve, then satisfactory agreement between the predicted and experimental curves should be obtained.

The procedure employed to determine the pseudocritical constants may be summarized as follows:

1. Pseudocritical temperature

- a. Calculate a mixture acentric factor from

$$\omega' = \sum_i y_i \omega_i \quad (6-13)$$

- b. Read the minimum value of Z^0 for each T_r in Pitzer's acentric factor tables.
- c. Read a value of Z' at the T_r and P_r corresponding to the minimum Z^0 values.
- d. Calculate a Z minimum from

$$Z_{\min} = Z^0_{\min} + \omega' Z' \quad (6-14)$$

- e. Plot $Z_{\min}$ versus the corresponding T_r .
- f. Read the minimum value of Z for the mixture being studied for several isotherms of the experimental data.
- g. For each isotherm, locate the experimental minimum Z value on the plot discussed in

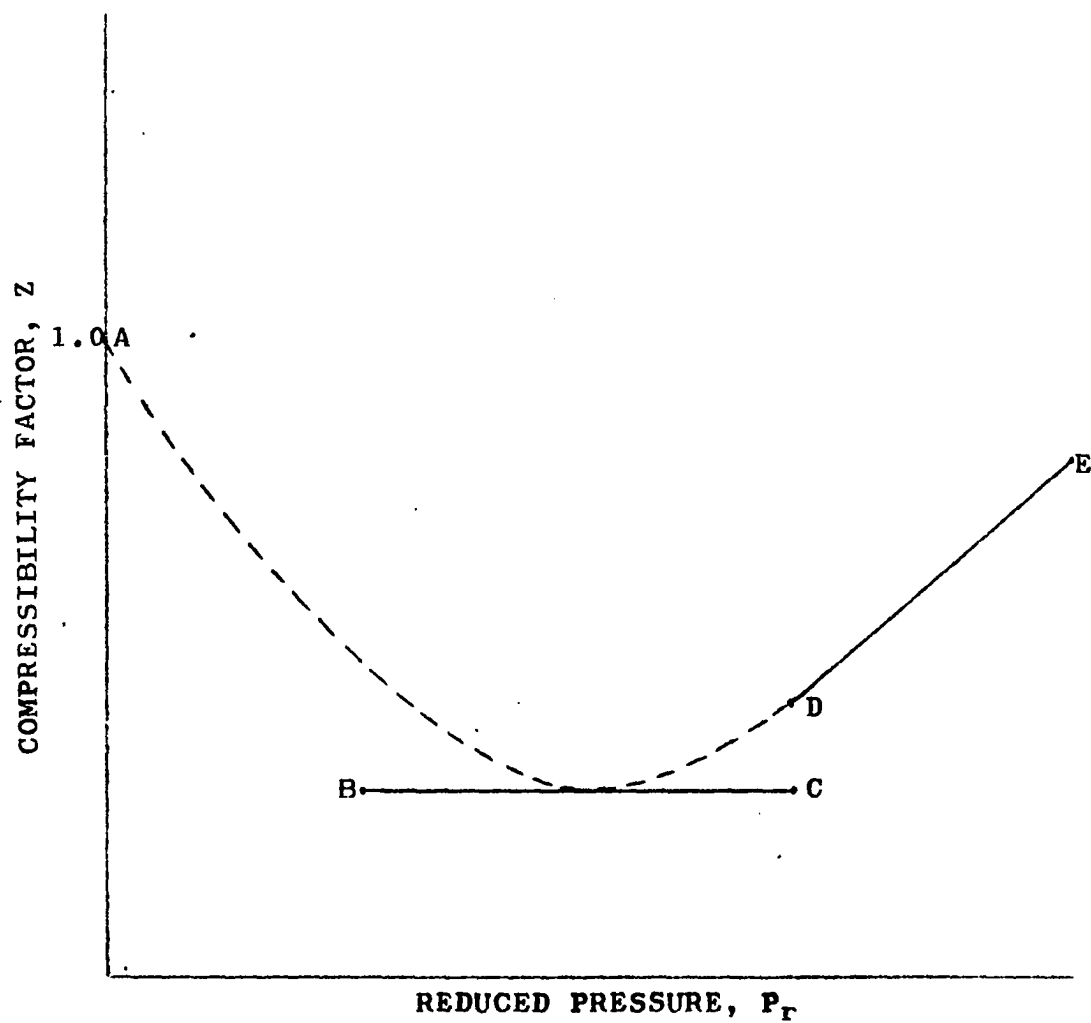


FIGURE VI-2. CONTROL OF THE GEOMETRY OF AN ISOTHERM
AFFECTED BY THE GRAPHICAL DETERMINATION
OF THE PSEUDOCRITICAL CONSTANTS

step e. Record the corresponding T_r value.

- h. By knowing the temperature of the experimental isotherm and the reduced temperature at which the minimum Z was found, the pseudocritical temperature may be calculated from

$$T_c' = T/T_r . \quad (6-15)$$

2. Pseudocritical pressure

- a. Plot the experimental compressibility factors, for an isotherm of the mixture being studied, versus pressure.
- b. With the graphically determined pseudocritical temperature, calculate a reduced temperature for the isotherm.
- c. Using ω' of the mixture, the calculated reduced temperature, and Pitzer's charts, calculate a compressibility factor for several of the larger values of P_r compatible with the experimental data.
- d. Locate the compressibility factor for the largest value of P_r on the plot discussed in step a and record the corresponding pressure.
- e. With the value of P_r and the pressure read from the plot, a value of the pseudocritical pressure may be calculated from

$$P_c' = P/P_r . \quad (6-16)$$

- f. Using this value of P_c' , calculate the pressure corresponding to the other values of P_r and plot the compressibility factors for these pressures. If they do not agree with the experimental curve, adjust the pseudocritical pressure to obtain the best agreement for all of the points.

To illustrate the procedure, the plot discussed under 1 - e for the fifty per cent C_3H_8 in a $C_3H_8 - CO_2$ system is plotted in Figure VI-3. For this system $\omega' = 0.1885$. The experimental data (59) gives a minimum value of the Z of the $160^\circ F.$ isotherm as 0.3374. When this point is located on the curve, the corresponding value of the reduced temperature is 1.062. From the temperature of the isotherm, $160^\circ F.$, and the reduced temperature, 1.062, the pseudocritical temperature calculates to be $583.8^\circ R$. The average value of the pseudocritical temperature obtained from six isotherms was $584.5^\circ R$.

The experimental data of the $160^\circ F.$ isotherm for this system is plotted in Figure VI-4. Using the average value of $584.5^\circ R$ for the pseudocritical temperature and an acentric factor of 0.1885, compressibility factors for values of P_r of 6.0, 7.0, 8.0 and 9.0 were calculated. The compressibility factor for P_r of 9.0 was 1.087. When this value is located on the experimental curve, a corresponding pressure of 6,500 psia may be read. Since a reduced pressure of 9.0 corresponds

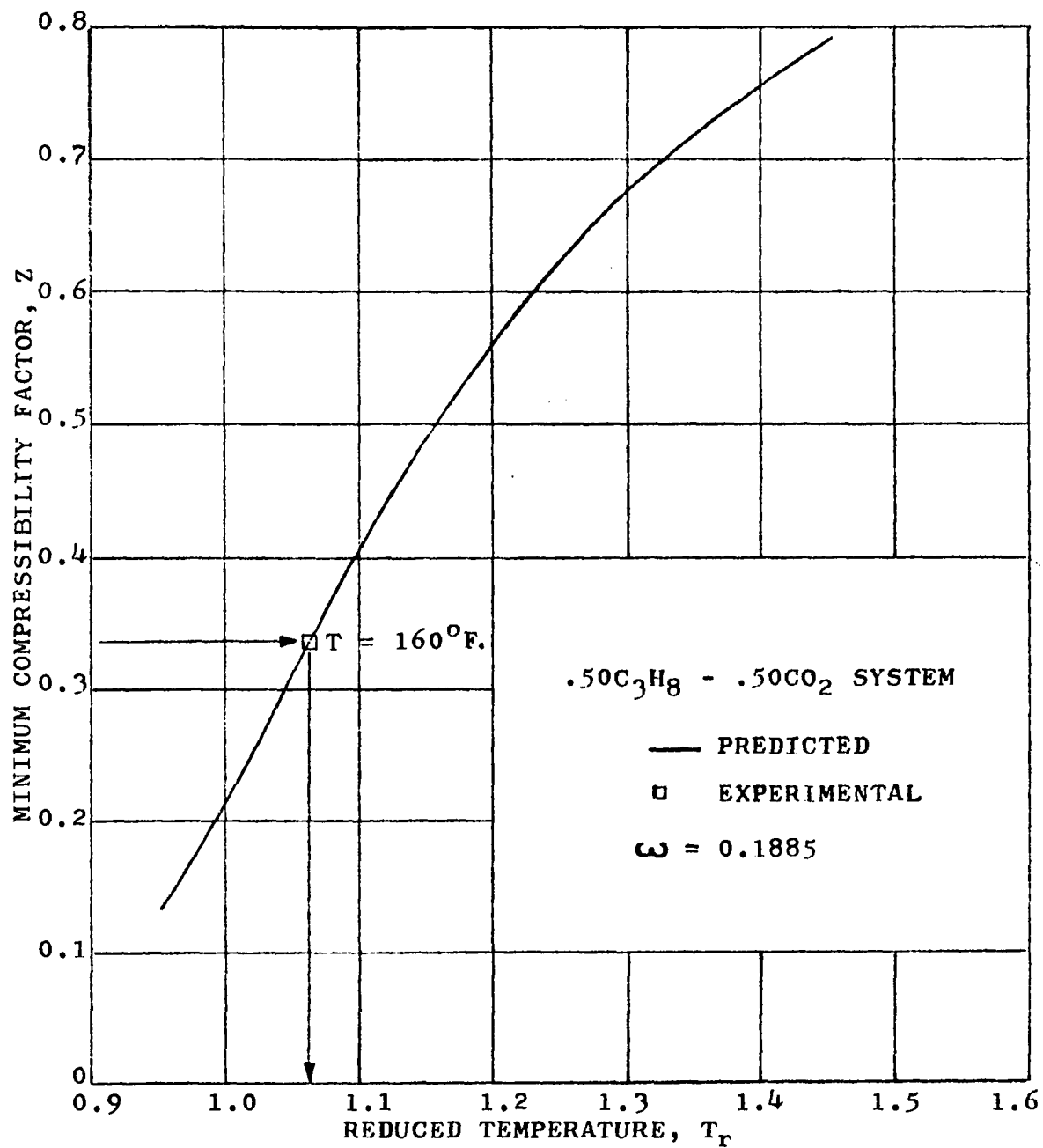


FIGURE VI-3. MINIMUM COMPRESSIBILITY FACTORS FROM THE ACENTRIC FACTOR TABLES FOR DETERMINATION OF THE PSEUDOCRITICAL TEMPERATURE

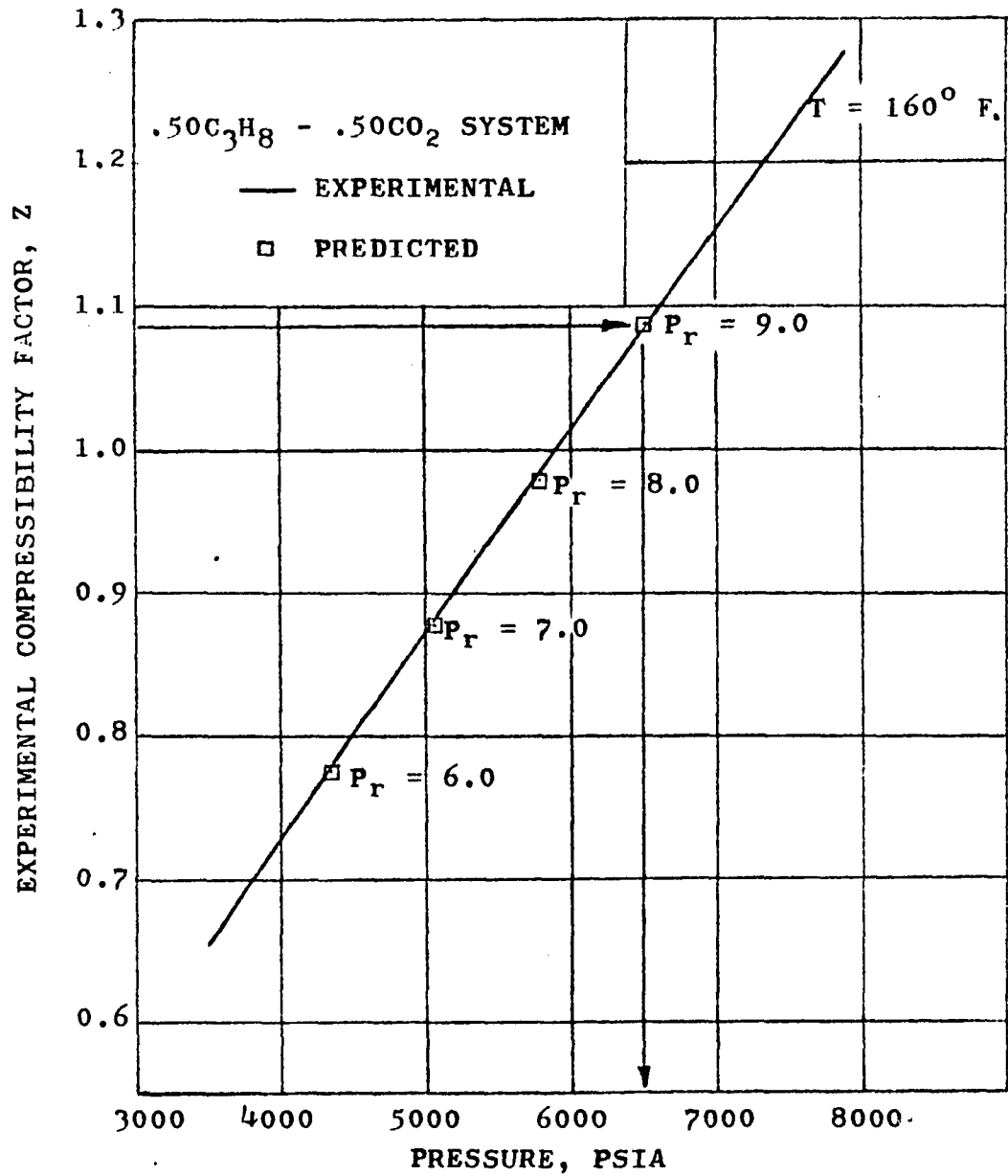


FIGURE VI-4. EXPERIMENTAL COMPRESSIBILITY FACTORS
 VERSUS PRESSURE FOR DETERMINATION OF THE
 PSEUDOCRITICAL PRESSURE

to a pressure of 6,500 psia, the pseudocritical pressure must be 722.2 psia. Using this value of the pseudocritical pressure, pressures corresponding to reduced pressures of 6.0, 7.0 and 8.0 were calculated and the compressibility factors were plotted on the figure. The points agree quite well with the experimental isotherm indicating that a pseudocritical pressure of 722.2 psia and a pseudocritical temperature of 584.5° R. will allow this portion of the isotherm to be predicted. The average pseudocritical pressure obtained for four different isotherms was 722.0 psia.

The results of the graphical determination of the pseudocritical constants are tabulated in Table 2 of Appendix E. The results for the hydrocarbon - carbon dioxide binaries are shown in Figures VI-5 through VI-8.

The selection of the isotherm to be used for a particular binary was arbitrary. There was a small variation with temperature in the determined constants. For this reason, the pseudocritical constants for several isotherms were averaged to obtain the values listed in Table C-2. Since the experimental data for the methane-ethane system only went to 3,000 psia and since the fluctuation of pseudocritical constants with temperature was the most pronounced for this system, the listed pseudocriticals for this system are not as reliable as the others.

A comparison of the graphically determined pseudocritical constants with those calculated from Kay's rule

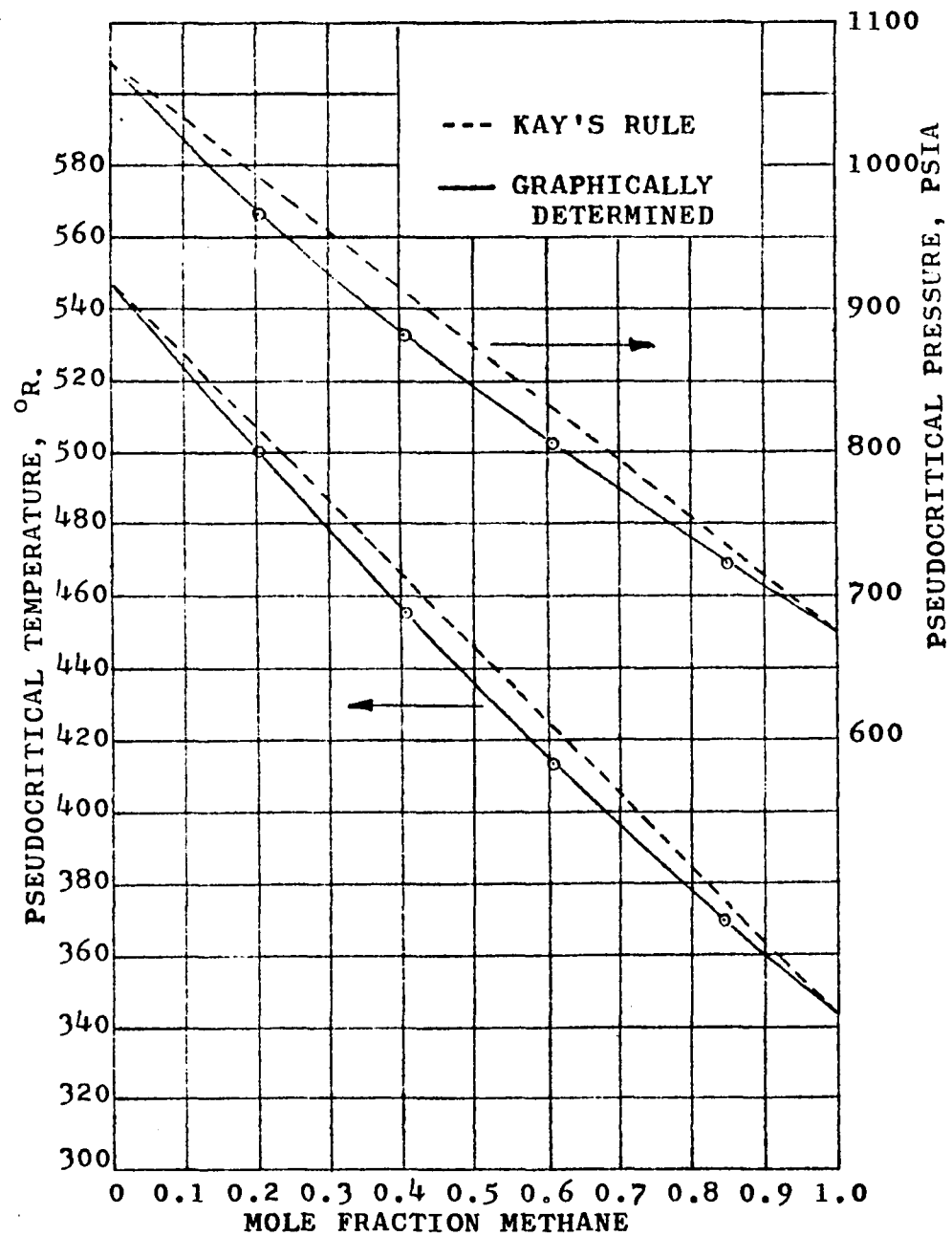


FIGURE VI-5. METHANE-CARBON DIOXIDE BINARY
PSEUDOCRITICAL CONSTANTS AS A FUNCTION
OF COMPOSITION

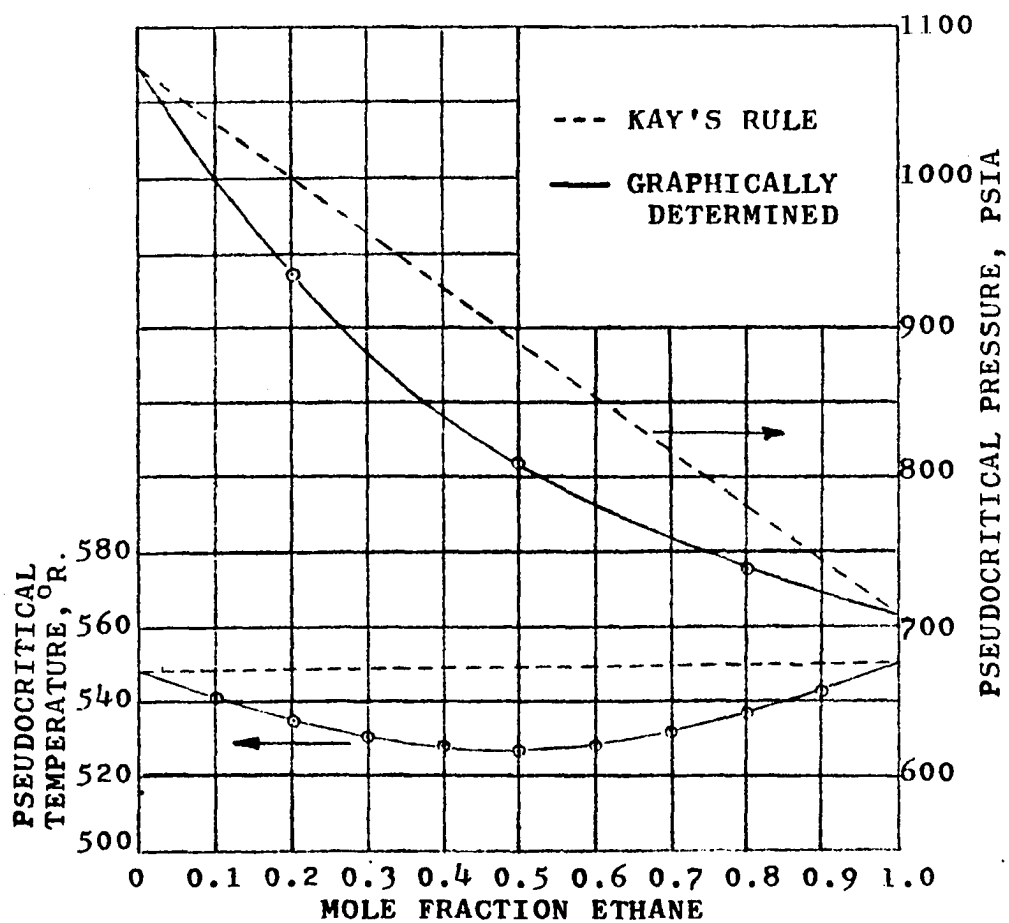


FIGURE VI-6. ETHANE-CARBON DIOXIDE BINARY PSEUDOCRITICAL CONSTANTS AS A FUNCTION OF COMPOSITION

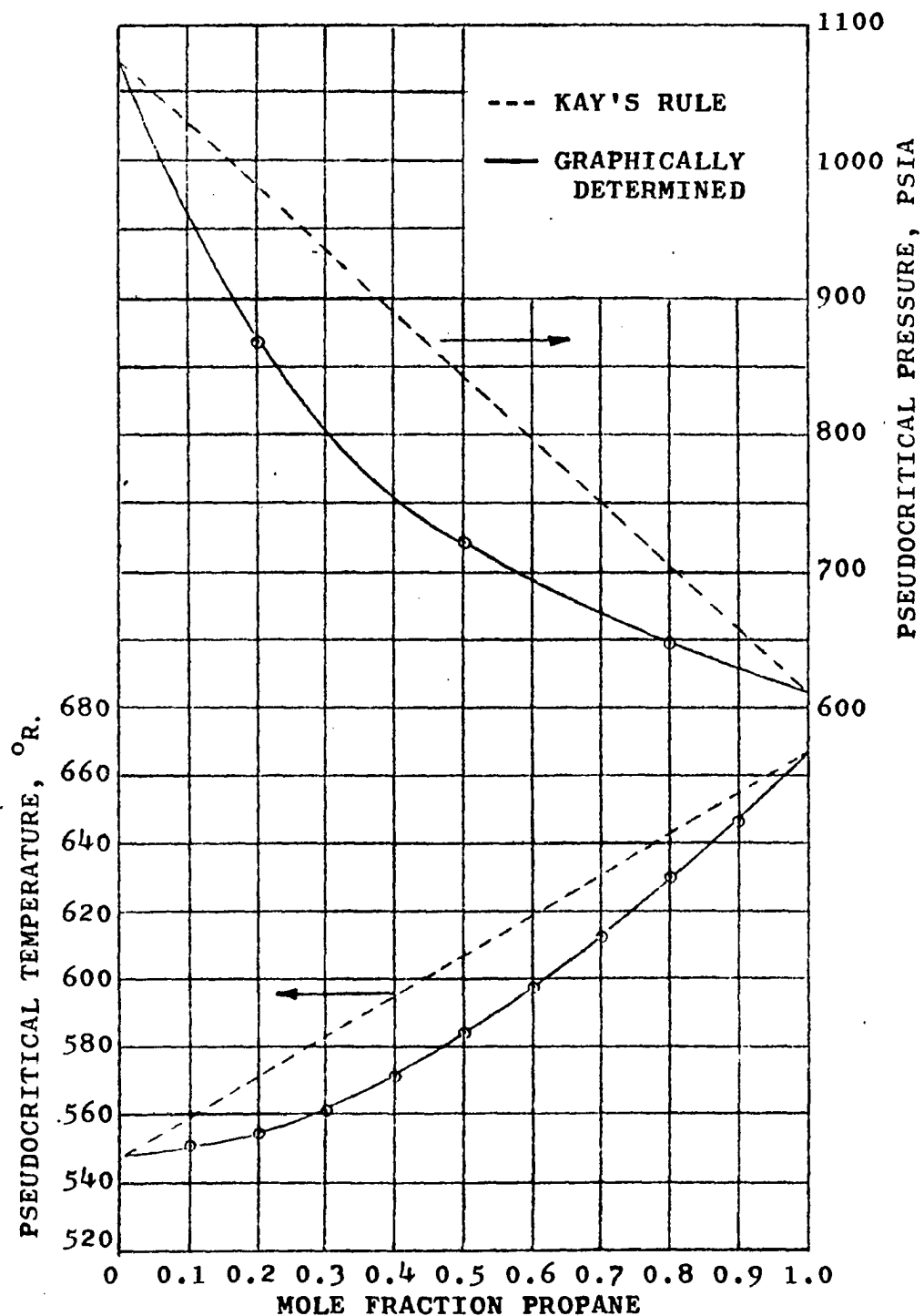


FIGURE VI-7. PROPANE-CARBON DIOXIDE BINARY PSEUDOCRITICAL CONSTANTS AS A FUNCTION OF COMPOSITION

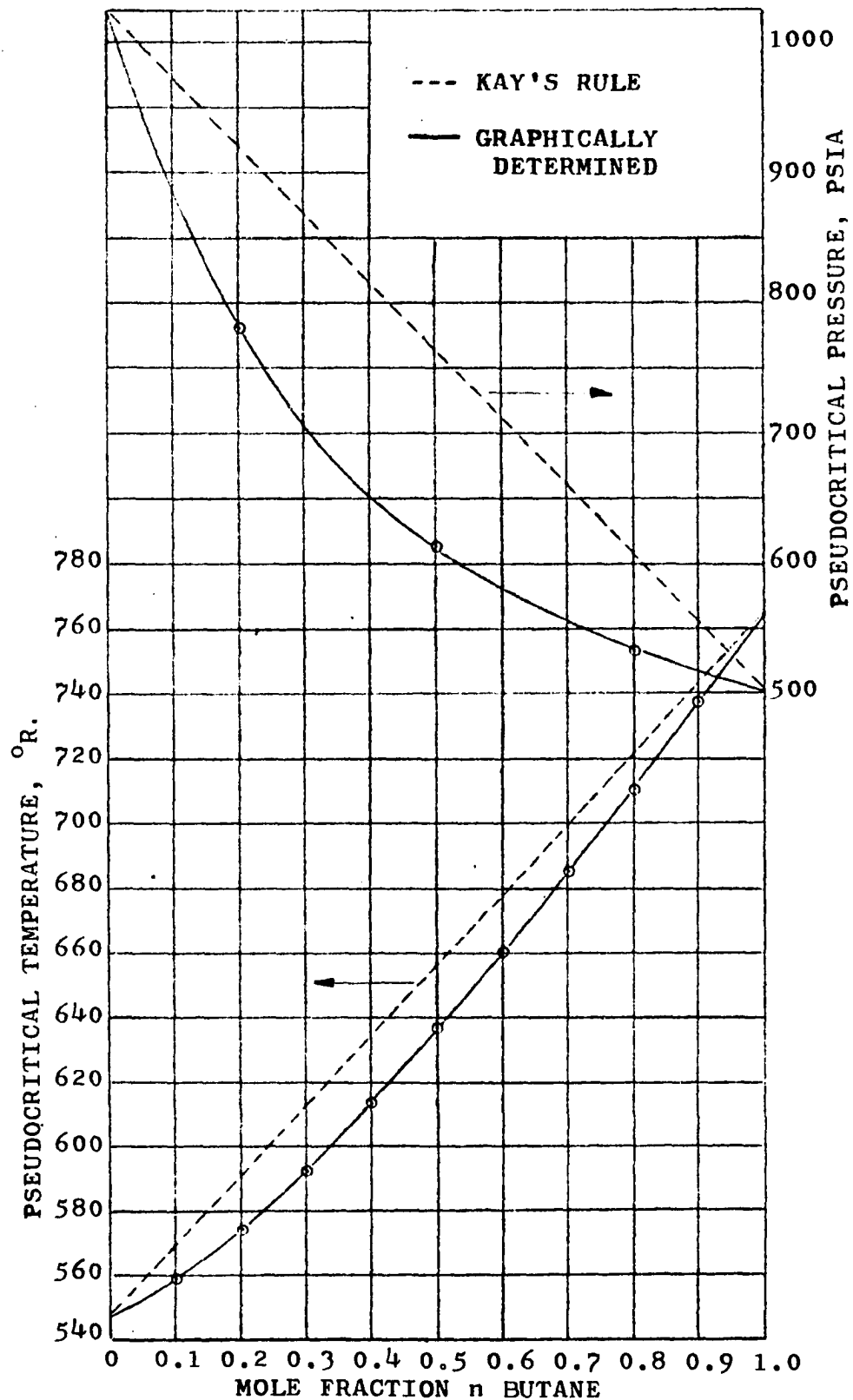


FIGURE VI-8. BUTANE-CARBON DIOXIDE BINARY PSEUDOCRITICAL CONSTANTS AS A FUNCTION OF COMPOSITION

reveals that for all of the hydrocarbon - carbon dioxide and the hydrocarbon - hydrogen sulfide binaries, the pseudocritical temperatures and pressures fall below those calculated with Kay's rule. For the hydrocarbon - hydrocarbon binaries, the pseudocritical constants lie above those predicted by Kay's rule. Pitzer and Hultgren (41) postulated that in the case of the hydrocarbon - hydrocarbon binaries, where the principle intermolecular attractive force is the London force between C - H bonding electrons, the positive deviation above an arithmetic average is due to the difference in the molecular size. For those binaries containing carbon dioxide or hydrogen sulfide, the negative deviation was postulated to be due to the fact that one component of the attractive force between unlike molecules is smaller than that for like molecules. Quadrupole forces are significant for the interaction of carbon dioxide molecules but are absent between carbon dioxide and hydrocarbon molecules. Dipole-dipole forces are important between hydrogen sulfide molecules but are absent between the hydrogen sulfide - hydrocarbon molecules.

The results of predicting the compressibility factors for the nine binary mixtures of Section A of this chapter using the empirically determined pseudocriticals are presented

in Table 1 of Appendix E. The average absolute deviations for the hydrocarbon - carbon dioxide and hydrocarbon - hydrogen sulfide system are considerably less than those predicted with any of the pseudocritical constant rules.

CHAPTER VII

PSEUDOCRITICAL CONSTANTS FOR NATURAL GAS

A basic requirement of any combination rule is that it must be able to account for not only the forces operating between similar molecules but also those between dissimilar molecules. The fact that some of the mixing rules are satisfactory for the prediction of the pseudocritical constants for hydrocarbon binaries is indicative that the methods of combining the pure component properties satisfactorily account for the forces between dissimilar hydrocarbon molecules. The principle forces to be considered between hydrocarbon molecules are London dispersion forces, but between two carbon dioxide molecules, the quadrupole force must also be considered. Between a hydrocarbon and a carbon dioxide molecule, this quadrupole force is not present. The failure of the mixing rules to predict the pseudocritical constants for hydrocarbon - carbon dioxide binaries is indicative that the methods of combining the pure component properties do not allow for the alteration in the intermolecular forces for this type of system.

One possible method for arriving at the pseudocritical

combination rule satisfactory for hydrocarbon - carbon dioxide systems would be to alter the rules for combining pure component constants to obtain constants for the mixtures. For example, the methods that Joffe used to combine the pure component a and b to arrive at the a' and b' of the mixture could be altered to obtain a rule that worked better for the hydrocarbon - carbon dioxide systems. From our present state of knowledge, this would of necessity have to be done empirically.

Rather than alter the basic rule for each system, the author chose a somewhat different approach in this study. In working with natural gas, one is ordinarily only dealing with the normal paraffins. Occasionally, the engineer must also be concerned with the presence of a diluent such as carbon dioxide. The following paragraphs discuss how the pseudocritical constants, obtained from a combination rule which satisfactorily predicts the constants for the ordinary system, may be modified to account for the presence of a diluent such as carbon dioxide.

It was found in the previous chapter that method 3, the rules of Stewart, Burkhardt, and Voo satisfactorily predicted the pseudocritical constants for hydrocarbon binaries, but failed to adequately predict them for hydrocarbon - carbon dioxide binaries. This suggests that method 3, along with the acentric factor, may be used to predict the compressibility factor for natural gases containing only

hydrocarbons, but that method 3 would have to be modified in some way to be used for natural gases containing carbon dioxide.

Figure VI-1 shows that the deviations between the predicted and experimental compressibility factors for hydrocarbon - carbon dioxide binaries are dependent on both the carbon dioxide content and what hydrocarbon is in the mixture. In Figure VII-1, the difference between the pseudocritical constants of method 3 and those graphically determined is plotted versus the mole fraction of carbon dioxide in the mixture. It may be seen that this difference is also dependent upon the percentage carbon dioxide and what hydrocarbons are in the mixture.

Using Figure VII-1, a reliable prediction of the compressibility factor for hydrocarbon - carbon dioxide binaries could be made. The pseudocritical temperature could be calculated with method 3 and then adjusted by subtracting the difference between the calculated and graphically determined pseudocritical temperatures for the appropriate binary. Since, in method 3, the pseudocritical pressure is calculated from the pseudocritical temperature, an adjusted pseudocritical pressure could also be obtained.

While this scheme is possible for binaries of carbon dioxide with methane, ethane, propane, or n-butane, it would not be possible for mixtures containing more than one hydrocarbon since the graphically determined pseudocritical

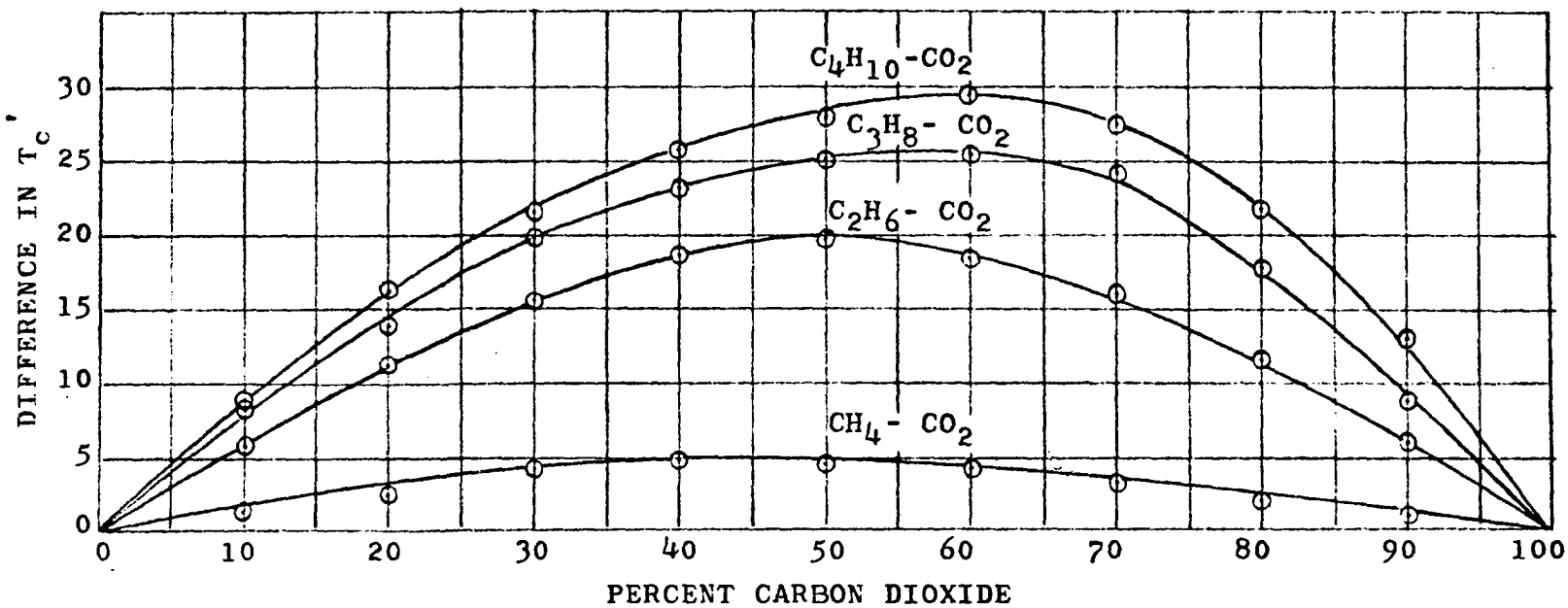


FIGURE VII-1. T_c' OF METHOD 3 MINUS THE GRAPHICALLY DETERMINED T_c' VERSUS PER CENT CARBON DIOXIDE

constants would not be available. It is possible to obtain the adjusting factor for the pseudocritical temperature of method 3 by treating the multi-component mixture of hydrocarbons and carbon dioxide as a binary of one hydrocarbon and carbon dioxide. This requires a characterization of the hydrocarbon present so that the appropriate binary may be used to obtain the adjusting factor.

In extending the use of the acentric factor to multi-component mixtures, it was assumed that the mixture may be characterized by a mixture acentric factor determined from

$$\omega' = \sum_i y_i \omega_i \quad (7-1)$$

Since this extension worked well for hydrocarbon mixtures, it should be possible to characterize the hydrocarbons in the mixtures of hydrocarbons and carbon dioxide by a mixture acentric factor.

The difference between the pseudocritical temperatures determined from method 3 and those graphically determined results from the fact that the method used to combine pure component constants failed to properly account for the variation of the multipole component of the attractive forces. This difference will hereafter be referred to as the multipole factor. To indicate that it is a correction in the pseudocritical temperature, the symbol $\mathcal{P}$ will hereafter be used to designate this factor. When $\mathcal{P}$ of Figure VII-1 is cross plotted versus the hydrocarbon acentric factor with the percentage carbon dioxide as a parameter, Figures VII-2

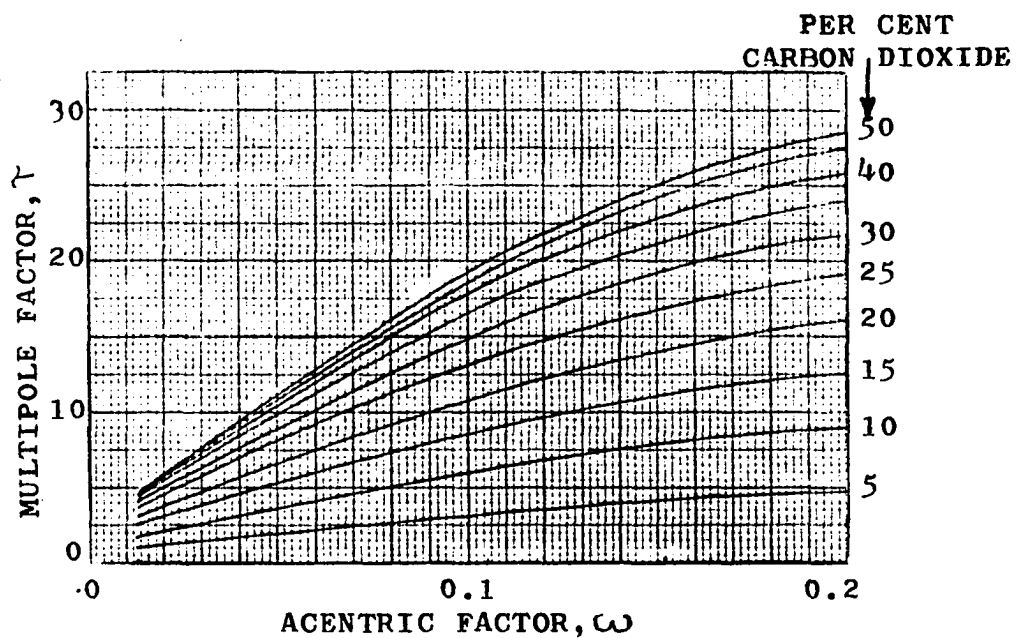


FIGURE VII-2.

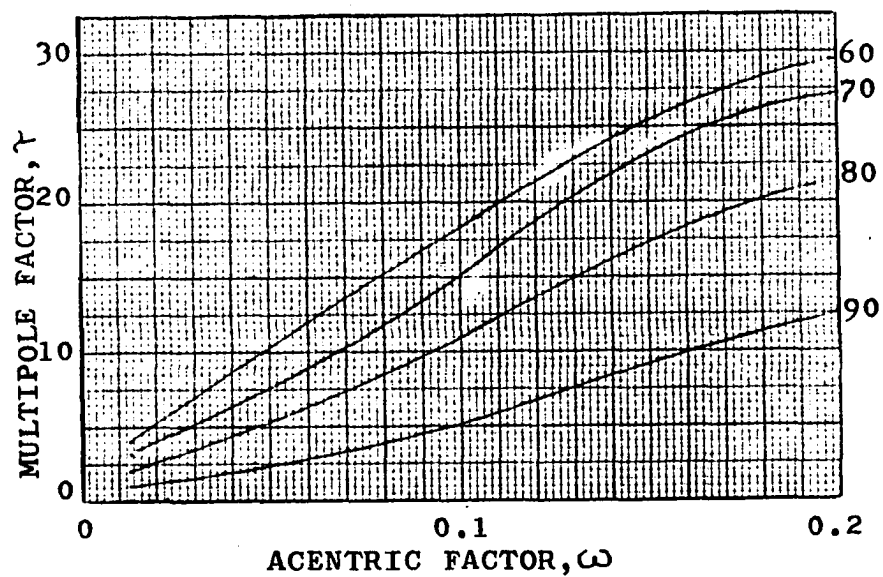


FIGURE VII-3. THE MULTIPOLE FACTOR VERSUS THE HYDROCARBON ACENTRIC FACTOR FOR VARIOUS PERCENTAGES OF CARBON DIOXIDE

and VII-3 are obtained. These figures may be used for multi-component mixtures by calculating the hydrocarbon mixture acentric factor, ω' , and reading γ for the appropriate percentage of carbon dioxide.

The procedure for predicting the compressibility factor for natural gases containing carbon dioxide would then be as follows:

1. Calculate T_c' and P_c' from

$$J = T_c' / P_c' = 1/3 \left(\sum_i y_i \frac{T_{ci}}{P_{ci}} \right) + 2/3 \left[\sum_i y_i \left(\frac{T_{ci}}{P_{ci}} \right)^{1/2} \right]^2 \quad (7-2)$$

$$k = T_c' / (P_c') = \sum_i y_i T_{ci} / (P_{ci})^{1/2} \quad (7-3)$$

$$T_c' = k^2 / J \quad (7-4)$$

$$P_c' = T_c' / J \quad (7-5)$$

2. Determine the hydrocarbon mixture acentric factor from

$$\omega_{hc} = \frac{\sum_j y_j \omega_j}{\sum_j y_j} \quad (7-6)$$

where the summations are for all hydrocarbon constituents.

3. Read γ from Figure VII-2 for the appropriate hydrocarbon acentric factor and percentage carbon dioxide.
4. Calculate the adjusted pseudocritical constants from

$$T_c'' = T_c' - \gamma \quad (7-7)$$

$$P_c'' = P_c' \cdot (T_c' - T) / T_c' \quad (7-8)$$

5. Find the total mixture acentric factor from

$$\omega' = \sum_i y_i \omega_i \quad (7-9)$$

where the summation is now taken over all components.

6. For the temperature and pressure of the system, calculate reduced constants from

$$T_r = T / T_c'' \quad (7-10)$$

$$P_r = P / P_c'' \quad (7-11)$$

7. With the reduced pseudocritical constants and the mixture acentric factor, values of Z^0 and Z' may be read from Pitzer's graphs or tables and the compressibility factor calculated from

$$Z = Z^0 + \omega' Z' \quad (7-12)$$

Another diluent of natural gas which causes a difficulty in the prediction of the compressibility factor is hydrogen sulfide. The multipole causing the difficulty in this case is the dipole of hydrogen sulfide. It would be desirable to have figures similar to Figures VII-2 and VII-3 to make a correction for the presence of hydrogen sulfide. Experimental data for hydrocarbon - hydrogen sulfide binaries are not available for enough mixtures to prepare similar plots.

When the difference between the graphically determined

pseudocritical temperature and that calculated by method 3 for the methane-hydrogen sulfide mixture is compared with the difference for the methane-carbon dioxide mixture, one finds that the difference has the same sign but is slightly larger for the methane-hydrogen sulfide mixture. This indicates that the pseudocritical temperature for hydrocarbon - hydrogen sulfide mixtures could be improved by using the same multipole factor as that obtained for the hydrocarbon - dioxide mixtures.

CHAPTER VIII

THE COMPRESSIBILITY FACTOR PREDICTION FOR SYSTEMS CONTAINING CARBON DIOXIDE OR HYDROGEN SULFIDE

To provide a test of the ideas presented in Chapter VII, the compressibility factors for ten multicomponent mixtures were determined by the proposed procedures. Five of the systems contained hydrocarbons and carbon dioxide and the other five contained hydrocarbons and hydrogen sulfide. The experimental compressibility factors for the hydrocarbon - carbon dioxide systems were determined in this study. The hydrocarbon - hydrogen sulfide data were determined by Satter (61). The analyses for these systems are given in Table 1 and 3 of Appendix F. Using the acentric factor tables and pseudocritical constants calculated by method 3 and adjusted with the multipole factor, γ , the average absolute deviation from experimental data for 270 points was 0.60 per cent. The maximum deviation was -2.27 per cent with only two points deviating by more than two per cent.

By using the acentric factor as a third parameter and pseudocritical constants predicted by method 3, it was

possible to predict the compressibility factor of the hydrocarbon - carbon dioxide systems experimentally determined for this study with an average absolute deviation of 0.92 per cent and a maximum deviation of -3.62 per cent. The results of comparing experimental and predicted compressibility factors indicate that carbon dioxide will not cause large deviations when the ethane and heavier hydrocarbons are at a low concentration and the carbon dioxide content is less than twenty per cent. Mixture 3 containing 20.16 per cent carbon dioxide and 4.74 per cent ethane showed an average absolute deviation of 1.22 per cent. With comparable ethane contents but lower carbon dioxide contents, the deviations for Mixtures 1 and 2 were considerably lower. Mixture 4, with a carbon dioxide content comparable to that of Mixture 2 but with the hydrocarbons heavier than methane raised to 13.16 per cent, showed a slightly larger deviation. Mixture 5, containing 28.67 per cent ethane and 12.92 per cent carbon dioxide, showed the largest deviation of any of the mixtures. The average absolute deviation in this case was 1.83 per cent with a maximum deviation of -3.62 per cent.

The compressibility factors for the hydrocarbon - carbon dioxide mixtures of this study were also predicted using method 3 pseudocritical constants adjusted with the multipole factor. Using γ , the average absolute deviation was reduced to 0.55 per cent and the maximum deviation was reduced to -2.27 per cent.

The multipole factor for all the systems of this study was small. The maximum γ for the five mixtures was 4.0° for Mixture 5. Because of the small γ corrections, the compressibility factors predicted with and without the multipole factor were comparable. Except for Mixture 1, where both methods satisfactorily predicted the compressibility factor, the use of the multipole factor always improved the compressibility factor prediction.

For the five mixtures of methane, ethane, and hydrogen sulfide, the compressibility factors were predicted, by method 3 and the acentric factor, with an average absolute deviation of 0.94 per cent and a maximum deviation of -3.63 per cent. By using the γ correction that was based on carbon dioxide data, the average absolute deviation was reduced to 0.68 per cent and the maximum deviation was reduced to -1.95 per cent.

The discussion that was presented for the carbon dioxide - hydrocarbon systems is also applicable for this type of system. That is, hydrogen sulfide presents no real difficulty in the prediction of compressibility factors using method 3 and the acentric factor unless the components heavier than methane are appreciable or the hydrogen sulfide content is above twenty per cent. Although the multipole factor improved the prediction for every mixture, the compressibility factors predicted when γ was not used did not deviate greatly from the experimental data.

A summary of the results of comparing predicted and experimental compressibilities for this system is presented in Table 4 of Appendix F. Example calculations for the hydrocarbon - carbon dioxide systems are presented in Appendix D.

The result of the comparisons between the predicted and experimental compressibility factors for the ten mixtures discussed above attests to the reliability of using the acentric factor as a third parameter for characterizing natural gas systems. For the systems studied, the pseudo-critical constants calculated with the rules of Stewart, Burkhardt, and Voo are satisfactory but the agreement with experimental data can be improved by adjusting these constants with the multipole factor.

CHAPTER IX

CONCLUSIONS

As a result of this study it has been possible to develop a multipole factor that provides a simple means of better characterizing the complex microscopic parameters governing the behavior of lean natural gas-carbon dioxide mixtures. It has also been concluded that:

1. The use of microscopic parameters to easily characterize the behavior of non-spherical, globular, or polar gas molecules is impractical with gas mixtures when more than one of these factors are causing the non-ideal fluid behavior. For natural gases, it is far more practical to use a third parameter (based on some bulk property) in which all of the causes of non-ideal fluid behavior are manifest.
2. For the constituents of natural gas, a nearly linear relationship exists between the general parameters that have been proposed to account for deviations from the Principle of Corresponding States. Because of this relationship, the

selection of one parameter over another is rather arbitrary.

3. The third parameter proposed by Pitzer, the acentric factor, is a suitable third parameter for such mixtures and is therefore used in this work. If the pseudocritical constants are adequately predicted, the acentric factor tables will provide a reliable prediction of the compressibility factor.
4. The selection of a set of pseudocritical constant prediction rules cannot be made on a theoretical basis. This selection must be made by testing the rules on mixtures that are typical of the system under study.
5. When the pseudocritical constants are determined with the rules of Stewart, Burkhardt and Voo, the deviations which may be expected between the experimental and predicted compressibility factors for hydrocarbon - carbon dioxide systems are dependent on both the carbon dioxide content and what hydrocarbons are in the mixture.
6. When the pseudocritical constants of Stewart, Burkhardt, and Voo are adjusted with the multipole factor determined in this study, improved compressibility factors for hydrocarbon - carbon

dioxide mixtures are obtained.

7. While the multipole factor was determined from binary data of hydrocarbon - carbon dioxide systems, it may be used for hydrocarbon - hydrogen sulfide systems. When it is used for such systems, the deviation between predicted and experimental compressibility factors is reduced.

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APPENDIX A

NOMENCLATURE

TABLE A - I

NOMENCLATURES

a	= Constant in equations of state of pure gases
a'	= Constant in equations of state of mixtures
a_0	= Radius of a molecule
a_r	= Reduced molecular radius
b	= Constant in equations of state of pure gases
b'	= Constant in equations of state of mixtures
$B(T)$	= Second virial coefficient
c	= A positive constant
$C(T)$	= Third virial coefficient
$^{\circ}C$	= Degrees Centigrade
d	= Density
d_c	= Critical density
d_r	= Reduced density (Equation 5-7)
F	= Dimensionless molecular parameter
$^{\circ}F$	= Degrees Fahrenheit
$f()$	= A universal function
$f_k()$	= Denotes a function dependent on k
$f_{\theta}()$	= Denotes a function dependent on θ
$g()$	= Function describing angular dependence of the interaction of two dipoles
h	= Plank's constant
i	= Subscript denoting i th component
J	= T_c'/P_c' (Equation 6-5)

j	= Subscript denoting j th component
K	= $T_c' / (P_c')^{\frac{1}{2}}$ (Equation 6-6)
$^{\circ}K$	= Degrees Kelvin
k	= Boltzman's constant
L	= Distance between force centers of a molecule
L_r	= Dimensionless distance between force centers (Equation 2-46)
L_o	= Length of a molecule
L'	= Sum of the bond lengths in the longest molecular chain
M	= Molecular weight
M_o	= Mean curvature of a molecule
m	= Mass of a molecule
N	= Number of molecules in a system
N_o	= Avogadro's Number
n	= Number of components in a system
n_g	= Moles of gas
n_o	= Number of force centers of a molecule
n_r	= Refractive index
P	= Absolute pressure
P^*	= Reduced pressure (Equation 2-15)
P_c	= Critical pressure
P_r	= Reduced pressure (Equation 2-6)
P_c'	= Pseudocritical pressure
P_r^o	= Reduced vapor pressure
Q	= Quadrupole moment

Q_r	= Reduced quadrupole moment (Equation 2-53)
Q'	= Quantum deviation parameter (Equation 2-33)
R	= Universal Gas constant
R_d	= Molecular refraction of a pure gas
R_d'	= Molecular refraction of a mixture
$^{\circ}R$	= Degrees Rankine
r	= Distance between two molecules
r'	= A parameter in pseudocritical temperature equation (Equation 3-91)
S_o	= Surface area of a molecule
s	= A parameter in pseudocritical temperature equation (Equation 3-91)
T	= Absolute temperature
T^*	= Reduced temperature (Equation 2-17)
T_c	= Critical temperature
T_r	= Reduced temperature (Equation 2-5)
T_c'	= Pseudocritical temperature
T_c''	= Corrected Pseudocritical temperature (Equation 7-7)
U	= Potential energy
U_o	= Maximum negative potential energy
V	= Total volume
$\underline{V}$	= Specific molar volume
V^*	= Reduced volume (Equation 2-16)
$\underline{V}_c$	= Critical specific molar volume
$\underline{V}_r$	= Reduced volume (Equation 2-7)
V_o	= Volume of Kihara's Molecular Core

v	= Volume of mercury relative to volume at 60°F
X	= Denotes third parameter in PCS
y	= Mole fraction
Z	= Compressibility factor
Z^0	= Compressibility factor of a substance with zero acentric factor
Z'	= Slope of the compressibility factor versus acentric factor curve at a given reduced temperature and pressure
Z_c	= Critical compressibility factor of a pure gas
Z_c'	= Critical compressibility factor of a mixture
α	= Empirical exponent (Equation 3-67)
α_k	= Riedel's third parameter (Equation 2-63)
β	= Compressibility of mercury
δ^c	= Rowlinson's third parameter (Equation 2-61)
ϵ	= Parameter in intermolecular function. It is the maximum energy of interaction
ϵ_{cl}	= Maximum energy of interaction of classical mole- cules
ϵ_q	= Maximum energy of interaction of quantum molecules
$\phi(r)$	= Intermolecular potential function
ϕ	= Ratio of quantum to classical collision diameters cubed
ϕ	= Azimuthal angle
Λ	= Quantum third parameter
Λ^*	= Reduced quantum third parameter (Equation 2-29)

- Λ_r = Reduced quantum third parameter (Equation 2-27)
 μ = Dipole moment
 μ_r = Reduced dipole moment (Equation 2-50)
 w = Pitzer's acentric factor for a pure gas
 w' = Acentric factor for a mixture
 w_{hc} = Acentric factor for the hydrocarbons in a mixture
 ρ = Shortest distance between molecular cores
 ρ_0 = Shortest distance between molecular cores at the energy minimum
 σ = Parameter in the intermolecular potential function.
 It is the collision diameter for two molecules with negligible kinetic energy
 σ_{cl} = Collision diameter for classical molecules
 σ_q = Collision diameter for quantum molecules
 θ = Ratio of quantum to classical energies of interaction
 e = Angle which dipoles make with the axis connecting them
 θ_k = Arbitrary exponent (Equation 3-76)
 τ = Multipole factor. A correction to the pseudo-critical temperature (Equation 7-7)

APPENDIX B

**CRITICAL PROPERTIES AND THIRD PARAMETER
FOR THE COMPONENTS OF NATURAL GAS**

TABLE B-1

PHYSICAL CONSTANTS

Component	Molecular Weight	Critical Temperature °F.	Critical Pressure Psia	Critical Volume ft ³ /lb
CH ₄	16.042	-116.5	673.1	0.0993
C ₂ H ₆	30.068	+90.09	708.3	0.0787
C ₃ H ₈	44.094	206.26	617.4	0.0730
nC ₄ H ₁₀	58.120	305.62	550.7	0.0704
nC ₅ H ₁₂	72.146	385.92	489.5	0.0690
C ₆ H ₁₄	86.172	454.5	439.7	0.0685
C ₇ H ₁₆	100.198	512.62	396.9	0.0682
C ₈ H ₁₈	114.224	565.2	362.1	0.0682
C ₉ H ₂₀	128.250	613	345	0.0673
C ₁₀ H ₂₂	142.276	655	320	0.0671
CO ₂	44.010	88.0	1073	0.0348
H ₂ S	34.076	212.7	1306	

TABLE B-2

THIRD PARAMETERS

Component	Z_c	ω	δ^c	α_k	R_d	L/σ	F	F/Z_c
CH ₄	0.290	.013		5.86	6.54	0.0	.096	.33
C ₂ H ₆	0.285	.105	.05	6.28	11.425	0.19	.048	.17
C ₃ H ₈	0.277	.152	.08	6.54	16.245	0.25	.033	.12
nC ₄ H ₁₀	0.274	.201	.11	6.77	20.64	0.39	.024	.09
nC ₅ H ₁₂	0.269	.252	.13	7.03	25.286		.019	.07
nC ₆ H ₁₄	0.264	.290		7.27	29.928		.016	.06
nC ₇ H ₁₆	0.260	.352		7.53	34.565		.014	.054
nC ₈ H ₁₈	0.256	.399		7.76	39.209		.012	.047
nC ₉ H ₂₀		.444			43.842		.010	.04
nC ₁₀ H ₂₂	0.247	.487		8.18	48.503		.090	.04
CO ₂	0.275	.225	.10	6.92		0.29	.046	.17
H ₂ S	0.284	.100		6.25			.047	.16

APPENDIX C

CALIBRATION AND CORRECTION DATA

TABLE C-1

COMPRESSIBILITY AND RELATIVE VOLUME OF MERCURY

VOLUMES ARE RELATIVE TO VOLUME AT 60° F

Temperature °F.	Compressibility $\beta \times 10^7$ (Vol/Vol Psi)	Relative Volume V
60	2.72	1.000000
70	2.75	1.001009
80	2.78	1.002018
90	2.81	1.003028
100	2.84	1.004038
110	2.87	1.005049
120	2.90	1.006060
130	2.93	1.007072
140	2.96	1.008084
150	3.00	1.009097
160	3.03	1.010110
170	3.06	1.011124

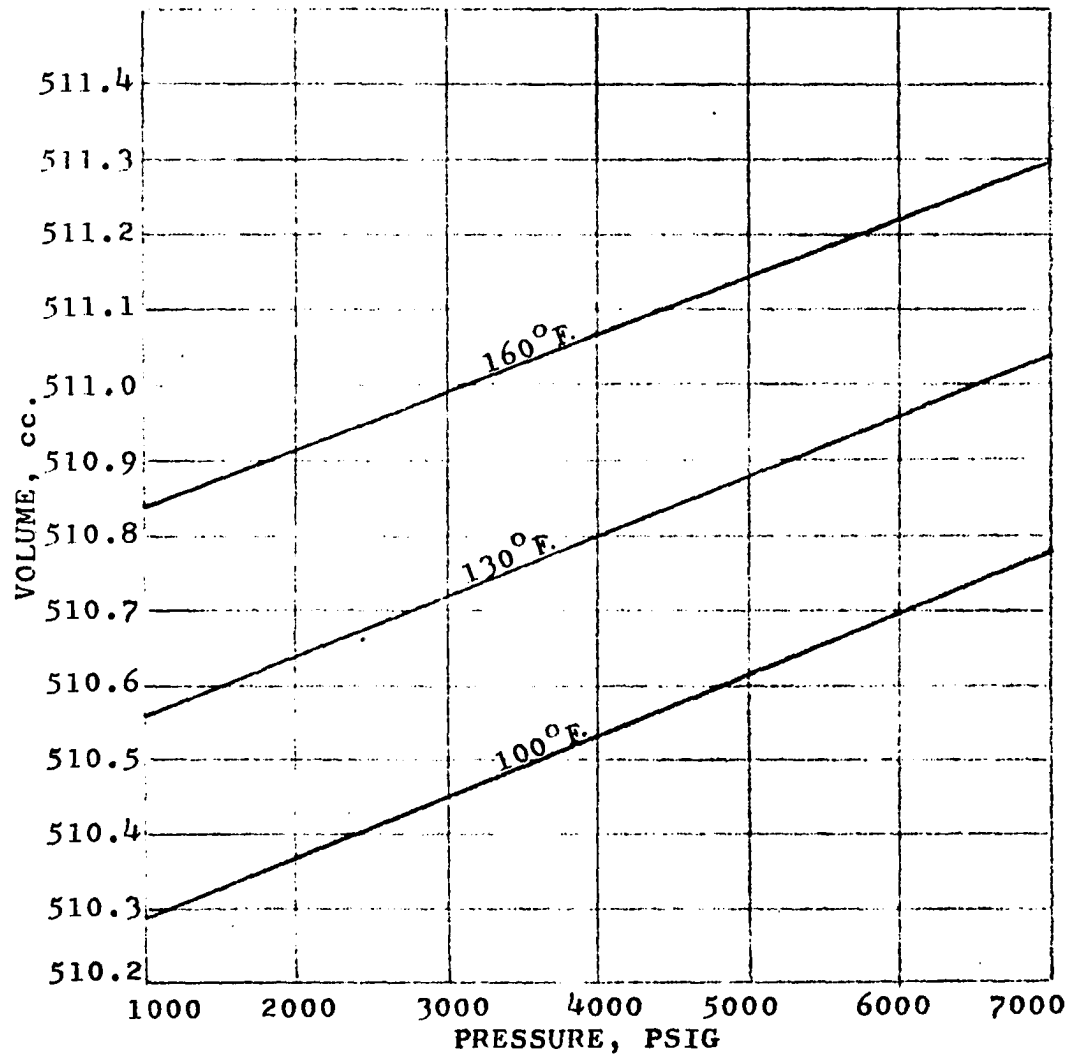


FIGURE C-1. HIGH PRESSURE CELL VOLUME AS A FUNCTION OF TEMPERATURE AND PRESSURE

APPENDIX D

SAMPLE CALCULATIONS

TABLE D-1

SAMPLE CALCULATION FOR PREPARING MIXTURES

Mixture 1

Component	Desired Concentration Mole Fraction
1. Methane	0.90
2. Ethane	0.05
3. Carbon Dioxide	0.05

The cell is initially filled with component 1.

Temperature of P-V-T cell = 100° F.

Room temperature = 77° F.

Volume of P-V-T cell at 3,000 psig
(from Figure C-1) = 510.430 cc.

Volume of Mercury in the cell at

3,000 psig and 77° F. = 404.670 cc.
(read on pump)

Calculation of the volume of component 1 at 3,000
psig and 100° F.

$$V_{\text{gas}} = V_{\text{cell}} - V_{\text{mercury}}$$

$$V_{\text{mercury}} = V_2 = V_1 \left[(1 + 3000\beta_1) \left(\frac{v_2}{v_1} \right) (1 - 3000\beta_2) \right]$$

Values for β and v are read from Table C-1.

The subscripts 1 and 2 refer to 77 and 100° F. respectively.

$$V_{\text{mercury}} = V_1 (1.002197) = 405.559 \text{ cc.}$$

$$V_{\text{gas}} = 510.430 - 405.559 = 104.871 \text{ cc.}$$

TABLE D-1--CONTINUED

Calculation of total moles and moles of each component.

at 3,000 psig and 100° F.

$$Z_1 \text{ (from Ref. 59) } = 0.8562$$

$$N_1 = PV/ZRT = .9884 \text{ g. moles}$$

$$N_t = N_1/0.90 = 1.098 \text{ g. moles}$$

$$N_2 = N_3 = 0.05(1.098) = 0.0549 \text{ g. moles}$$

Calculation of volumes of components 2 and 3 to be

injected at 2,000 psig and 77° F.

$$Z_2 \text{ (from Ref. 59) } = 0.410$$

$$Z_3 \text{ (from Ref. 58) } = 0.293$$

$$V_{\text{comp.2}} = ZNRT/P = 4.01 \text{ cc.}$$

$$V_{\text{comp.3}} = ZNRT/P = 2.86 \text{ cc.}$$

TABLE D-2

SAMPLE CALCULATION OF COMPRESSIBILITY FACTORS
FROM EXPERIMENTAL DATA

Mixture 3

Temperature of P-V-T cell = 100° F.
 Room temperature = 77° F.
 Heise Gauge Pressure = 1000 psig
 Barometric Pressure = 14.2 psia
 Pressure correction due to head of mercury between
 cell and gauge = 12 psi
 Absolute Pressure in cell = 1026.2 psia
 Volume of P-V-T cell at 1,000 psig and 100° F (from
 Figure C-1) = 510.290 cc.
 Volume of mercury in the P-V-T cell at 3,000 psig
 and 77° F (read from
 pump) = 134.815 cc.

Calculation of gas volume at 1,000 psig and 100° F.

$$V_{\text{gas}} = V_{\text{cell}} - V_{\text{mercury}}$$

$$V_{\text{mercury}} = V_2 = V_1 \left[(1 + P_1 \beta_1) \left(\frac{V_2}{V_1} \right) (1 - P_2 \beta_2) \right]$$

where $P_1 = 3,000$ psig

$$T_1 = 77^\circ \text{ F.}$$

$$\beta_1 = 2.77 \times 10^{-7}$$

$$v_1 = 1.001715$$

TABLE D-2--CONTINUED

$$P_2 = 1,000 \text{ psig}$$

$$T_2 = 100^\circ \text{ F}$$

$$\beta_2 = 2.84 \times 10^{-7}$$

$$V_2 = 1.004038$$

$$V_{\text{mercury}} = 134.875(1.002767) = 135.248 \text{ cc.}$$

$$V_{\text{gas}} = 375.042 \text{ cc.}$$

Calculation of moles of gas in sample

$$\text{Temperature of low pressure system} = 100^\circ \text{ F.}$$

$$\text{Volume of gas burette} = 997.34 \text{ cc.}$$

$$\text{Volume of steel expansion cell + lines} = 250.0 \text{ cc.}$$

$$\begin{aligned} \text{Volume of gas in put cell @ atm. pressure and} \\ 100^\circ \text{ F.} \end{aligned} = 216.33 \text{ cc.}$$

$$\text{Number of expansions into gas burette} = 31$$

Total volume of gas at 100° F. and atmospheric

$$\text{Pressure} = 31(997.34) + 250.0 + 216.33 = 31,204.68 \text{ cc.}$$

Pressure of gas(atmospheric

$$\text{pressure}) = 737.05 \text{ mm of Hg.}$$

$$N = PV/RT = 1.1861 \text{ g. moles}$$

Calculation of the compressibility factor

$$T = 100^\circ \text{ F.} = 310.94^\circ \text{ K.}$$

$$P = 1026.2 \text{ psia} = 69.83 \text{ atm.}$$

$$V = 375.042 \text{ cc.}$$

$$N = 1.1861$$

$$R = 82.055 \text{ cc. atm./}^\circ \text{ K g mole}$$

$$Z = PV/NRT = 0.8652$$

TABLE D-3

A SAMPLE CALCULATION USING THE PROPOSED
PROCEDURE FOR PREDICTING
COMPRESSIBILITY FACTORS

Mixture 5

Component	Mole Fraction	w	T _c , ° R.	P _c , psia
CH ₄	0.5841	0.013	343.3	673
C ₂ H ₆	0.2867	0.105	549.7	708
C ₃ H ₈	0.1292	0.225	547.6	1071

Pressure = 5026 psia

Temperature = 130° F.

Experimental Z = 0.9209

Calculation of Z without correcting for CO₂

$$w' = \sum_i y_i w_i$$

$$w' = 0.0668$$

$$J = T_c' / P_c' = 1/3 \left(\sum y_i \frac{T_{ci}}{P_{ci}} \right) + 2/3 \left[\sum y_i \left(\frac{T_{ci}}{P_{ci}} \right)^{1/2} \right]^2$$

$$K = T_c' / (P_c')^{1/2} = \sum_i y_i T_{ci} / P_{ci}^{1/2}$$

$$T_c' = K^2 / J = 429.1^\circ \text{ R.}$$

$$P_c' = T_c' / J = 736.2 \text{ psia}$$

$$T_r = T / T_c' = 589.6 / 429.1 = 1.374$$

TABLE D-3--CONTINUED

$$P_r = P/P_c' = 5026/736.2 = 6.827$$

From Figures III-3 and III-4 or interpolated from
Pitzer's acentric factor tables

$$Z_o = 0.9041$$

$$Z' = 0.040$$

$$Z = Z_o + \omega Z'$$

$$Z = 0.9067$$

Calculation of Z using γ to correct for CO₂

$$\omega_{hc} = \frac{\sum y_j \omega_j}{\sum y_j}$$

$$\omega_{hc} = 0.0433$$

From Figure V-2

$$\gamma = 4.0 \text{ R.}$$

$$T_c'' = T_c' - 4.0 = 429.1 - 4.0$$

$$T_c'' = 425.1^\circ \text{ R.}$$

$$P_c'' = P_c' \times T_c''/T_c'$$

$$P_c'' = 736.2 \times \frac{425.1}{429.1} = 729.3 \text{ psia}$$

$$T_r = \frac{589.6}{425.1} = 1.387$$

$$P_r = \frac{5026}{723.3} = 6.892$$

TABLE D-3--CONTINUED

From Figures III-3 and III-4 or interpolated from
Pitzer's acentric factor tables

$$Z_0 = .9110$$

$$Z' = 0.040$$

$$Z = Z_0 + \omega 'Z'$$

$$Z = 0.9137$$

APPENDIX E

BINARY MIXTURES

TABLE E-1

SUMMARY OF COMPRESSIBILITY FACTOR CALCULATIONS
FOR BINARY MIXTURES

Binary	Mole Frac. 1st Comp.	Temp. Range °F.	Press. Range Psia	Number of Points
CH ₄ CO ₂	0.6050	100-280	1,000- 10,000	56
C ₂ H ₆ CO ₂	0.500	100-280	1,000- 9,000	40
C ₃ H ₈ CO ₂	0.500	100-280	1,000- 7,000	32
nC ₄ H ₁₀ CO ₂	0.500	160-340	1,000- 7,000	31
CH ₄ H ₂ S	0.500	100-280	1,000- 10,000	43
CH ₄ C ₂ H ₆	0.500	70-150	1,000- 3,000	20
CH ₄ C ₃ H ₈	0.500	100-280	1,000- 8,000	35
CH ₄ nC ₄ H ₁₀	0.500	100-280	1,500- 7,000	25
CH ₄ nC ₅ H ₁₂	0.500	60-280	2,000- 5,000	12

TABLE E-1--CONTINUED

METHOD 1				METHOD 2			
AAD*	MD**	PMD***		AAD*	MD**	PMD***	
%	%	T _r	P _r	%	%	T _r	P _r
1.89	-4.57	1.32	4.22	0.85	-2.63	1.34	4.28
7.90	-33.22	1.02	1.12	6.14	-45.98	1.03	1.17
12.46	-37.51	1.02	1.18	9.02	-43.29	1.02	1.27
13.72	-20.64	0.94	1.23	8.61	-19.92	1.11	2.06
4.45	-17.16	1.10	2.02	1.63	-3.72	1.26	4.17
3.37	+5.50	1.32	2.90	2.44	+3.73	1.31	3.56
2.86	+9.68	1.23	2.33	0.62	+3.67	1.20	1.51
3.09	+13.55	1.23	2.45	0.51	+1.68	1.29	3.18
2.14	+8.52	1.24	3.44	0.83	-1.89	1.09	3.39

* Per cent average absolute deviation

** Per cent maximum deviation

*** Point of maximum deviation

TABLE E-1--CONTINUED

METHOD 3				METHOD 4			
AAD*	MD**	PMD***	P _r	AAD*	MD**	PMD***	P _r
%	%	T _r		%	%	T _r	
0.77	-2.43	1.34	4.27	1.94	-4.62	1.32	4.21
6.25	-40.01	1.02	1.17	6.86	-43.73	1.02	1.17
9.37	-49.25	1.02	1.28	9.09	-52.91	1.00	1.26
8.52	-18.93	1.11	2.06	6.85	-26.79	1.09	2.02
1.88	-7.20	1.31	2.84	4.52	-7.22	1.13	2.07
2.40	+4.38	1.31	2.84	3.20	+3.94	1.31	2.83
0.62	+3.61	1.20	2.26	2.23	-3.74	1.08	2.23
0.55	+1.93	1.18	2.38	2.96	-3.12	1.06	3.11
0.71	+3.34	0.90	6.78	3.10	-5.87	1.07	3.28

TABLE E-1--CONTINUED

METHOD 5				USING GRAPHICALLY DETERMINED PSEUDO- CRITICAL CONSTANTS			
AAD* %	MD** %	PMD*** T _r	P _r	AAD* %	MD** %	PMD*** T _r	P _r
0.81	-2.52	1.34	4.28	0.41	+1.01	1.79	6.19
6.66	-49.87	1.02	1.17	1.15	-22.97	1.06	1.23
10.84	-43.20	1.02	1.28	1.25	-18.80	1.06	1.39
11.07	-15.05	1.13	2.09	0.54	-3.57	1.16	2.26
2.03	-17.32	1.10	2.02	0.66	+5.52	1.15	1.06
1.90	+5.65	1.32	2.85	1.38	-10.55	1.15	2.12
1.03	+9.76	1.23	2.39	0.78	-3.12	1.07	2.25
1.77	+13.20	1.23	2.45	0.54	-2.33	1.17	2.38
3.49	+8.80	1.24	3.51	0.41	-1.80	1.08	3.41

TABLE E-2

PSEUDOCRITICAL CONSTANTS BINARY MIXTURES

Binary	Mole Frac. 1st Comp.	Graphically Determined		Method 1		Method 3	
		T_c'	P_c'	T_c'	P_c'	T_c'	P_c'
CH ₄ -CO ₂	0.2035	500.4	965.0	506.0	990.0	502.0	982.7
	0.4055	455.5	882.7	464.8	909.6	459.0	898.7
	0.6050	413.7	807.3	424.0	830.2	417.5	819.0
	0.8469	369.9	721.6	374.6	733.9	371.5	728.0
C ₂ H ₆ -CO ₂	0.1	541.0					
	0.2	535.0	936.0	548.0	998.0	546.7	974.0
	0.3	530.5					
	0.4	528.0					
	0.5	527.0	811.0	548.7	890.0	546.8	855.0
	0.6	528.5					
	0.7	532.0					
	0.8	537.0	739.0	549.3	781.0	548.2	761.0
	0.9	543.0					
C ₃ H ₈ -CO ₂	0.1	549.0					
	0.2	553.3	869.0	571.3	980.0	572.7	933.0
	0.3	561.0					
	0.4	571.5					
	0.5	584.5	722.0	606.7	844.0	609.3	783.0
	0.6	598.5					
	0.7	615.0					
	0.8	632.0	648.0	642.1	708.0	643.9	675.0
	0.9	649.0					

TABLE E-2--CONTINUED

Binary	Mole Frac. 1st Comp.	Graphically Determined		Method 1		Method 3	
		T _c '	P _c '	T _c '	P _c '	T _c '	P _c '
nC ₄ H ₁₀ -CO ₂	0.1	559.5					
	0.2	575.0	831.0	591.2	967.0	596.8	899.0
	0.3	593.0					
	0.4	614.0					
	0.5	637.5	664.0	656.5	811.0	665.5	727.9
	0.6	661.0					
	0.7	686.0					
	0.8	711.0	584.0	721.7	655.0	727.4	611.0
	0.9	738.0					
CH ₄ -H ₂ S	0.20	591.8	1152.0	606.7	1179.0	598.2	1164.0
	0.50	487.2	941.0	507.9	990.0	494.6	965.0
	0.80	395.3	772.0	409.1	800.0	400.6	784.0
CH ₄ -C ₂ H ₆	0.20	513.0	710.0	508.4	701.0	510.5	709.0
	0.50	461.0	706.0	446.5	691.0	449.7	704.0
	0.80	399.0	691.0	384.6	680.0	386.0	690.0
CH ₄ -C ₃ H ₈	0.20	613.0	638.0	601.3	628.0	608.3	638.0
	0.50	521.0	666.0	504.5	645.0	515.7	664.0
	0.80	419.0	685.0	407.8	662.0	415.1	678.0
CH ₄ -nC ₄ H ₁₀	0.20	693.0	584.0	680.9	575.0	693.5	583.0
	0.50	580.0	630.0	554.3	612.0	574.9	629.0
	0.80	454.0	670.0	427.7	649.0	441.5	666.0
CH ₄ -nC ₅ H ₁₂	0.20	771.0	530.0	745.1	526.0	763.5	528.0
	0.50	629.0	586.0	594.4	581.0	624.2	590.0
	0.80	466.0	645.0	443.8	636.0	464.7	650.0

APPENDIX F

MULTICOMPONENT MIXTURES

TABLE F-1

COMPOSITION OF THE EXPERIMENTAL
MIXTURES OF THIS STUDY

Components	Mixture 1	Mixture 2	Mixture 3	Mixture 4	Mixture 5
CH ₄	0.8977	0.8520	0.7458	0.7593	0.5841
C ₂ H ₆	0.0464	0.0410	0.0474		0.2867
C ₃ H ₈				0.1316	
N ₂	0.0053	0.0057	0.0052		
CO ₂	0.0506	0.1013	0.2016	0.1091	0.1292

TABLE F-2

EXPERIMENTAL COMPRESSIBILITY FACTORS

Pressure Psia	Mixture 1			Z	Mixture 2		
	100°F.	130°F.	160°F.		100°F.	130°F.	160°F.
1026	0.8805	0.9044	0.9246		0.8813	0.9040	0.9234
1526	0.8437	0.8752	0.8993		0.8378	0.8715	0.8987
2026	0.8183	0.8547	0.8847		0.8117	0.8501	0.8824
2526	0.8108	0.8508	0.8793		0.8043	0.8443	0.8766
3026	0.8223	0.8574	0.8845		0.8148	0.8509	0.8825
3526	0.8455	0.8771	0.9007		0.8377	0.8697	0.8985
4026	0.8778	0.9041	0.9225		0.8708	0.8968	0.9210
4526	0.9166	0.9373	0.9537		0.9096	0.9304	0.9492
5026	0.9591	0.9741	0.9881		0.9520	0.9688	0.9832
6026	1.0502	1.0562	1.0640		1.0445	1.0516	1.0583
7026	1.1456	1.1430	1.1428		1.1397	1.1392	1.1385

TABLE F-2--CONTINUED

Pressure Psia	Mixture 3			Z	Mixture 4		
	100°F.	130°F.	160°F.		100°F.	130°F.	160°F.
1026	0.8652	0.8887	0.9095	0.8128	0.8509	0.8739	
1526	0.8141	0.8519	0.8818	0.7500	0.7985	0.8344	
2026	0.7783	0.8251	0.8600	0.7142	0.7703	0.8101	
2526	0.7676	0.8136	0.8499	0.7140	0.7633	0.8037	
3026	0.7783	0.8196	0.8549	0.7369	0.7779	0.8134	
3526	0.8037	0.8393	0.8704	0.7754	0.8080	0.8361	
4026	0.8380	0.8669	0.8933	0.8206	0.8454	0.8665	
4526	0.8787	0.9022	0.9239	0.8707	0.8892	0.9030	
5026	0.9231	0.9408	0.9562	0.9226	0.9361	0.9449	
6026	1.0178	1.0261	1.0339	1.0312	1.0350	1.0359	
7026	1.1156	1.1158	1.1154	1.1408	1.1361	1.1279	

TABLE F-2--CONTINUED

Mixture 5

Z

Pressure Psia	100°F.	130°F.	160°F.
1026	0.7932	0.8298	0.8614
1526	0.7154	0.7715	0.8132
2026	0.6755	0.7360	0.7832
2526	0.6783	0.7298	0.7753
3026	0.7078	0.7481	0.7863
3526	0.7508	0.7820	0.8112
4026	0.8007	0.8238	0.8465
4526	0.8548	0.8709	0.8885
5026	0.9104	0.9209	0.9333
6026	1.0242	1.0253	1.0286
7026	1.1379	1.1312	1.1267

TABLE F-3

COMPOSITION OF THE HYDROCARBON-HYDROGEN-SULFIDE MIXTURES

Components	Mixture A	Mixture B	Mixture C	Mixture D	Mixture E
CH ₄	0.871	0.831	0.836	0.800	0.713
C ₂ H ₆	0.064	0.071	0.117	0.107	0.090
H S	0.065	0.098	0.047	0.093	0.197

TABLE F-4

SUMMARY OF CALCULATED COMPRESSIBILITY FACTORS
FOR MULTICOMPONENT SYSTEMS

Temperature range for all mixtures was 100 - 160° F.
Pressure range for all mixtures was 1026 - 7026 psia.

Mixture	Number of Points	AAD*	Method 3 MD**	PMD***		Method 3 with γ AAD	MD	PMD	
				T_r	P_r			T_r	P_r
1	33	0.46	+1.08	1.71	5.80	0.67	+1.32	1.72	5.82
2	33	0.46	-0.85	1.59	4.25	0.17	-0.42	1.52	7.10
3	33	1.22	-1.98	1.43	3.38	0.49	-0.95	1.45	6.78
4	33	0.65	-1.86	1.36	4.25	0.50	+1.60	1.37	1.45
5	33	1.83	-3.60	1.30	4.11	0.91	-2.27	1.32	4.15
A	28	1.32	-2.11	1.57	4.24	1.00	-1.76	1.58	4.26
B	28	1.30	-2.48	1.45	2.77	0.88	-1.77	1.46	2.78
C	28	0.29	-0.91	1.47	2.86	0.22	+0.71	1.63	9.96
D	28	0.41	-0.90	1.43	2.77	0.37	+0.92	1.51	1.41
E	28	1.40	-3.63	1.34	3.85	0.91	-1.95	1.35	3.89

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- * Per cent average absolute deviation
 ** Per cent maximum deviation
 *** Point of maximum deviation