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OF GASEOUS MIXTURES

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EQUILIBRIUM WATER CONTENT
OF GASEOUS MIXTURES

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EQUILIBRIUM WATER CONTENT OF GASEOUS MIXTURES

CHAPTER I

THE PROBLEM

In spite of the extensive work done in the experimental determination of equilibrium water content of pure gases (hydrocarbons and non-hydrocarbons) and natural gases, which are mixtures of various components, there exists a wide gap between these two extreme cases. From time to time various correlations have been proposed to correlate the existing data and to predict the equilibrium water content of various systems. Most of these correlations are satisfactory in the case of pure gases. The ones based on the concept of intermolecular forces have produced the highest degree of accuracy but, unfortunately, the limited data available for this approach bar the wide application of those correlations.

For complex gaseous mixtures, the approach based on the concept of intermolecular forces becomes too complicated and any correlation based on this approach eluded the past investigators. Consequently, no serious attempt

has so far been made to predict the quantitative effect of the presence of non-hydrocarbons e.g. nitrogen, carbon dioxide, hydrogen sulfide, on the equilibrium water content of gaseous mixtures. The dire need for a correlation to achieve this object prompted the present investigation.

Through this investigation an attempt will be made to study the effect of the presence of ethane, nitrogen, carbon dioxide and hydrogen sulfide separately on the equilibrium water content of methane, the chief component of all natural gases, thus filling partly the gap existing in the experimental water content data. The results thus obtained will be utilized to propose a correlation capable of correlating the existing data and predicting the equilibrium water content of other gaseous mixtures.

However, it is recognized that it will be impossible to propose a correlation capable of handling cases of extreme composition or in an unlimited range of temperature and pressure. Consequently, this whole investigation will be limited to systems with less than 20 mole per cent of any component except methane from nominal temperature of 100 to 160°F between 200 and 2,000 pounds per square inch pressure.

CHAPTER II

GENERAL CONSIDERATIONS

This study is aimed mainly at the behavior of the vapor phase of a two phase vapor-liquid system in equilibrium. The compositions of both phases are functions of the original dry gas composition, assuming that the liquid phase originally consisted of pure water. Any system in a state of equilibrium can be fully defined by fixing some of its physical or empirical properties. Composition is not very convenient to work with, especially for complex systems like natural gas-water. In its place the "escaping tendency," an empirical property of the system, is found to be more convenient. It can be expressed in different forms like chemical potential, free energy and fugacity. Using fugacity, which has the units of pressure, any vapor-liquid system in equilibrium can be defined fully by the following three criteria:

$$T^v = T^l \quad (2-1)$$

$$P^v = P^l \quad (2-2)$$

$$\bar{f}_i^v = \bar{f}_i^l, \quad (2-3)$$

where the superscripts v and l designate vapor and liquid phases while subscript "i" refers to any component. The bar above f designates the value of the fugacity in a mixture. P and T are the pressure and temperature of the system.

For the same system the equilibrium phase distribution ratio, K, can be represented as:

$$K_i = \frac{y_i}{x_i} = \frac{\text{mole fraction of component "i" in vapor phase}}{\text{mole fraction of component "i" in liquid phase}} \quad (2-4)$$

Introduction of the concept of fugacity into Equation (2-4) gives

$$K_i = \frac{\bar{f}_i^l / x_i}{\bar{f}_i^v / y_i} \quad (2-5)$$

Assuming the Lewis and Randall Fugacity Rule to hold, fugacities $\bar{f}_i^v$ and $\bar{f}_i^l$ can be determined by the following relations:

$$\bar{f}_i^v = y_i f_i^v \quad (2-6)$$

$$\bar{f}_i^l = x_i f_i^l \quad (2-7)$$

Combining Equations (2-6) and (2-7) with Equation (2-5) gives the following relation for the ideal K value:

$$K_{\text{ideal}} = \frac{f_i^l}{f_i^v} \quad (2-8)$$

To facilitate the evaluation of fugacities, system pressure, P , and vapor pressure, P^0 , are introduced by multiplying the numerator in Equation (2-8) by (P_i^0/P_i^0) and the denominator by (P/P) , giving:

$$K_{\text{ideal}} = \frac{f_i^l/P_i^0}{f_i^v/P} \frac{P_i^0}{P} \quad (2-9)$$

which is a corrected form of:

$$K_{\text{ideal}} = \frac{P_i^0}{P} \quad (2-10)$$

Assuming Dalton's law and Raoult's law for ideal vapor and liquid states to hold good.

Fugacity of any component "i" in the liquid state can be determined from Equation (2-3) written in the following form:

$$\frac{f_i^l}{P_i^0} = \frac{f_i^v}{P_i^0} \quad (2-11)$$

where subscript P_i^0 designates the fugacity of component "i" at its vapor pressure and system temperature. $f_{P_i^0}^v$ can be determined from Figure 5-2.

The system pressure is higher or lower than the vapor pressures of most of the components in a mixture. The effect of this difference in pressures is taken into consideration by applying the basic equation for the fugacities between the vapor pressure and the system pressure as follows:

$$RT \ln \frac{f_P^l}{f_{P_i}^l} = \int_{P_i}^P V dp \quad (2-12)$$

where f_P^l = liquid fugacity of a component at system pressure, P , and system temperature, T .

Replacing V by $\frac{ZRT}{P}$ and integrating Equation (2-12) with an average compressibility factor of component "i" in liquid state, gives:

$$\ln \frac{f_P^l}{f_{P_i}^l} = Z_{av} \ln \frac{P}{P_i}$$

or

$$f_P^l = f_{P_i}^l \left(\frac{P}{P_i} \right)^{Z_{av}} \quad (2-13)$$

Combining Equations (2-9) and (2-13) gives the expression

$$K_{ideal} = \frac{P_i^o}{P} \left(\frac{f_{P_i}^v / P_i^o}{f_P^v / P} \right) \left(\frac{P}{P_i^o} \right)^{Z_{av}} \quad (2-14)$$

Equation (2-14) assumes ideal liquid and vapor states for which Amagats law of additive volumes holds good. The value of K for any component in a mixture, as obtained from Equation (2-14), is a function of system temperature and pressure only and is independent of composition. But for real systems this is hardly true. The intermolecular forces alter the ideal conditions which in turn affect the true properties of the system.

For determining the true properties of a real gaseous phase various equations of state have been proposed (31). But the two particularly useful for the present study will be discussed briefly:

A. Statistical Equation of State

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

$$P = kT \left(-\frac{\ln Q}{V} \right)_{T,N} \quad (2-15)$$

$$P = \frac{NkT}{V} - \frac{N^2}{6V^2} \int g(r)r \frac{dU}{dr} 4\pi r^2 dr \quad (2-16)$$

where k = Boltzmann constant

V = total volume of the system

N = number of molecules in the system

U = the potential energy of interaction

B. Virial Equation of State

In this approach the equation of state is expressed in the form of a power series in terms of volume or

pressure, i.e.:

$$PV = RT \left[1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^4} + \dots \right] \quad (2-17)$$

or

$$PV = RT + B'(T)P + C'(T)P^2 + D'(T)P^4 + \dots \quad (2-18)$$

where $B(T)$, $C(T)$, . . . , $B'(T)$, $C'(T)$, . . . are functions of temperature only and are called, respectively, the second, third and fourth virial coefficients.

The most widely accepted method for evaluating the second virial coefficient for simple non-polar spherical molecules utilizes the Lennard-Jones potential function:

$$U(r) = 4E \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2-19)$$

where $U(r)$ = intermolecular potential function

E = maximum energy of attraction

σ = the collision diameter for low velocity
collision between two molecules

r = distance between two molecules.

Equation (2-19) shows that the attractive potential energy of a pair of molecules has an inverse sixth power dependence on separation and an inverse twelfth power dependence on repulsive energy.

For simple polar molecules, the Stockmeyer potential function, which is a superposition of the

Lennard-Jones potential function and the interaction of two dipoles, is widely employed for evaluating the second virial coefficient. The third and to a lesser extent the fourth virial coefficients are still under development.

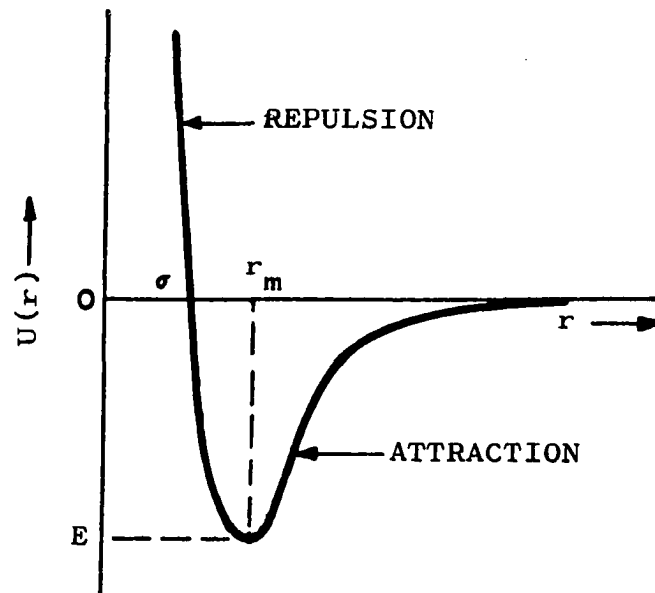


FIGURE 2-1. TYPICAL LENNARD-JONES POTENTIAL ENERGY CURVE

CHAPTER III

EXISTING CORRELATIONS

An extensive search of literature revealed various correlations for determining the equilibrium water content of the gaseous phase of a two phase vapor-liquid system. They are reviewed briefly in the following sections.

A. Theoretical Correlations

Assuming ideal behavior of co-existing phases i.e. Dalton's law of partial pressures for the vapor phase and Raoult's law for the liquid phase to hold good in a two phase aqueous system in equilibrium, the following relation can be written:

$$\frac{y_w}{x_w} = \frac{P_w^0}{P} \quad (3-1)$$

Assuming solubility of gaseous phase in the water rich liquid phase as negligible ($x_w \approx 1.0$) Equation (3-1) may be written as:

$$y_w = \frac{P_w^0}{P} \quad (3-2)$$

At low pressures where all gases tend to approach ideal behavior, Equation (3-2) will describe the water content of hydrocarbon gases with reasonable accuracy but at elevated pressures this relationship would involve serious errors.

To account for the non-ideality of the vapor phase, if P_w^0 and P in Equation (3-2) are replaced with fugacities of water in liquid and vapor phase respectively, the above equation can be written as:

$$y_w = \frac{f_w^l}{f_w^v} \quad (3-3)$$

Equations (3-2) and (3-3) were used to calculate the equilibrium water content of methane at 340°F and plotted in Figure 3-1 by Lukacs (45). The discrepancy of experimental values from those obtained using Equation (3-3) is due to the fact that at any pressure and temperature fugacity of water has to be determined in both the vapor and liquid phases. However, outside the two phase region for pure water, one of the phases will be hypothetical and the fugacity of this phase is usually obtained by extrapolating into the two phase region. In cases where extended extrapolation is required this procedure can lead to considerable error.

Bartlett (2) proposed a corrected form of Equation (3-2):

$$y_w = \frac{p_w^o}{P} \times Z \quad (3-4)$$

where Z = compressibility factor of the gas at system pressure and temperature.

The author further corrected Equation (3-4) by introducing Poynting's correction factor to account for the change in vapor pressure of water with change in system pressure.

However, experimental results obtained by other investigators did not even qualitatively correspond to the results calculated by the proposed corrected equation.

From Equations (2-6) and (2-7), Olds, et al. (55) defined a constant of proportionality:

$$\beta = f_w^l \frac{x_w}{y_w} \quad (3-5)$$

which is equal to f_w^v in the pure state. And assuming:

- (a) Dalton's law of partial pressures to hold good
- (b) ideal gas behavior

$$(c) \left(\frac{dV_{lw}}{dP} \right)_T = 0$$

they proposed the following relationship:

$$\log \frac{y_w P}{p_w^o} = \frac{V_{lw} (P - p_w^o)}{2.303 RT} \quad (3-6)$$

where V_{lw} = average specific volume of liquid water.

B. Semi-empirical Correlations

Leland et al. (41) proposed the following relation based on the theoretical work of Scatchard (80) and Hildebrand:

$$y_w = \left(\frac{V_g}{V_w}\right) e^{-\left[1 - \frac{V_w}{V_g} + \frac{V_w(U_{gg} - 2U_{gw} + U_{ww})}{RT}\right]} \quad (3-7)$$

where V_g = molal volume of pure hydrocarbon at system pressure and temperature

V_w = molal volume of pure water at system pressure and temperature

U_{gg} = intermolecular potential energy between pairs of hydrocarbon molecules per unit volume of pure hydrocarbon

U_{ww} = intermolecular potential energy between pairs of water molecules per unit volume of pure water

U_{gw} = a function analogous to U_{gg} and U_{ww} terms, which accounts for the intermolecular potential energy between pair composed of unlike molecules

The U_{gg} and U_{ww} terms may be evaluated from the expression:

$$U_{ii} = \left[\frac{(E_o)_i - (E_p)_i}{V_i} \right]_T \quad (3-8)$$

where $(E_o)_i$ = molal internal energy of pure component i at system temperature and zero pressure

$(E_p)_i$ = molal internal energy of pure component i at temperature and pressure of the system.

The U_{gw} term is evaluated from an empirical relation:

$$U_{gw} = a'(U_{gg} + U_{ww}) \quad (3-9)$$

where a' is an empirically derived constant having these average values:

$$a' = 0.26 \text{ for paraffins} \quad (3-10)$$

$$a' = 0.29 \text{ for the olefin, 1-butene} \quad (3-11)$$

The assumptions involved in this correlation are:

1. The mutual energy of two molecules depends only upon the distance between them and their relative orientation and not at all on the nature of the other molecules between or around them, or on temperature.

2. The distribution of the molecules in position and in orientation is random i.e. independent of the temperature and the nature of the other molecules present.

3. The change in volume on mixing at constant pressure is zero.

Rigby and Prausnitz (72) combining Equations (2-11) and (2-12) with the definitions of fugacity coefficient, ϕ , and activity coefficient, γ , derived this equation:

$$y_w \phi_w^P = \gamma_w^{(P^r)} x_w f_w^o(P^r) e^{\int_{P^r}^P \frac{\bar{v}_w^1}{RT} dP} \quad (3-12)$$

where ϕ_w = vapor-phase fugacity coefficient

$\gamma_w^{(P^r)}$ = liquid-phase activity coefficient

$f_w^o(P^r)$ = reference fugacity of water at system temperature and reference pressure, P^r

$\bar{v}_w^1$ = partial molar volume of water in liquid state.

In the pressure and temperature range of interest assuming solubility of the gas in water to be negligible and water to be essentially incompressible the following relations hold good:

$$\gamma_w^{(P^r)} = 1.0 \quad (3-13)$$

$$\bar{v}_w^1 = v_w^1 \quad (3-14)$$

$$\frac{dv_w^1}{dP} = 0 \quad (3-15)$$

Substituting Equations (3-13), (3-14) and (3-15) in Equation (3-12) the following relation was obtained:

$$y_w = \frac{x_w \cdot f_w^o(P^r)}{\phi_w^P} e^{\left[\frac{v_w^1(P-P^r)}{RT} \right]} \quad (3-16)$$

From the empirical virial equation of state:

$$\ln \phi_w = \frac{2}{V} (y_w B_{12} + y_g B_{11}) + \dots - \ln \frac{PV}{RT} \quad (3-17)$$

where V = vapor molar volume

B_{11} = second virial coefficient of water

B_{12} = second virial cross coefficient between water and gas molecules.

From the solubility data for binary aqueous mixtures, virial cross coefficients for nitrogen, argon and methane were obtained and reported by the authors.

C. Empirical Correlations

Bukacek (8) proposed the following correlation:

$$y_w = \frac{A}{P} + B' \quad (3-18)$$

where y_w = water content of vapor phase in pounds per million cubic feet of gas

B' = an experimentally determined temperature dependent constant

A = a constant defined by the following relation:

$$A = P_w^o \frac{18 \times 10^6 \cdot P_b}{10.73(459.6 + T_b) Z_b} \quad (3-19)$$

where P_b , T_b and Z_b are the pressure, temperature and compressibility factor at the base conditions chosen for gas volume measurements. Values of A and B' for different temperatures (-40 to 460°F) have been reported.

Townsend (88) proposed the following equation for the equilibrium water content of a binary aqueous system:

$$y_w = K_w \cdot \frac{\phi_w''}{\phi_w'} \cdot x_w \cdot \gamma_w \quad (3-20)$$

where ϕ_w'' = activity coefficient of water in liquid phase which accounts for deviations from real solutions caused by differences in molecular or chemical type

ϕ_w' = activity coefficient of water in the vapor phase

γ_w = activity coefficient of water in the liquid phase which takes into account deviations from ideal solutions caused by differences in molecular size or volatility

Values of K_w were obtained by integrating Equation (2-12) and combining with Equation (2-8).

For methane-water system, assuming $\frac{\phi_w''}{\phi_w'} \cdot x_w = 1.0$, values of γ_w were reported at 80°F and pressure ranging between 14.7 and 3000 pounds per square inch absolute.

D. Equilibrium Water Content Charts

Due to the lack of any workable correlation for the determination of equilibrium water content of a natural gas at given pressure and temperature, various

investigators (9, 17, 19, 30, 40, 46, 50, 74, 83) have reported experimental results in the form of water content charts. Of these the most widely used are the two prepared by McCarthy, et al. (46) and McKetta and Wehe (50) as reproduced in Figures 3-2 and 3-3 respectively.

McCarthy, et al used the data obtained with essentially nitrogen free natural gas whereas McKetta and Wehe used the data reported by other investigators, mainly those of Dodson and Standing (19).

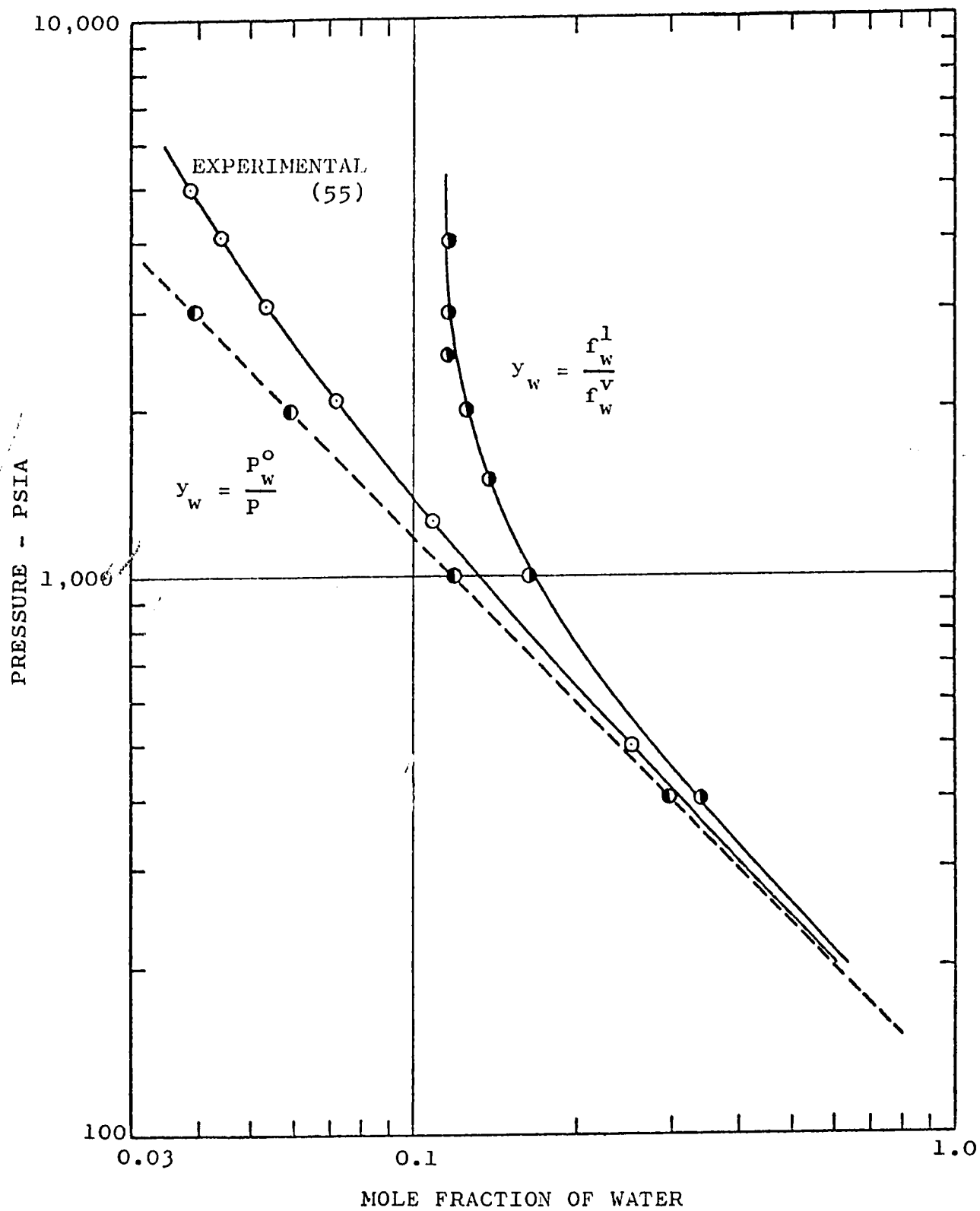


FIGURE 3-1. WATER CONTENT OF METHANE AT 340°F

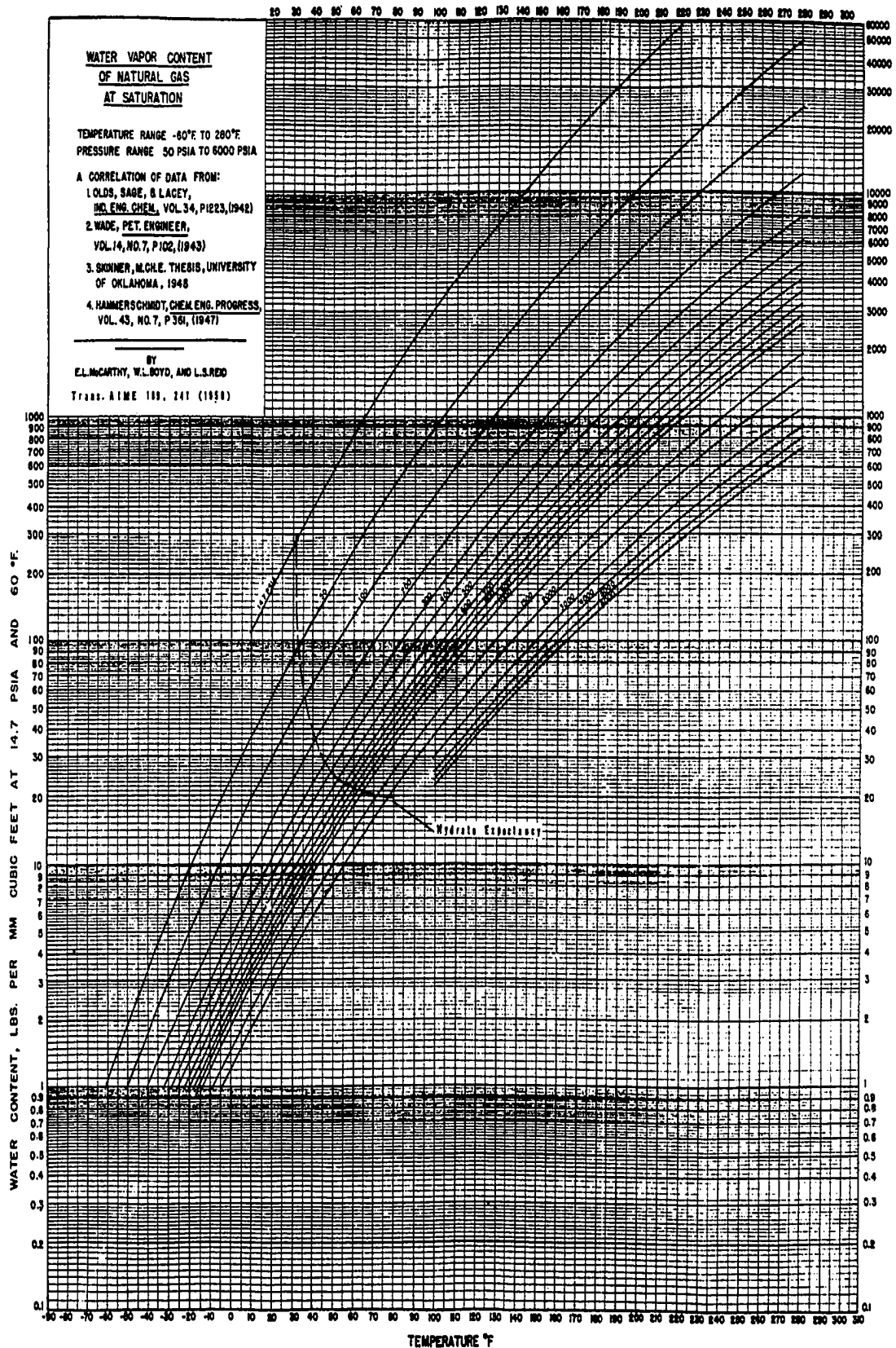


FIGURE 3-2. WATER VAPOR CONTENT OF NATURAL
GAS AT SATURATION

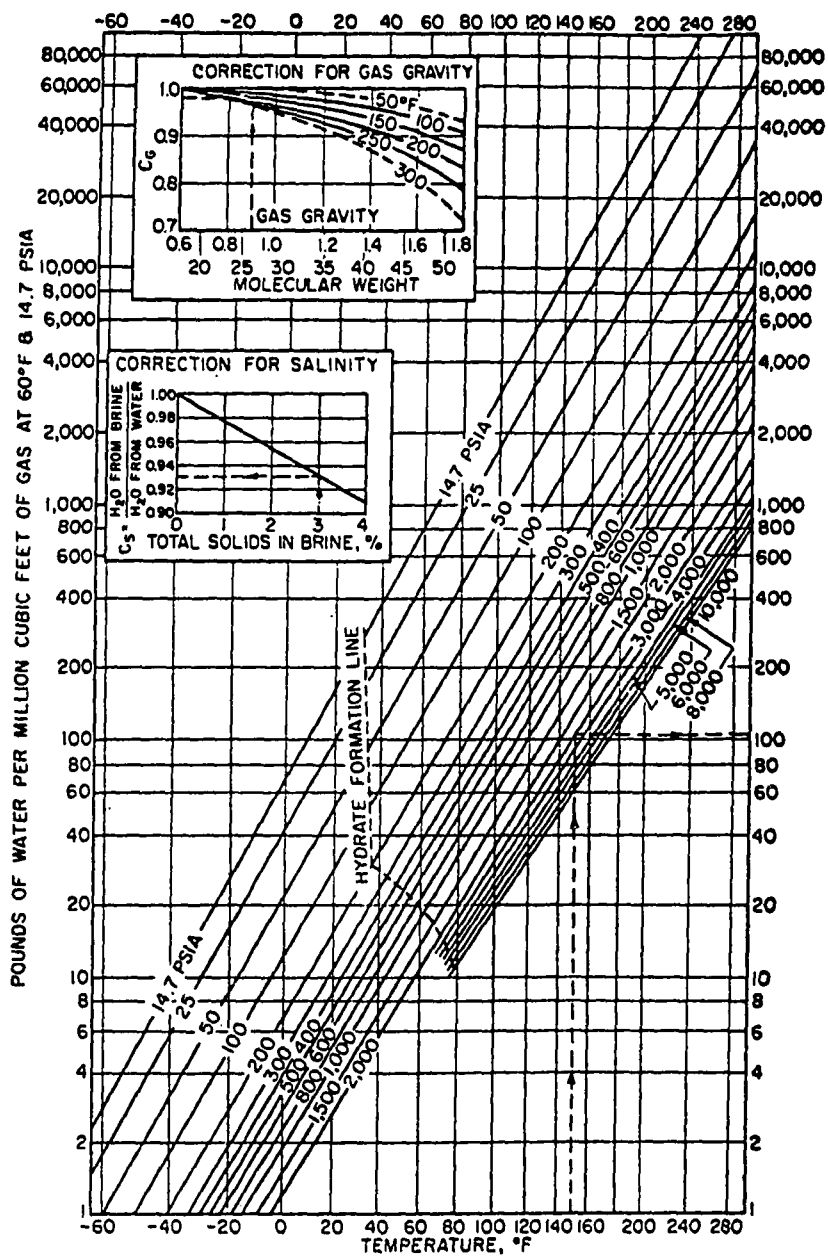


FIGURE 3-3. WATER VAPOR CONTENT OF NATURAL GASES AS A FUNCTION OF PRESSURE, TEMPERATURE, SALINITY AND GRAVITY OF THE GAS

CHAPTER IV

FACTORS INFLUENCING EQUILIBRIUM WATER CONTENT

As indicated in Appendix B, various investigators have studied the equilibrium water content of different systems mostly as a function of system pressure and temperature without considering the composition of the gaseous phase as any significant variable. All of these investigators concluded from their experimental data that equilibrium water content of any vapor phase is a direct function of system temperature and an inverse function of system pressure. Different interpretations of these two significant conclusions led others to propose various correlations for equilibrium water content as reviewed in the previous chapter. Lack of any workable correlation for determining the equilibrium water content of a natural gas points sharply to a closer study of the factors influencing the water content, which is the object of this chapter.

The degrees of freedom of a natural gas- water two phase system in a state of equilibrium can be determined from the Phase Rule (42):

$$F = C - \Phi + 2 \quad (4-1)$$

where F = degrees of freedom at equilibrium

C = number of components in the system

Φ = number of phases present at equilibrium.

For the system under study $\Phi=2$, which leads to the relation:

$$F = C \quad (4-2)$$

In addition to the system pressure and temperature, for a two component natural gas, composition of the system is the only degree of freedom which must be specified to define that system completely. However, even for a natural gas consisting of several components, the phase rule indicates that temperature, pressure and composition are still the variables to be specified to define that system in equilibrium. Each of these variables is considered separately in the following sections.

A. Effect of System Pressure

Assuming ideal liquid and vapor states, the water content of any gas in equilibrium with liquid water at a given temperature may be written as:

$$\frac{y_w}{x_w} = \frac{p_w^0}{P} \quad (2-10)$$

Considering solubility of the gas in liquid water to be very small ($x_w \approx 1.0$).

$$y_w = \frac{p_w^0}{P} \quad (4-3)$$

But it should be well recognized that in real systems, assumptions made for Equation (2-10) do not hold good.

At this stage, if the system pressure is increased by introducing some gas to the system, keeping the volume and temperature constant, the system will undergo these changes:

- (a) space available for the molecules of water vapor will be reduced, owing to the increase in space occupied by the gas molecules.
- (b) intermolecular attraction between the molecules of water vapor and those of the gas will be increased due to the decrease in the average distance between any two molecules.
- (c) as a result of (b) compressibility factor, Z , of the gas will be affected.
- (d) due to the increase in system pressure, the vapor pressure of water will be increased.
- (e) the solubility of gas in liquid water will be affected.

As a result of these effects the concentration of water in the vapor space increases as reported by Deaton and Frost (17) and McHaffie (47). But at the same time mole fraction of water in the vapor phase decreases as confirmed by all the experimental work done to date. This leads to the conclusion that the increase in the

moles of water in the vapor phase is smaller than the moles of gas introduced to cause that increase in system pressure.

It is impossible to predict theoretically the decrease in mole fraction of water in the vapor phase as a result of all the effects cited above, especially for complex gaseous mixtures containing one or more non-hydrocarbons. However, the problem can be simplified by considering the vapor phase as a pseudo binary with water vapor as one component and the dry gas (consisting of various components) as the other component and introducing fugacities of these two pseudo components as the measure of their "escaping tendencies." To facilitate their determination and easy handling, they are represented as:

$$\frac{f_w^v}{P} = \phi_w \quad (4-4)$$

$$\frac{f_g}{P} = \phi_g \quad (4-5)$$

where subscripts w and g represent the components of the pseudo binary.

From the conclusion reached earlier it is assumed that the water content of the vapor phase in equilibrium with liquid water is a direct function of ϕ_w/ϕ_g .

Changes (a) and (b) mentioned earlier led many investigators to propose numerous equations of state (79) to describe the volumetric behavior of pure gases and as

a means of correlating experimental data. Some of these equations are specific for a particular pure gas in a specified range of pressure and temperature, while others have been generalized by virtue of more and more adjustable parameters. The two distinct approaches followed by those investigators are based on thermodynamic and statistical mechanical treatments.

In statistical mechanics the equation of state is fundamentally related to the law of force between the individual molecules and the experimental data are used to determine empirically the adjustable parameters. The important equations of state have been discussed briefly in Chapter II.

The effect of system pressure on the compressibility factor (an empirical entity proposed to account for the non-ideality of a system), Z , can be vividly observed from the most celebrated equation of state proposed by van der Waals:

$$p = \frac{RT}{V-b} - \frac{a}{V^2} \quad (4-6)$$

where a = intermolecular force correction constant

b = molecular volume correction constant.

From the equation of state for an ideal gas, p_i may be written as:

$$p_i = \frac{RT}{V} \quad (4-7)$$

where p_i = pressure of the same gas if it were in an ideal state.

From equations (4-6) and (4-7), Z for the gas can be defined as:

$$Z = \frac{p}{p_i} = \frac{V}{V-b} - \frac{a}{RTV} \quad (4-8)$$

As p increases and V decreases, Z will at first diminish due to the effect of $\frac{a}{RTV}$ in Equation (4-8). But when V becomes sufficiently small, Z will increase due to $\frac{V}{V-b}$ being the dominating term. Table 4-1 shows this behavior for Nitrogen at 32°F.

From the second column in Table 4-1, Z for Nitrogen begins to increase at some pressure between 50 and 100 atmospheres. Whereas, ϕ_g is minimum somewhere between 150 and 200 atmosphere before it starts to increase. Agreement between Z and ϕ_g is extremely good especially in the low pressure range.

Assuming that the same trend is followed by a multicomponent gaseous phase, its compressibility factor, Z , becomes important and will contribute significantly to its water content, in equilibrium with liquid water. The contribution of changes (d) and (e) to the overall effect on the equilibrium water content, due to the increase in system pressure can be partially accounted for by considering the equilibrium distribution constant for water, K_w , as calculated by Equation (2-14). As pointed out earlier in Equation (3-20), equilibrium water content is a direct function of K_w .

TABLE 4-1
COMPARISON OF Z AND ϕ_g FOR NITROGEN AT 32°F

Pressure (atm)	Z*	ϕ_g^*	% Deviation
1	0.99955	0.99955	0.00
10	0.9957	0.9956	+ 0.01
50	0.9850	0.9812	+ 0.39
100	0.9854	0.9703	+ 1.53
150	1.0030	0.9672	+ 3.56
200	1.0363	0.9721	+ 6.24
400	1.2566	1.0620	+15.49
800	1.7964	1.4950	+11.21
1000	2.0700	1.839	+11.16
$\% \text{ Deviation} = \frac{Z - \phi_g}{Z} \times 100$			

*From Lewis and Randall (42), p. 189.

B. Effect of System Temperature

If the temperature of a gas-water equilibrium system is increased keeping the volume constant, it will undergo these changes:

- (a) there will be an increase in pressure and to bring it back to the initial value, some of the gas will have to be withdrawn from the system which will make more space available for the molecules of water vapor to move around.
- (b) intermolecular forces between the molecules of water and those of the gas will be altered.
- (c) compressibility factor of the gas will be increased.
- (d) vapor pressure of water, being a direct function of the temperature, will be increased appreciably.
- (e) the solubility of the gas in the liquid water will be altered depending upon the range of temperature the system is in and the nature of the gas.

Changes (a) and (d) directly lead to a higher concentration and mole fraction of water in the vapor phase which is the overall effect of increase in system temperature, as confirmed by all available experimental data. In the absence of any adequate theoretical treatment to predict the overall effect from different phenomena cited above, the ratio of "escaping tendencies" of the pseudo binary mixture, $\frac{\phi_w}{\phi_g}$, and the compressibility factor, Z , of the gaseous mixture along with K_w will vary

well account for all of them.

C. Effect of Gas Composition

Of all the factors affecting the equilibrium water content of a gaseous mixture, composition has received the minimum attention. Some investigators have only observed qualitatively the effect of the presence of nitrogen in natural gases (8, 17, 26, 64). Lack of any appreciable quantitative data has considerably boosted the importance of this aspect. Consequently, much attention has been devoted to composition of gaseous mixtures throughout this investigation.

If the gas composition of a gas-water equilibrium system is changed without affecting the pressure, temperature and volume of that system, the following changes are likely to take place:

- (a) intermolecular forces between the molecules of water and those of the gaseous mixture will be altered.
- (b) the compressibility factor, which is a function of critical pressure and temperature of the gaseous mixture, will be affected.
- (c) the solubility of the gas in liquid water will be affected, which in turn will alter the vapor pressure of water.

From time to time different investigators (41, 72, 92) have been successful in correlating the equilibrium water content of binary aqueous systems to the inter- and

intramolecular forces through the Virial equation of State (Equations 3-7, 3-16, 3-17). But for systems having the gaseous phase consisting of more than three components the lack of adequate second virial coefficient data and the adequate mixing rules makes it extremely difficult to attempt such correlations.

However, the ratio of "escaping tendencies," $\frac{\phi_w}{\phi_g}$, along with the compressibility factor, Z , of the gaseous phase, being function of the gas composition, adequately accounts for changes (a) and (b). And consequently the overall effect of gas composition on the equilibrium water content of the vapor phase can well be accounted for by $\frac{\phi_w}{\phi_g}$, Z and K_w .

Of these variables, ϕ_g and Z are functions of critical pressure and critical temperature which account for any change in composition of the gaseous mixture. And the only way one can truly ascertain how good (or bad) these variables can account for the above mentioned changes is by determining how well the critical properties of the mixture represent its microscopic properties.

The general approach to mixtures has been to combine pure component critical properties through some combination rule to arrive at "pseudocritical" properties characteristic of the mixture. These properties are then used in the pure component relationships to predict

ϕ and Z for that mixture. This approach conspicuously disregards the problem of the interaction between the dissimilar molecules in the system. This problem is even more acute in cases where the mixture contains one or more polar components. Consequently it is imperative in the present investigation that the true critical properties be used instead of the pseudocritical properties of the mixture.

In the opinion of the author the method proposed by McLeod (51) is the best to date to determine the true critical properties of a gaseous mixture, and will be discussed in Chapter V.

CHAPTER V

PROPOSED CORRELATION

After establishing that K_w , ϕ_w , ϕ_g and Z can very well account for the change in equilibrium water content of the vapor phase in a two phase gas-water system due to any changes in temperature, pressure and gas composition in Chapter IV, each entity will be considered separately at this stage.

The equilibrium ratio for pure water, K_w , as calculated from Equation (2-14) is a function of system pressure, temperature, critical properties (pressure and temperature) of water and the compressibility of water which, in turn, is a function of the composition of water. Throughout this investigation the solubility of gas in water is assumed to be small which leads to the constant values of the critical properties of water. The effects of system pressure and temperature on K_w are depicted in Figure 5-7. The effect of any impurity dissolved in water will be a decrease in P_w^O which will cause a corresponding decrease in the value of K_w .

The fugacity coefficient of water, ϕ_w , is a function of system pressure and temperature and is independent

of the composition of the system. Figure 5-8 shows its change with pressure and temperature.

The fugacity coefficient, ϕ_g , and the compressibility factor, Z , of the gaseous mixture are functions of system pressure, temperature and critical pressure and critical temperature of the mixture. Any change in the composition will be depicted in the true critical properties which, in turn, will affect both ϕ_g and Z . And their combined effect will adequately represent any change in the force patterns between similar and dissimilar molecules in the mixture. Any change in system pressure will affect ϕ_g and Z similar to the way it affects these characteristics for nitrogen as shown in Table 4-1. An increase in system temperature will cause corresponding increases in ϕ_g and Z .

Because of the higher values of critical pressure and critical temperature for water as compared with those for any component of a gaseous mixture, it can be concluded from Figure 5-2 that for any increase in system pressure the corresponding decrease in ϕ_w will be more than the decrease in ϕ_g , which results in a net decrease in the ratio ϕ_w/ϕ_g . Also any increase in system temperature will result in an increase in the ratio ϕ_w/ϕ_g , though not very appreciable at relatively low pressures.

Behavior of the ratio ϕ_w/ϕ_g with any change in system pressure or temperature is the same as the behavior

of equilibrium water content of the vapor phase of a gas-water system. This confirms the assumption made in Chapter IV and paves the way for a workable correlation.

A. Proposed Correlation

From these considerations the following correlation is suggested for the determination of equilibrium water content of a gaseous mixture of known composition and at specified system pressure, P and temperature, T :

$$y_w = K_w \left(\frac{\phi_w}{\phi_g} \right)^Z \quad (5-1)$$

Utilizing Equations (4-4) and (4-5) the above relation can also be represented as:

$$y_w = K_w \left(\frac{f_w^v}{f_g} \right)^Z \quad (5-2)$$

Both these relations are dimensionally consistent if K_w and y_w are represented as mole fractions.

Different terms in the above relations can be determined as below:

K_w is calculated from equation (2-14):

$$K_w = \frac{P_w^o}{P} \left(\frac{f_w^v P_w^o / P_w^o}{f_w^v / P} \right) \left(\frac{P}{P_w^o} \right)^{Z_{av}} \quad (5-3)$$

where : P_w^o = vapor pressure of pure water at system temperature T , as determined from Figure 5-1.

$$f_w^v P_w^o / P_w^o = \phi_{P_w^o} = \text{fugacity coefficient of water at its}$$

vapor pressure and system temperature, as

determined from Figure 5-2.

$f_w^V/P = \phi_w$ = fugacity coefficient of water at system temperature and pressure, as determined from Figure 5-2.

Z_{av} = average compressibility factor of liquid water at log-mean average pressure, as determined from Figure 5-3.

For determining the fugacity coefficient, ϕ_g and compressibility factor, Z , of a gaseous mixture different methods are available in the literature but the one proposed by McLeod (51) is the most suitable for complex gaseous mixtures containing one or more non-hydrocarbons, e.g., N_2 , CO_2 , H_2S . This method is described here briefly.

B. McLeod's Equation of State

This equation of state makes use of Eykman Molecular Refraction (EMR) as a third parameter and can be functionally represented as:

$$Z = F' (P_R, T_R, EMR) \quad (5-3)$$

This characteristic parameter, EMR, is particularly useful because it recognizes both intermolecular forces and molecular structure of the constituents of the gaseous mixture. The linear relationship between EMR and molecular weight for pure components as well as their mixtures (in a given homogeneous series), the constancy of EMR with change in temperature and pressure,

and the fact that all substances have approximately the same refractive index at the critical points, have enhanced its value as a characteristic parameter in this improved equation of state.

The mixing rule proposed for this equation of state consists mainly in splitting up the gaseous mixture into a pseudo binary. Methane, along with the other non-hydrocarbons (N_2 , CO_2 , H_2S , etc.) formed one group of the binary and the remaining hydrocarbons formed the other. The additive EMR for each group was determined and a critical temperature and pressure of the mixture was determined graphically from Figures 5-4 and 5-5.

Using the critical pressure and temperature determined above, the fugacity coefficient, ϕ_g , of the gaseous mixture is determined from Figure 5-2 and the compressibility factor, Z , from Figure 5-6.

C. Procedure for the Application of the Proposed Correlation

1. Using equation (5-3), calculate K_w for the given pressure, P , and temperature, T . (For values at 100, 130 and 160°F go to Figure 5-7 and read off K_w .)
2. From Figure 5-2, read off value of ϕ_w for the given P and T . (For values at 100, 130, and 160°F go to Figure 5-8 and determine ϕ_w .)
3. Divide the gaseous mixture into two groupings, i.e.

Group 1--Methane, carbon dioxide, hydrogen sulfide,

nitrogen;

Group 2--Ethane plus hydrocarbons.

4. For each grouping in the pseudobinary calculate EMR:

$$EMR_1 = \sum y_i^* (EMR)_i$$

$$EMR_2 = \sum y_i^* (EMR)_i$$

5. With $(EMR)_1$ obtain $(T_c/P_c)_1$ for group 1 from curve 1 in Figure 5-4 and with $(EMR)_2$ obtain $(T_c/P_c)_2$ for group 2 from curve 2 in Figure 5-4.

$$\frac{T_c}{P_c} = (y_i)(T_c/P_c)_1 + (y_j)(T_c/P_c)_2$$

6. Obtain $(EMR)_{mix}$. This can be obtained by two methods:

(a) Before step 3

$$(EMR)_{mix} = \sum_{i=1}^n y_i (EMR)_i$$

(b) After step 3

$$(EMR)_{mix} = y_i (EMR_1) + y_j (EMR_2)$$

7. With a value of $(EMR)_{mix}$ go to Figure 5-5 and read off T_c/P_c
8. With values for T_c/P_c and $T_c/\sqrt{P_c}$ solve for P_c and T_c .
9. $P_R = \frac{P}{P_c}$
- $T_R = \frac{T}{T_c}$

10. From Figure 5-2 read off value of ϕ_g using values of P_R and T_R obtained in step 9.
11. From Figure 5-6 read off values of Z for P_R and T_R obtained in step 9.
12. To obtain Y_w , substitute values of K_w , ϕ_w , ϕ_g , and Z , as obtained above, in Equation 5-1.

To check the range of applicability of this correlation, experimental work was done during the course of this work. Methane, being the main component of all natural gases, was also taken as the main component of all gaseous mixtures tested experimentally for determination of their equilibrium water content. The experimental procedure and set-up are described in Chapter VI and the compositions of all gaseous mixtures are reported in Appendix D.

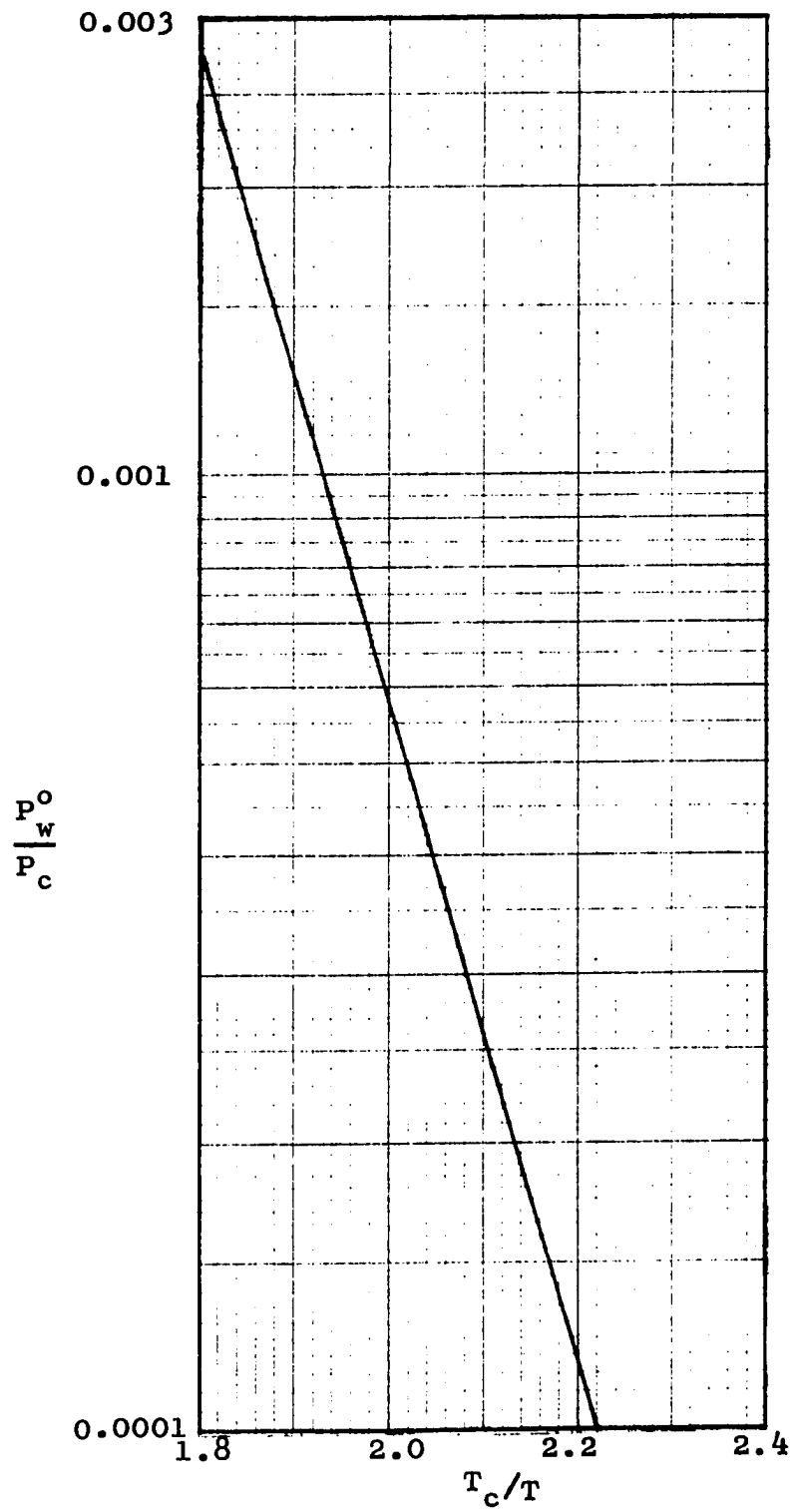


FIGURE 5-1. REDUCED VAPOR PRESSURE OF WATER

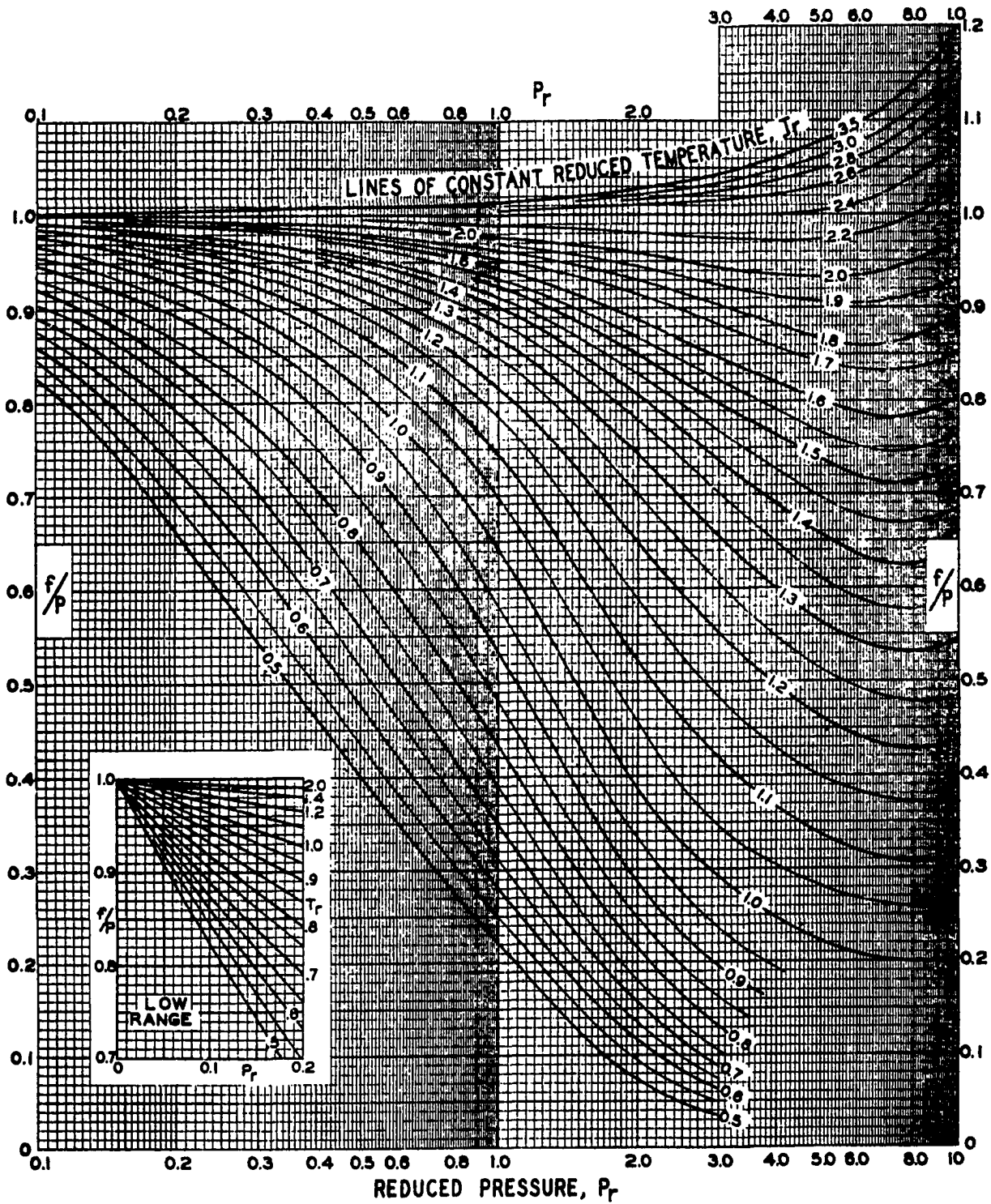


FIGURE 5-2. GENERALIZED FUGACITY COEFFICIENT FOR VAPORS

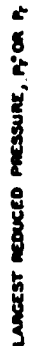


FIGURE 5-3. EXPONENT FOR PRESSURE CORRECTION
TO THE LIQUID FUGACITY OF WATER

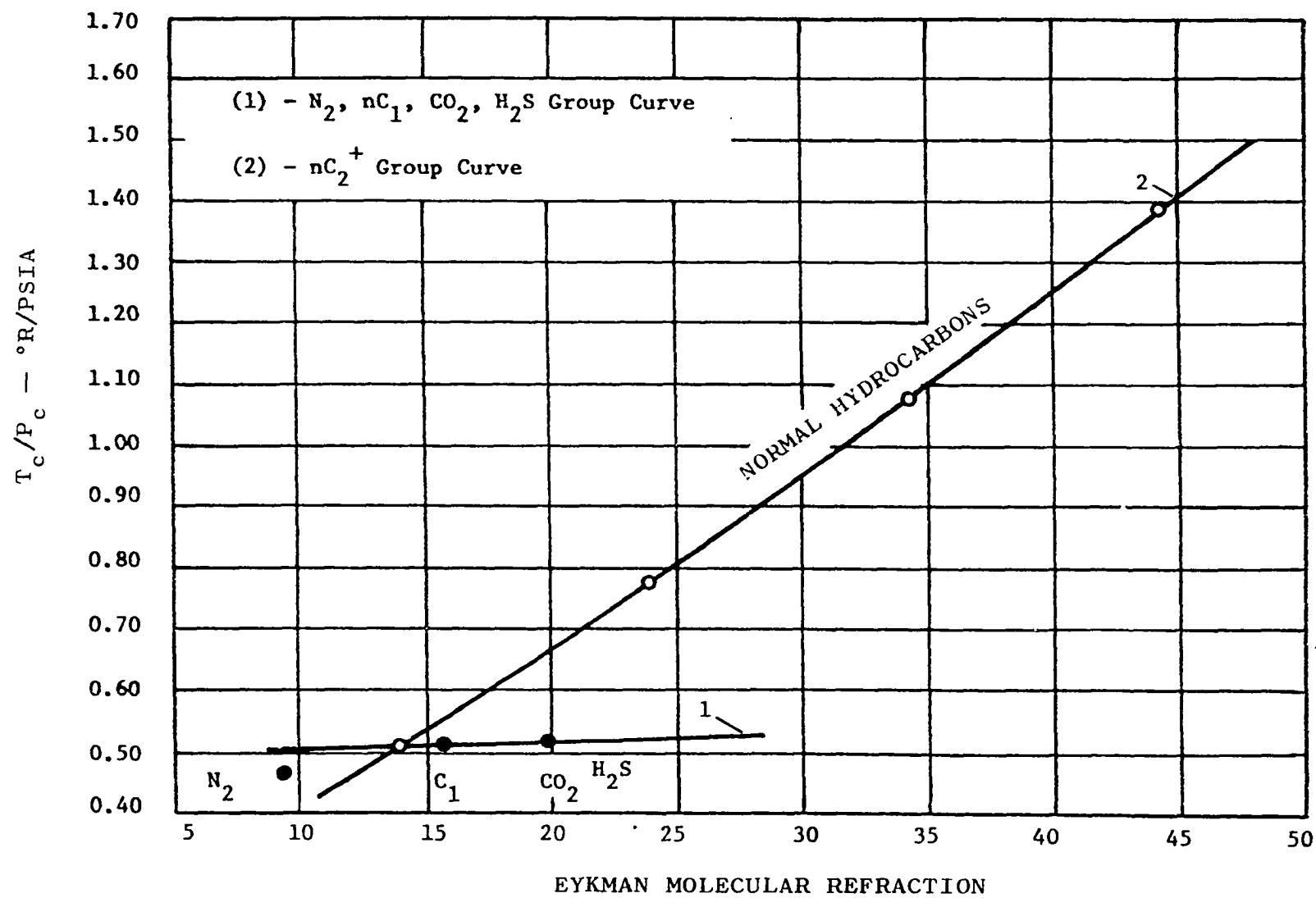


FIGURE 5-4. CORRELATION OF T_c/P_c AND EMR

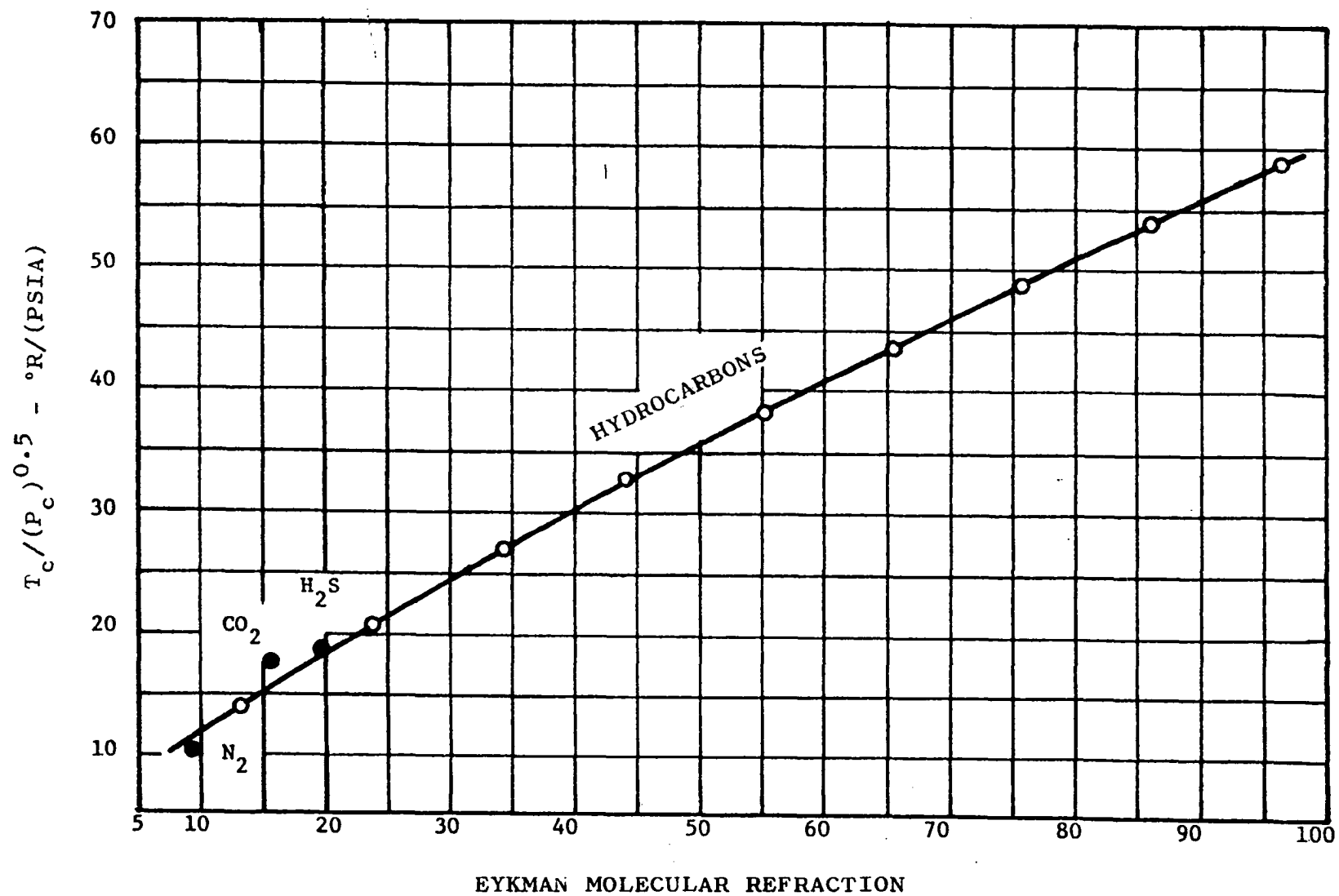


FIGURE 5-5. CORRELATION OF $T_c/(P_c)^{0.5}$ AND EMR

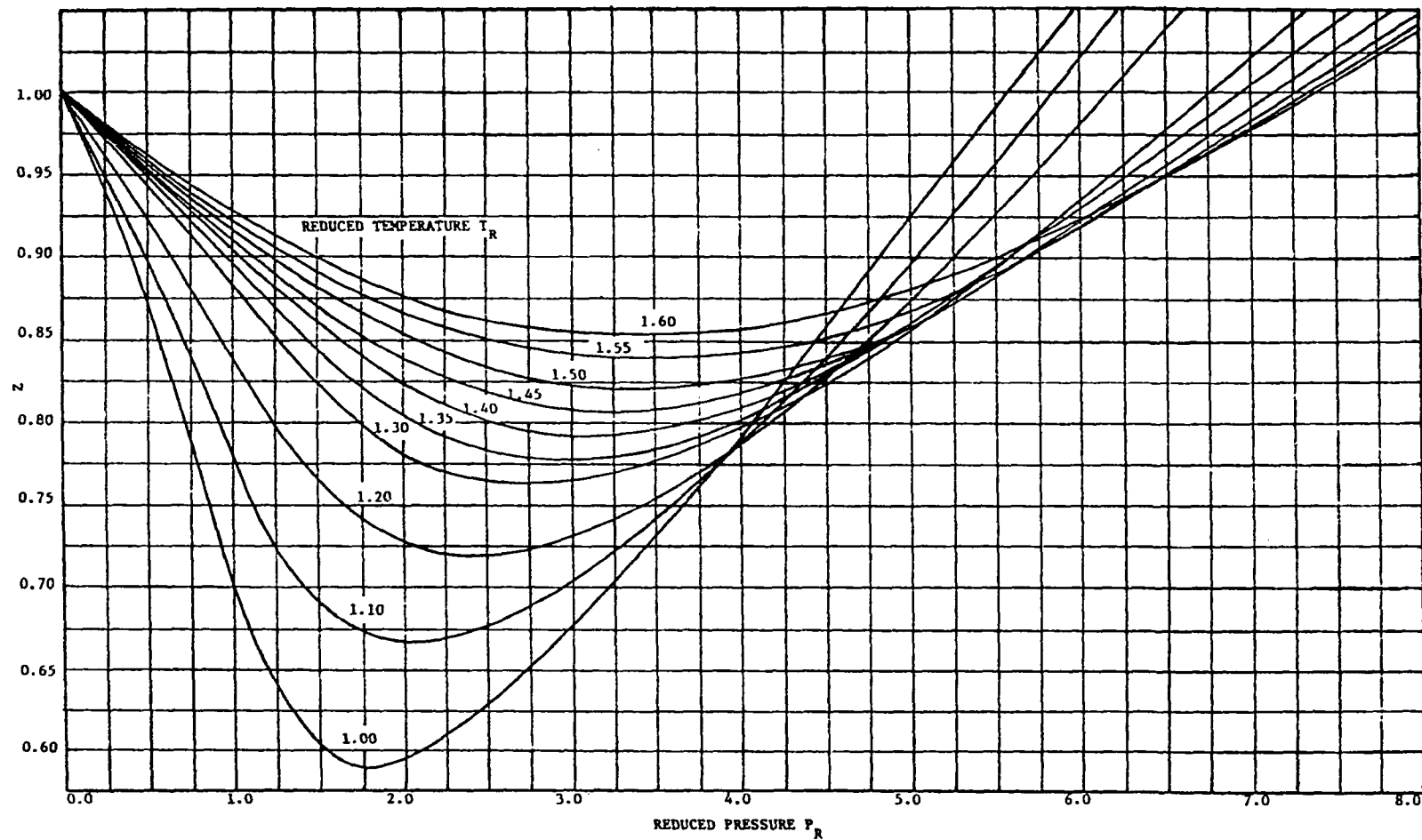


FIGURE 5-6. GENERALIZED COMPRESSIBILITY FACTOR Z AT REDUCED TEMPERATURES AND PRESSURES

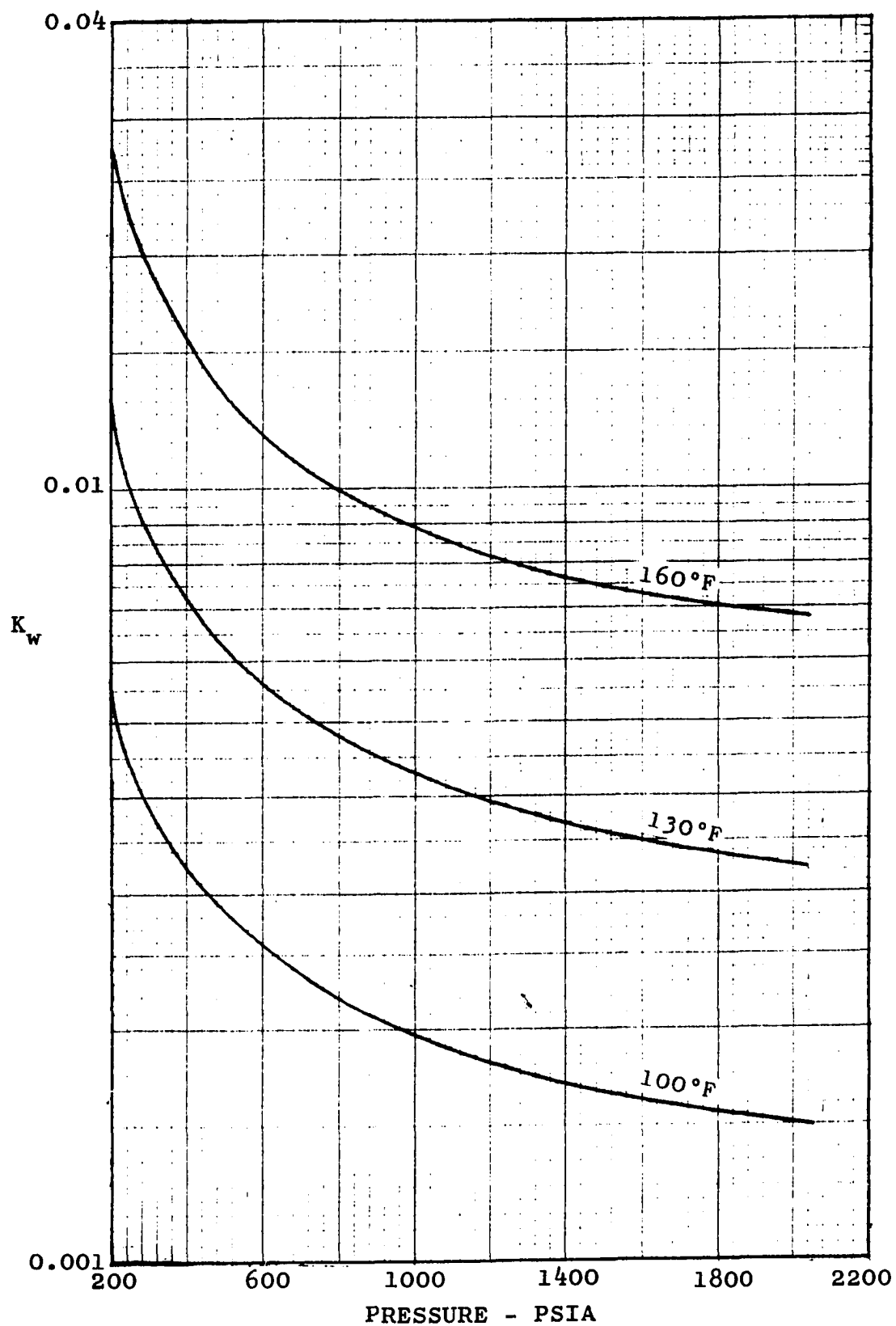


FIGURE 5-7. EQUILIBRIUM RATIO FOR WATER

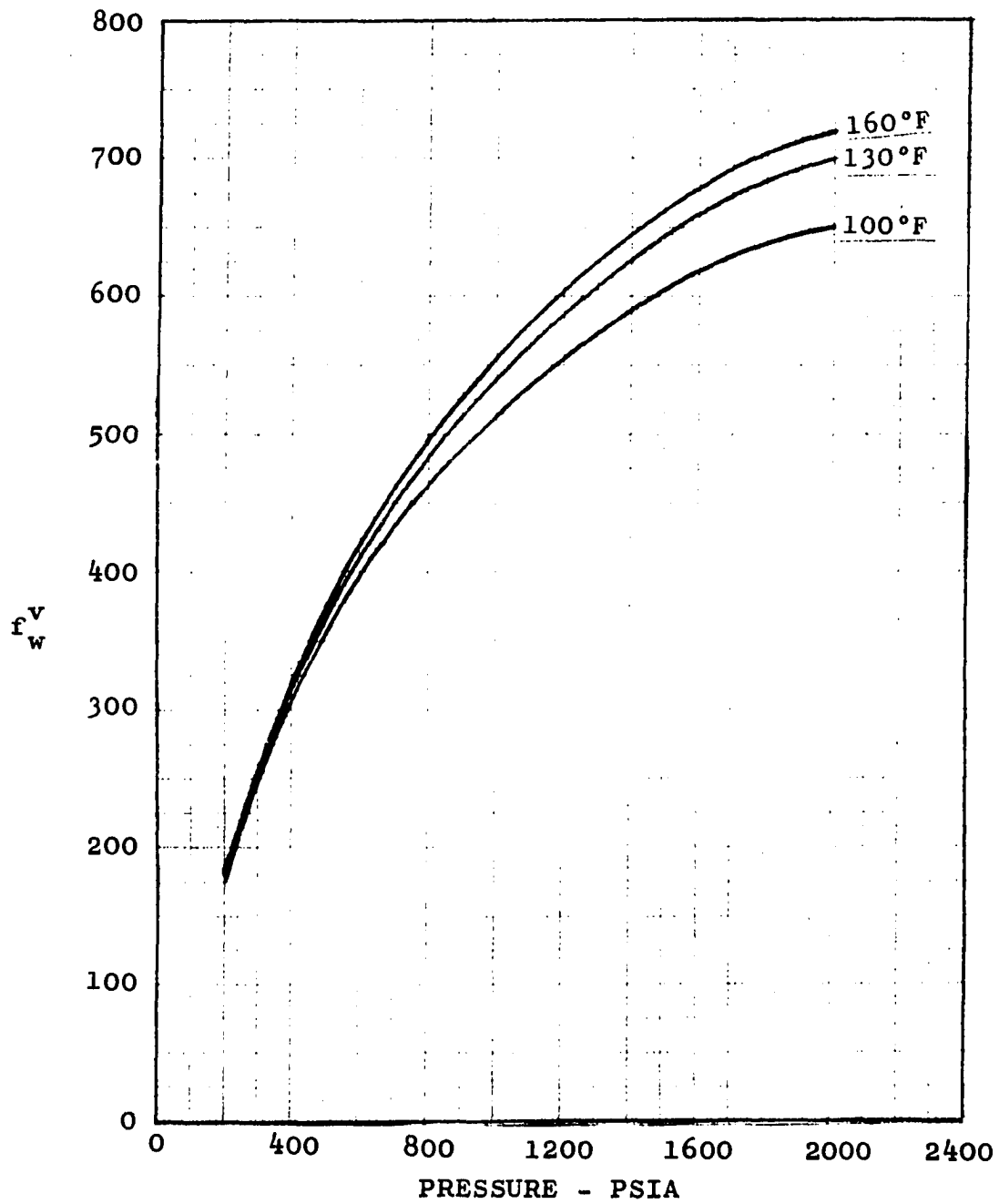


FIGURE 5-8. FUGACITY OF WATER

CHAPTER VI

EXPERIMENTAL INVESTIGATIONS

While the literature provides enough experimental data on the equilibrium water content of pure gases (hydrocarbons and non-hydrocarbons) and natural gases, the data available for binary hydrocarbon mixtures are meager. And no such data are available for binary or ternary gaseous mixtures of hydrocarbons and non-hydrocarbons.

The experimental phase of this study consisted in providing equilibrium water content data of binaries of methane and each of ethane, nitrogen, carbon dioxide and hydrogen sulfide. Equilibrium water contents of eight selected gaseous mixtures were determined at nominal temperatures of 100, 130 and 160°F and at pressures ranging from 200 to 2,070 psig.

A close examination of the various methods available for the determination of equilibrium water content of gases (1, 8, 71) revealed the gravimetric method to be the most suitable for the present work. This method consists in removing water from the saturated gas by passing it through anhydrous magnesium perchlorate and measuring the

effluent gas by a wet test meter. The increase in the weight of the adsorbent represents the amount of water present in the amount of gas measured by the gas meter.

The reliability of the equipment and experimental procedure selected was established by obtaining data for pure methane and comparing the measured values with those published in the literature (55). The accuracy of the experimental data was sufficient for the purpose of this investigation.

A. Materials Used

The gases used for this study were pure methane, ethane, nitrogen, carbon dioxide, hydrogen sulfide and helium. Methane, supplied by Phillips Petroleum Company, was of pure grade and a quoted minimum purity of 99 mole per cent. Ethane, obtained from the same company, was also of pure grade and had the quoted minimum purity of 99 mole per cent. The extra dry grade of nitrogen was supplied by Matheson Company and had a minimum purity of 99.7 mole per cent. Carbon dioxide, obtained from the same source, was bone dry grade with a minimum purity of 99.8 mole per cent. The technical grade hydrogen sulfide with minimum purity of 98.5 mole per cent was also obtained from Matheson Company. Helium, used as carrier gas in the chromatograph, was of grade A supplied by the U.S. Bureau of Mines.

The anhydrous magnesium perchlorate used was C. P. Grade supplied by J. T. Baker Chemical Company under the trade name "Anhydrone." Ordinary laboratory distilled water was used as the liquid phase throughout this investigation.

B. Experimental Equipment

The experimental equipment used in obtaining the equilibrium water content data consisted of a high pressure cell enclosed in an insulated air bath, a mixing cell, 250 cc Ruska mercury pump with a Heise pressure gauge, Beckman GC-2 gas chromatograph, Magnesium perchlorate filled glass tubes, a wet test meter, a vacuum pump and other necessary accessories. Figure 6-1 shows the schematic diagram of the experimental set-up.

1. High Pressure Cells

Two stainless steel high pressure cells supplied by Ruska Instrument Corporation were used. One of the cells was windowed with a capacity of 650 cc and was used as the mixing cell to prepare the required gaseous mixtures. The other cell was a blind one with a capacity of 550 cc and was used as the equilibrium cell inside the constant temperature air-bath. Both these cells were provided with stands on which they could be rocked. And both of them had pressure rating of 12,000 psig at 350°F.

2. Constant Temperature Bath

The blind cell was kept in a 3'x3'x2' constant temperature air-bath. Insulated with one inch insulation board and a double layer of aluminum foil, the plywood box could stand temperature of 200°F and had a double layer of safety glass with an insulating air space between to provide visual access to the equilibrium cell. Constant temperature was maintained by a thermostat with a 150 watt light bulb serving as a heat source. For attaining and maintaining comparatively higher temperatures (higher than 130°F) a heating element and another 200 watt bulb were also provided. A small fan was used to keep the temperature uniform throughout the air-bath. The temperature in this bath could be controlled within $\pm 1^\circ\text{F}$. To check the temperature of the bath at all times, two mercury expansion thermometers were used, one near the back-wall of the bath and the other one was kept next to the glass window inside the air bath.

3. Mercury Pump and Pressure Gauge

Pressure and volume control of the system was achieved by the hand-operated Ruska mercury pump. It was designed for a maximum pressure of 10,000 psig and had the maximum working displacement of 250 cc. It was calibrated to read 0.01 cc.

This pump was connected to a 10,000 psig Heise

gauge which was calibrated in increments of 10 psi. This gauge was checked with a dead weight tester provided with a diaphragm differential pressure indicator and after the dial of the gauge was adjusted, no error was detected in its scale readings from those of the tester.

4. Wet Test Meter

"Precision" wet test meter made by Precision Scientific Company was used to measure the gas volumes. It was calibrated to read 0.001 cubic foot and had a quoted accuracy of 0.5 per cent under normal operating conditions. It was checked against a graduated aspirator and was found to be accurate within one per cent.

5. Gas Chromatograph

The analyses of the gas samples from the mixing cell were performed on a Beckman GC-2 gas chromatograph equipped with a thermal conductivity detector cell. Power for this unit was supplied by a Sola constant voltage transformer. The signal generated by the chromatograph was recorded on a Bristol Potentiometric strip-chart recorder. The column used for this work was a twelve-foot, stainless steel, silicone column with a 1/4 inch diameter. It was packed with 42-60 mesh crushed C-22 Johns-Manville firebrick, coated with Dow-Corning Silicone fluid, type 550. This kind of silicone column can be used for experimental temperatures as high as 300°F.

6. Accessories

All Swagelok 1/8-inch valves, fittings and tubing were made of high pressure 316 stainless steel capable of withstanding pressures up to 20,000 psig. In addition to the above equipment mercury-in-glass thermometers, Cenco-Megavac vacuum pump, analytical chainomatic balance, graduated cylinder and other accessories were used during the course of this experimental work.

C. Experimental Procedure

The whole sequence of the procedure consisted of a preliminary checking and preparing of the equipment, making and analyzing the gas mixtures and determining the water content of that mixture.

1. Preliminary Preparations

After the apparatus was assembled, it was necessary to make a few adjustments before the equipment was ready for use. Prior to and during each run visual checks were made to be sure the system was absolutely leakproof. Before some runs checks were made by establishing the ability of the system to hold vacuum for several hours.

After completing the installation procedures for the chromatograph it was put into operation strictly according to the procedure outlined in Section 4 of the Instruction Manual for GC-2 Gas Chromatograph. A warm-up period of 24 hours was allowed before the first gas sample

was analyzed. A few tests were made with pure gases and standard mixtures to establish the following operating conditions:

Carrier Gas (Helium)	15 psi
Katharometer Current	250 ma
Katharometer Temperature	40°C
Column Temperature	40°C
Sample Size	1.5 cc

These temperatures were measured potentiometrically using an iron-constantan thermocouple and were never found to vary by more than $\pm 0.1^\circ\text{C}$.

During the course of this investigation the chromatograph was not used continuously but it was found advantageous to leave the power turned on by keeping the chromatograph switch set to "on." This kept the detector and the column constantly at 40°C , the temperature selected for the present work. This also kept certain detector circuits in ready condition without actually supplying current to the detector filament. It was also found expedient to leave a small amount of helium (5 psi) passing through the chromatograph at all times. This prevented moist air from entering the sensitive detector cell and column therefore eliminating a 3 to 4 hours reconditioning period needed to restore normal column behavior. With this the time required from the time of setting the operating

conditions detailed earlier until the instrument was ready for use was about thirty minutes. For the recorder a warm-up period of about 4 hours was allowed before it was ready for operation.

2. Preparation and Analysis of Mixture

A mixture was prepared by introducing gases into the mixing cell evacuated for several hours. The component having the lower vapor pressure was introduced first to a predetermined mixing pressure. This pressure could also be arbitrarily fixed to obtain the final mixture within certain pressure range. A sample calculation for the final mixing pressure is presented in Table E-2 in the Appendix. After the mixture was prepared, it was agitated by injecting and withdrawing some mercury from the cell a couple of times. Then it was allowed to stand for 24 hours. During this time, the cell was rocked occasionally. At the end of this period a sample of the mixture was analyzed in the chromatograph. Eight different mixtures were prepared and analyzed and their results are presented in Table D-1 in the Appendix.

In order to be able to use the results of a chromatographic analysis to determine the composition of an unknown mixture, the chromatograph had to be calibrated after establishing some relation between the area or peak height and the percentage of the component it represented.

Because of the relatively high pressure gases involved in the present work, the method used in this work was based on the assumption that the detector response, as characterized by the peak height, for each of the components analyzed was a linear function of the amount of that component in the sample.

Before each analysis a standard sample, consisting of light hydrocarbons, was run through the chromatograph and component peaks were determined. For components not included in the standard sample, peaks for pure gases were determined. Then the actual sample was run and the component peaks were determined. These peaks could then be used to read the per cent composition from the calibration readings. This procedure eliminated the need to reproduce analytical conditions exactly from run to run.

3. Measurement of Water Content

While allowing the gaseous mixture to mix in the Mixing cell for 24 hours, the Equilibrium cell was evacuated through valve 4, keeping valves 1, 2, 7, 9 and 10 closed, for several hours. When the mixture was ready a small stream of gas was passed through the system to purge it of any foreign vapors. Pressure was allowed to come to atmospheric conditions in the Equilibrium cell, keeping the mixing cell at the desired pressure and the remainder of the system filled with the gaseous mixture at atmospheric

pressure. By closing valve 6 and opening valve 10, 20 cc of distilled water were injected into the cell by gravity feed. 50 cc of distilled water were introduced in case of gaseous mixture with hydrogen sulfide as one of the components. Valves 2 and 6 were opened to fill the system with the gaseous mixture and the maximum amount of the mixture was transferred to the Equilibrium cell by injecting mercury into the Mixing cell. All valves were closed. The pressure in the Equilibrium cell was raised to about 2000 psig by injecting some mercury through valves 8 and 9. In the meantime the temperature of the air-bath was raised to the required temperature and set at about 2 degrees above the system temperature. The cell was rocked manually with the help of a steel tubing tied to its bottom and passing through the front wall of the air-bath. The rocking motion was given for about two hours and after that it was repeated for ten minutes after every two hours. The inside cell temperature was checked potentiometrically by an iron-constantan thermocouple inserted from its top. After 24 hours the temperature and pressure inside the cell were constant. Maximum variation in temperature was never more than 0.5°F.

In the meantime the gas mixture trapped between valves 2 and 6 was used for the chromatographic analysis by using valve 4 as the inlet for the chromatograph gas sampling valve.

To minimize weighing error, two one inch pieces of 1/8-inch pyrex glass tubing were used as the absorption tubes. After cleaning these tubes they were filled with anhydrous magnesium perchlorate and supported on both ends with glass wool. From valve 4, the gas mixture was passed through these tubes for 5 minutes to replace air in the dessicant with gas. Then they were weighed on an analytical balance and were connected between valve 11 and the wet test meter. All connections between tubings were secured with short sections of tygon tubing. Before this, however, the tube section between valves 7 and 11 had been evacuated for about an hour and the gas meter had been checked for water and horizontal level. The steel tubing section before the weighing tubes, along with valve 11, was kept at a temperature of about 180°F by constant heating with a heating tape in order to prevent any condensation of water vapor in this section.

Valve 7 was then slowly opened. Next the throttling valve 11 in the sampling line was gradually opened, allowing the gas to flow from the cell to the weighing tubes and on to the gas meter. And the injection of mercury into the Equilibrium cell was immediately begun, keeping the pressure in the cell constant. When the desired quantity of gas was withdrawn from the cell valves 11 and 7 were closed. The weighing tubes were disconnected. Short pieces of tygon tubing were secured to both free ends and plugged

with small pieces of glass rod, which acted as glass stoppers. After about ten minutes the tubes were weighed with a minimum of handling and the increases in weights of both tubes were recorded. The runs were rejected in cases where the increase in weight of second tube was more than 5% of the increase in weight of the first tube. Total increase in weight of both tubes was taken as the amount of water absorbed from the amount of gas recorded on the gas meter at temperature and pressure as shown by the thermometer and the manometer respectively.

The pressure in the Equilibrium cell was reduced to the next system pressure keeping the temperature constant. The cell was rocked for fifteen minutes every hour for three hours which was the time found sufficient for the system to achieve equilibrium conditions. Once again the whole procedure was repeated and the amount of water absorbed from a known volume of gas was recorded.

To adsorb a minimum amount of 20 milligrams of water it was found necessary to pass 0.4 cubic foot of the gas. The gas was passed at a rate of about 2 cubic feet per hour. And each run took between 10 and 20 minutes.

The calculation of equilibrium water content from the measured data has been presented in Table E-3 in the Appendix.

D. Accuracy of the Experimental Method

As mentioned earlier in this chapter the reliability of the equipment and the procedure selected was established by obtaining data for pure methane and comparing the measured values with those published by Olds, et al (55). The comparison at nominal temperatures of 100, 130 and 160°F and up to a pressure of 2070 psig is presented in Table 7-1. An excellent agreement between the data of these two different sources and the consistency of the values of the present work are obvious. No special trend of deviations is visible from this comparison.

The deviation of the experimental values from the published values may be a combined contribution of various factors. High degree of purity of methane (99.9 mole per cent) used by Olds et al could account for some deviation. The discrepancy between the actual system pressure and the gauge pressure, due to the compressibility of the varying amounts of mercury could be a source of error. The change in room temperature and pressure could contribute to the deviation. These effects were, though, minimized because of the short time (10 to 20 minutes) required for each run. Some error could be introduced by a small change in composition because each gaseous mixture is prepared more than once. In no case was there a difference in composition of any component by more than 0.2 per cent.

The most important sources of error were, however, the uncertainty in measuring effluent gas and weighing drying tubes. As mentioned earlier, the uncertainty due to gas measurement was not more than one per cent in any case. Whereas, in the majority of the runs the possible error due to uncertainty in the weighings was one per cent or less. Numerous tests with the analytical balance used depicted an uncertainty of ± 0.2 milligram. And since the smallest amount of water adsorbed was 20 milligrams in any run, the largest possible error was 2 per cent.

Due to all these factors the maximum possible error in the experimental values could not have been more than 3.5 per cent, which leads to the conclusion that the experimental equipment and procedure were reliable and accurate enough for the present work.

After establishing the reliability of this procedure equilibrium water content of eight different binary mixtures were determined. The results of these determinations will be presented in the next chapter along with the results for pure methane.

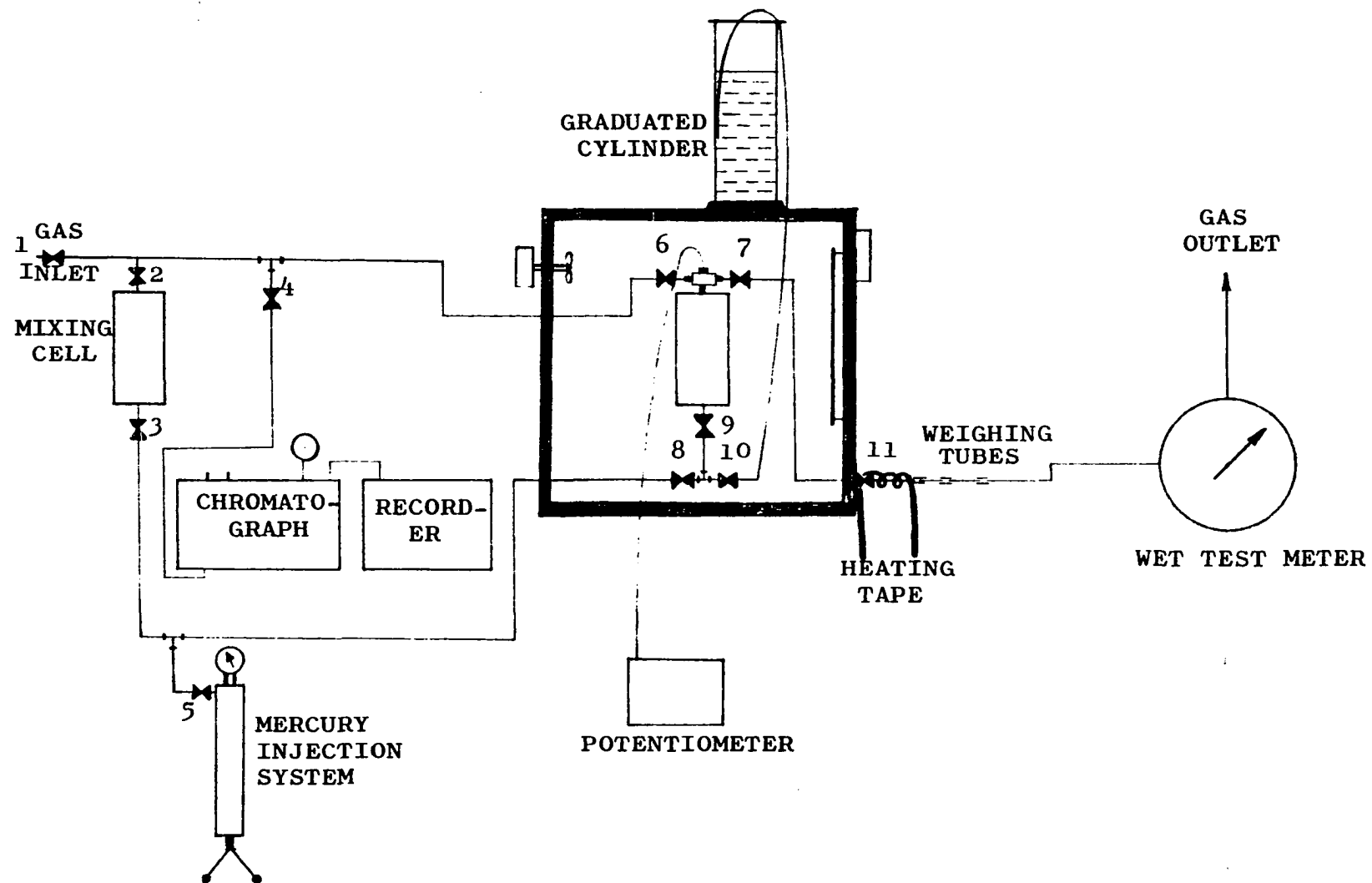


FIGURE 6-1. SCHEMATIC DIAGRAM OF EXPERIMENTAL EQUIPMENT

CHAPTER VII

RESULTS AND DISCUSSION

During the experimental phase of this study only vapor phase equilibrium water contents of different systems were determined. All determinations were conducted at nominal temperatures of 100, 130 and 160°F and over a pressure range of 200-2070 pounds per square inch gauge. The data obtained are presented in both tabular and graphical forms throughout this chapter. Chromatographic analyses of different systems (Mixtures 1 to 8) studied experimentally are presented in Appendix D, along with the analyses of other systems as reported in literature. The range of compositions for these gaseous mixtures was selected keeping in mind the compositions of natural gases normally encountered in the gas industry.

The results of different systems are discussed in the following sections:

A. Methane-Water System

To establish the applicability of the proposed experimental set-up to the present investigation, equilibrium water content of pure methane was determined at

nominal temperatures of 100, 130 and 160°F and pressures ranging from 200 to 2070 pounds per square inch in Table 7-1 and illustrated in Figure 7-1. Agreement between these results and the data available in literature was found to be excellent.

The experimental data are then compared with the calculated equilibrium water contents of methane using the proposed correlation and the results are presented in Table 7-2. The average calculated water content is 2 to 5% less than the experimental value in the pressure and temperature range of investigation. The calculated values used were taken from the smoothed calculated curves in Figure 7-1.

Figure 7-1 also depicts an excellent agreement between the calculated and the reported water content data for methane at 220°F, which is beyond the range of temperature selected for this investigation.

The small average absolute errors at different temperatures of comparison are a good indication of the validity of different assumptions made in Chapter IV and warrant further investigation in the case of mixtures of hydrocarbons and non-hydrocarbons with methane.

As reported in Appendix F (Table F-1) the agreement between ϕ_g and Z for methane is excellent (deviation less than 3%).

TABLE 7-1

EQUILIBRIUM WATER CONTENT OF METHANE

Temperature (°F)	Pressure (PSIA)	Experimental (Mole fraction)	Literature Smoothed (55) (Mole fraction)	Experimental % Deviation
100	214.19	0.005160	0.005050	+2.18
	614.20	0.001882	0.001900	-0.95
	1014.14	0.001341	0.001250	+7.28
	1514.12	0.000919	0.000940	-2.23
	2014.10	0.000754	0.000762	-1.05
Average Deviation				2.74%
130	214.04	0.01130	0.01180	-4.24
	614.10	0.00430	0.00460	-6.93
	1014.10	0.00279	0.00276	+1.09
	1514.10	0.00193	0.00205	-5.85
	2084.17	0.00171	0.00162	+5.61
Average Deviation				4.75%
160	214.05	0.02565	0.02600	-1.35
	614.14	0.00933	0.00910	+2.52
	1014.14	0.00550	0.00580	-5.17
	1514.12	0.00425	0.00425	0.00
	2014.14	0.00368	0.00340	+8.23
Average Deviation				3.45%

TABLE 7-2

EQUILIBRIUM WATER CONTENT OF METHANE

Temperature (°F)	Pressure (PSIA)	Experimental (Mole fraction)	Calculated (Mole fraction)	% Error
100	214.19	0.005160	0.004630	+10.28
	614.20	0.001882	0.001890	- 0.43
	1014.14	0.001341	0.001280	+ 4.55
	1514.12	0.000919	0.000952	- 3.59
	2014.10	0.000754	0.000772	- 2.39
Average Error				+ 1.68%
Average Absolute Error				4.25%
130	214.04	0.01130	0.01070	+ 5.31
	614.10	0.00430	0.00413	+ 3.95
	1014.10	0.00279	0.00272	+ 2.51
	1514.10	0.00193	0.00205	- 6.22
	2084.17	0.00171	0.00165	+ 3.51
Average Error				+ 1.81%
Average Absolute Error				4.30%
160	214.05	0.02565	0.02300	+10.32
	614.14	0.00933	0.00860	+ 7.83
	1014.14	0.00550	0.00560	- 1.82
	1514.12	0.00425	0.00418	+ 1.65
	2014.14	0.00368	0.00345	+ 6.25
Average Error				+ 4.85%
Average Absolute Error				5.57%

B. Methane-Ethane-Water System

Equilibrium water content data for methane-ethane mixtures containing 8.27 and 15.96 mole per cent ethane are presented in Figures 7-2 and 7-3 respectively. Tables 7-3 and 7-4 present comparison between the experimental and the calculated water content data for the same mixtures.

At relatively low pressures the calculated values are lower than the experimental values but after some point between 1000 and 1500 pounds per square inch pressure the trend is reversed and the per cent error increases with pressure. With the present data it cannot be ascertained whether the present trend will continue in the higher pressure range. But the higher average absolute error and rather poor agreement between ϕ_g and Z for the mixtures (Table F-2) warrant a look at these properties for ethane-water system.

Tables 7-15 and F-10 for ethane-water system show the same trend. Deviation between ϕ_g and Z also follows the same trend reaching a maximum of 54.5 per cent at 100°F and 2000 pounds per square inch absolute. This is in contradiction with the assumption made in Chapter IV and may be responsible for a higher error in the case of methane-ethane-water system. Hence, while dealing with gaseous mixtures containing large amounts of ethane this anomaly should not be overlooked.

TABLE 7-3

EQUILIBRIUM WATER CONTENT OF MIXTURE 1

Temperature (°F)	Pressure (PSIA)	Experimental (Mole fraction)	Calculated (Mole fraction)	% Error
100	214.14	0.005200	0.004700	+ 9.62
	614.14	0.001892	0.001850	+ 2.22
	1014.19	0.001320	0.001270	+ 3.79
	1514.14	0.000924	0.000950	- 2.82
	2014.19	0.000753	0.000805	- 6.91
Average Error				+ 1.18%
Average Absolute Error				5.07%
130	214.14	0.012500	0.010800	+13.60
	614.19	0.004510	0.004180	+ 7.32
	1014.20	0.002805	0.002790	+ 0.54
	1514.12	0.002225	0.002090	+ 6.06
	2014.12	0.001720	0.001720	0.00
Average Error				+ 5.504%
Average Absolute Error				5.504%
160	214.14	0.02565	0.02330	+ 9.15
	614.14	0.00919	0.00875	+ 4.79
	1014.14	0.00566	0.00575	- 1.59
	1514.14	0.00415	0.00425	- 2.41
	2054.14	0.00338	0.00349	- 3.25
Average Error				+ 1.34%
Average Absolute Error				4.24%

TABLE 7-4

EQUILIBRIUM WATER CONTENT OF MIXTURE 2

Temperature (°F)	Pressure (PSIA)	Experimental (Mole fraction)	Calculated (Mole fraction)	% Error
100	214.14	0.005210	0.004750	+ 8.81
	614.12	0.001859	0.001900	- 2.21
	1014.07	0.001330	0.001300	+ 2.26
	1514.09	0.000912	0.000995	- 9.10
	2014.05	0.000740	0.000850	-14.87
Average Error				- 3.02%
Average Absolute Error				7.45%
130	214.09	0.012400	0.01080	+12.90
	614.12	0.004400	0.00413	+ 6.14
	1014.14	0.002795	0.00279	+ 0.18
	1514.20	0.002230	0.00211	+ 5.38
	2014.14	0.001711	0.00178	- 4.03
Average Error				+ 4.114%
Average Absolute Error				5.726%
160	214.10	0.02505	0.02300	+ 8.17
	614.10	0.00907	0.00880	+ 2.98
	1014.11	0.00569	0.00575	- 1.05
	1514.10	0.00417	0.00433	- 3.84
	2014.10	0.00358	0.00360	- 0.56
Average Error				+ 1.14%
Average Absolute Error				3.32%

Experimental determinations, however, show that less than 20 mole per cent ethane in a mixture of methane and ethane does not affect the equilibrium water content of methane to any appreciable extent and there is no visible trend to support any other conclusions. Data reported in literature (91) for methane-ethane mixtures containing up to 50 mole per cent ethane confirm this observation.

C. Methane-Nitrogen-Water System

Figures 7-4 and 7-5 depict the experimental equilibrium water content data for methane-nitrogen mixtures containing 8.55 mole per cent (Mixture 3) and 18.86 mole per cent (Mixture 4) nitrogen respectively. A comparison of experimental data with those obtained by using the proposed correlation is presented in Tables 7-5 and 7-6. That nitrogen lowers the water content of natural gases was qualitatively observed by earlier investigators (8, 17, 26, 64) and is confirmed by the present data.

For Mixture 3, the average absolute error lies between 2.99 and 3.72 per cent in the temperature range considered. Whereas, Table F-4 (Appendix F) shows that the addition of nitrogen has caused an average decrease of about 4.3 per cent in the calculated water content of methane at 2000 pounds per square inch pressure and does

TABLE 7-5

EQUILIBRIUM WATER CONTENT OF MIXTURE 3

Temperature (°F)	Pressure (PSIA)	Experimental (Mole fraction)	Calculated (Mole fraction)	% Error
100	214.02	0.004650	0.00450	+ 3.23
	614.02	0.001820	0.00181	+ 0.55
	1014.02	0.001310	0.00122	+ 6.87
	1514.01	0.000915	0.00900	+ 1.64
	1924.01	0.000717	0.00750	- 4.60
Average Error				+ 1.54%
Average Absolute Error				3.38%
130	214.13	0.01028	0.01040	- 1.17
	614.12	0.00425	0.00408	+ 4.00
	1014.12	0.002495	0.00269	- 7.80
	1514.12	0.00197	0.00195	+ 1.02
	2034.12	0.00148	0.00155	- 4.73
Average Error				- 1.74%
Average Absolute Error				3.72%
160	214.10	0.02155	0.02300	- 6.73
	614.09	0.00882	0.00865	+ 1.93
	1014.13	0.00541	0.00560	- 3.51
	1514.13	0.00397	0.00408	- 2.77
	2064.13	0.00326	0.00326	0.00
Average Error				- 2.22%
Average Absolute Error				2.99%

TABLE 7-6

EQUILIBRIUM WATER CONTENT OF MIXTURE 4

Temperature (°F)	Pressure (PSIA)	Experimental (Mole fraction)	Calculated (Mole fraction)	% Error
100	214.05	0.00442	0.00448	- 1.36
	614.07	0.001831	0.00181	+ 1.15
	1014.21	0.001230	0.00122	+ 0.81
	1514.19	0.000848	0.000895	- 5.55
	2014.13	0.000710	0.000722	- 1.69
Average Error				- 1.33%
Average Absolute Error				2.11%
130	214.13	0.00969	0.01040	- 7.34
	614.19	0.00392	0.00406	- 3.57
	1014.10	0.00252	0.00267	- 5.95
	1514.12	0.00184	0.00192	- 4.35
	2014.17	0.00161	0.00155	+ 4.10
Average Error				- 3.42%
Average Absolute Error				5.06%
160	214.18	0.02097	0.02230	- 6.34
	614.18	0.00826	0.00860	- 4.11
	1014.18	0.00545	0.00560	- 2.75
	1514.18	0.00363	0.00400	-10.20
	1994.09	0.00305	0.00320	- 4.92
Average Error				- 5.66%
Average Absolute Error				5.66%

not seem to be affected appreciably with system temperature. This decrease in calculated water content of methane increases with pressure and is the maximum (4.3 per cent) at 2000 pounds per square inch absolute.

For Mixture 4, the average error points to the trend that calculated values of equilibrium water content are higher than the experimental values by 1.33 to 5.66 per cent as the temperature is increased from 100 to 160°F. But the absence of such trend in the case of Mixture 3 prevents from reaching any valid conclusion. The decrease in the calculated water content of methane caused by the presence of nitrogen increases with system pressure but is virtually unaffected by the system temperature in the range of this investigation. The average decrease at 2000 pounds per square inch absolute is 6.4 per cent which leads to the conclusion that the decrease in water content of methane caused by nitrogen is some direct function of the mole fraction of nitrogen present in the mixture.

Agreement between ϕ_g and Z for the system is excellent.

D. Methane-Carbon Dioxide-Water System

Experimental equilibrium water content data for Mixture 5 (11.32 mole per cent carbon dioxide) and Mixture 6 (20.22 mole per cent carbon dioxide) are presented

in Figures 7-6 and 7-7 respectively. A comparison of experimental data with those calculated using the proposed correlation is presented in Tables 7-7 and 7-8 for both mixtures. Both experimental and calculated data show an increase over the calculated water content data for pure methane under similar conditions of pressure and temperature, thus confirming the conclusions reported by other investigators (32, 45).

At relatively low pressures the experimental data tend to be 2 to 5 per cent lower than the calculated data but somewhere between 200 and 600 pounds per square inch absolute the trend seems to reverse itself. The reason for this type of behavior may be the chemical reaction between carbon dioxide and liquid water resulting in lowering the K-value for water. After the reversed trend is achieved the increase in water contents of both Mixtures 5 and 6 over those of pure methane increases with pressure but seems to decrease with increasing temperature. At 2000 pounds per square inch absolute pressure the calculated per cent increases at various temperatures are:

	<u>Mixture 5</u>	<u>Mixture 6</u>
100°F	4.00	5.68
130°F	3.12	4.81
160°F	1.88	3.04

TABLE 7-7

EQUILIBRIUM WATER CONTENT OF MIXTURE 5

Temperature (°F)	Pressure (PSIA)	Experimental (Mole fraction)	Calculated (Mole fraction)	% Error
100	214.09	0.004600	0.004700	- 2.17
	614.11	0.001812	0.001810	+ 0.11
	1013.95	0.001361	0.001264	+ 7.12
	1414.11	0.000973	0.001011	- 3.91
	2013.98	0.000855	0.000804	+ 5.96
Average Error				+ 1.42%
Average Absolute Error				3.85%
130	214.19	0.01095	0.01090	+ 0.46
	614.19	0.00432	0.00412	+ 4.63
	1014.19	0.00282	0.00273	+ 3.19
	1514.19	0.00190	0.00205	- 7.90
	2014.20	0.00182	0.00172	+ 5.50
Average Error				+ 1.18%
Average Absolute Error				4.34%
160	214.21	0.02255	0.02300	- 2.00
	614.19	0.00828	0.00870	- 5.07
	1014.17	0.00602	0.00572	+ 4.98
	1514.15	0.00433	0.00423	+ 2.31
	2014.21	0.00374	0.00351	+ 6.15
Average Error				+ 1.27%
Average Absolute Error				4.10%

TABLE 7-8

EQUILIBRIUM WATER CONTENT OF MIXTURE 6

Temperature (°F)	Pressure (PSIA)	Experimental (Mole fraction)	Calculated (Mole fraction)	% Error
100	214.09	0.004410	0.00462	- 4.76
	614.01	0.001990	0.00188	+ 5.53
	1014.02	0.001270	0.00126	+ 0.79
	1514.12	0.000926	0.00096	- 3.67
	2014.12	0.000856	0.00082	+ 4.20
Average Error				+ 0.42%
Average Absolute Error				3.79%
130	214.14	0.010900	0.01110	- 1.83
	614.13	0.004440	0.00418	+ 5.86
	1014.13	0.002880	0.00279	+ 3.12
	1514.17	0.002050	0.00209	- 1.95
	2014.17	0.001852	0.00173	+ 6.59
Average Error				+ 2.36%
Average Absolute Error				3.87%
160	214.17	0.022450	0.02320	- 3.34
	614.15	0.008810	0.00872	+ 1.02
	1014.17	0.005950	0.00572	+ 3.86
	1514.18	0.004400	0.00422	+ 4.09
	2014.18	0.003635	0.00351	+ 3.44
Average Error				+ 1.81%
Average Absolute Error				3.15%

With the accuracy of the present experimental set up it is not possible to establish this trend but at a later date a more sophisticated set up may be able to confirm this.

However, the agreement between the experimental and calculated equilibrium water content of both mixtures is good. The agreement between ϕ_g and Z for both mixtures is also good; the maximum deviation being 7.4% at 100°F and 2000 psi. The deviation decreases with increasing temperature which is in tune with the premise that gases behave more ideally at higher temperatures and lower pressures.

E. Methane-Hydrogen Sulfide-Water System

Equilibrium water content data for Mixtures 7 and 8 as determined experimentally at 130°F and between 200 and 2000 psig are presented in Figures 7-8 and 7-9. Tables 7-9 and 7-10 depict a comparison between experimental and calculated water contents for the same mixtures.

A relatively higher average absolute error for these two cases may be attributed to the inadequacy of the present experimental set up using mercury as the confining medium in the P-V-T equilibrium cell. Hydrogen sulfide reacts with mercury in the presence of water thus affecting the vapor pressure and consequently the K value of water. The correlation seems to give water content

TABLE 7-9

EQUILIBRIUM WATER CONTENT OF MIXTURE 7

Temperature (°F)	Pressure (PSIA)	Experimental (Mole fraction)	Calculated (Mole fraction)	% Error
130	214.06	0.01040	0.01100	- 5.77
	614.10	0.00431	0.00408	+ 5.33
	1014.12	0.00303	0.00277	+ 8.59
	1514.09	0.00235	0.00208	+11.49
	2014.09	0.00187	0.00173	+ 7.49
Average Error				+ 5.426%
Average Absolute Error				7.734%

TABLE 7-10

EQUILIBRIUM WATER CONTENT OF MIXTURE 8

Temperature (°F)	Pressure (PSIA)	Experimental (Mole fraction)	Calculated (Mole fraction)	% Error
130	214.08	0.01030	0.01100	- 6.80
	614.11	0.00432	0.00415	+ 3.94
	1014.14	0.00327	0.00282	+13.78
	1514.14	0.00211	0.00215	- 1.90
	2014.14	0.00189	0.00182	+ 3.70
Average Error				+ 2.544%
Average Absolute Error				6.024%

values which are up to 14 per cent lower than the experimental values.

However, Table 7-10 presents a comparative study of the mixtures tested by Lukacs (45) using water as the confining medium in the P-V-T equilibrium cell and determining the equilibrium water content by a chromatographic method instead of the gravimetric method employed in the present investigation. In this case the water content data obtained using the correlation are 3.5 to 7 per cent lower than the experimental data reported. This is a good agreement. And the agreement between ϕ_g and Z for all the gaseous mixtures studied is found to be excellent (deviation less than 2.5 per cent).

The calculated increase in equilibrium water content of Mixture 7 at 130°F and 2000 psia over that of pure methane at same temperature and pressure is 5.41 per cent and that for Mixture 8 is 10.0 per cent. This increase is approximately twice the increase caused by the presence of carbon dioxide in Mixtures 5 and 6.

F. Natural Gas-Water System

Throughout this study it has been well recognized that the key to developing the correlation for predicting the equilibrium water content of a gaseous mixture is the understanding of the nature of interactions between dissimilar molecules in that mixture. Although, it is

TABLE 7-11
EQUILIBRIUM WATER CONTENT OF CH₄-H₂S SYSTEMS

Tempera- ture (°F)	Pres- sure (PSIA)	Mix- ture No.	Experimental* (Mole fraction)	Calculated (Mole fraction)	% Error
160	1395	9	0.00475	0.00457	+3.79
160	1010	10	0.00616	0.00587	+4.70
160	611	11	0.00930	0.00875	+5.91
160	358	12	0.01500	0.01389	+7.40
160	1392	13	0.00520	0.00492	+5.39
160	925	14	0.00690	0.00641	+7.10
Average Error					+5.715%

*Experimental values as reported by Lukacs (45).

impossible to express the water content as a function of absolute molecular forces of a complex gaseous mixture, true critical properties of that mixture have been assumed as good overall representatives of these intermolecular forces and thus used for the determination of fugacity coefficient and the compressibility factor in the proposed correlation. In the previous sections, through the analysis of results, this assumption has been shown to hold good for binary gaseous mixtures even when the molecules involved were widely different in size, shape and nature. But the validity of this assumption should also produce acceptable results in the case of natural gases which are complex mixtures of widely diversified molecular structures. This test will also establish the range of acceptability of the proposed correlation.

An extensive search of the literature revealed that only limited equilibrium water content data are available for natural gas-water systems with known composition of natural gas. However, data for three typical natural gases of known compositions, as reported in literature (19, 40, 74), have been utilized in the present study.

Calculated equilibrium water content data for Mixture 15 (containing no non-hydrocarbons components) are compared with the reported experimental data in Table 7-12. The agreement is remarkable with maximum

TABLE 7-12
EQUILIBRIUM WATER CONTENT OF MIXTURE 15

Temperature (°F)	Pressure (PSIA)	Experimental* (Mole fraction)	Calculated (Mole fraction)	% Error
100	500	0.002282	0.002170	+4.91
	1000	0.001251	0.001299	-3.70
	1500	0.000957	0.000992	-3.66
	2000	0.0008096	0.0008115	-0.23
150	500	0.008611	0.008450	+1.87
	1000	0.004710	0.004640	+1.49
	1500	0.003386	0.003435	-1.45
	2000	0.002800	0.002825	-0.89
Average Error				-0.21%
Average Absolute Error				2.275%

*Experimental data reported by Dodson & Standing (19).

deviation being less than 5%. The agreement between ϕ_g and Z for the gas (Table F-12) is also good; the maximum deviation being 6.81% at 100°F and at a pressure of 2000 pounds per square inch absolute.

Mixture 17, for which the experimental and calculated water content data are presented in Table 7-14, is a typical natural gas containing 13.5% ethane and small amounts of oxygen and carbon dioxide. In this case the calculated values are lower than the experimental values for relatively low pressure range which confirms the observation made in Section B of this chapter. The agreement between calculated and experimental data is good.

The agreement between ϕ_g and Z for the gas (Table F-13) is excellent.

All this discussion of various gas mixture-water systems indicates that the proposed correlation is valid for predicting the equilibrium water content of a gaseous mixture within the pressure, temperature and composition ranges selected for this study. The predicted results are expected to be within $\pm 6\%$ of the experimental data.

G. The Proposed Method and Recommendations for Future Work

The proposed method for determining the equilibrium water content of a gaseous mixture, as presented in Chapter V, consists mainly of two steps:

1. Determination of true critical properties of the gaseous mixture containing hydrocarbons and non-hydrocarbons.

2. Using these critical properties, determination of various terms for the proposed correlation.

This study has revealed that the two pseudo-binary approaches in steps 1 and 2 successfully recognize both intermolecular forces and molecular structure of the gaseous mixture. And this makes the proposed method the most accurate so far for quantitative determination of equilibrium water content of that mixture.

However, to widen its range of applicability the following recommendations may be made for future work:

1. A study of the gaseous mixtures containing different amounts of ethane to investigate the larger errors observed in this case.

2. An experimental study of different gaseous mixtures in the temperature, pressure and composition ranges beyond the ones selected for the present investigation.

3. A study of gaseous mixtures containing hydrogen sulfide with a modified experimental set-up.

TABLE 7-13

EQUILIBRIUM WATER CONTENT OF MIXTURE 16

Temperature (°F)	Pressure (PSIA)	Experimental* (Mole fraction)	Calculated (Mole fraction)	% Error
80	1500	0.000537	0.000569	-5.95
100	1000	0.001241	0.001271	-2.42
	1500	0.000946	0.000971	-2.64
	2000	0.000758	0.000806	-6.40
Average Error				-4.35%

*Experimental data reported by Russell, et al. (74).

TABLE 7-14

EQUILIBRIUM WATER CONTENT OF MIXTURE 17

Temperature (°F)	Pressure (PSIA)	Experimental* (Mole fraction)	Calculated (Mole fraction)	% Error
110	200	0.00693	0.00654	+5.63
	500	0.00297	0.00290	+2.36
Average Error				+3.995%

*Experimental data reported by Laulhere and Briscoe (40).

TABLE 7-15

EQUILIBRIUM WATER CONTENT OF ETHANE

Temperature (°F)	Pressure (PSIA)	Experimental* (Mole fraction)	Calculated (Mole fraction)	% Error
100	200	0.005007	0.005240	- 4.66
	400	0.002641	0.003169	-20.00
	800	0.001474	0.002100	-42.60
	1000	0.001244	0.001959	-57.40
	1500	0.000949	0.001760	-85.50
	2000	0.000812	0.001598	-96.90
130	200	0.01170	0.012600	- 7.69
	400	0.00600	0.006995	-16.58
	800	0.00325	0.004500	-38.45
	1000	0.00274	0.004030	-47.10
	1500	0.00202	0.003535	-75.00
	2000	0.00168	0.003235	-92.50
160	200	0.024450	0.025130	- 2.62
	400	0.012690	0.014660	-15.56
	800	0.006833	0.008950	-30.98
	1000	0.005675	0.008014	-41.20
	1500	0.004147	0.006790	-63.80
	2000	0.003409	0.006050	-77.40

*Experimental smoothed data reported by Reamer, et al. (65).

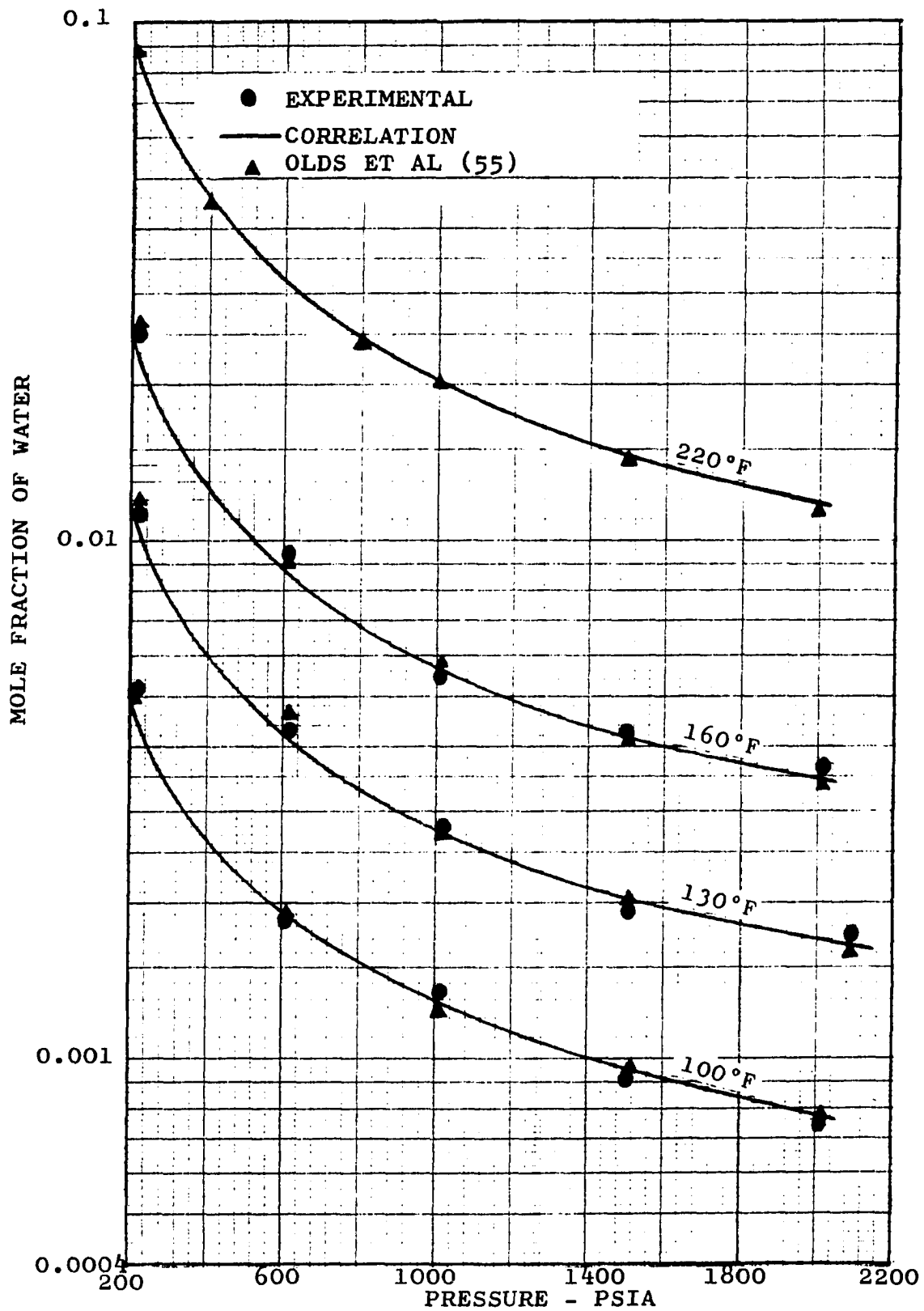


FIGURE 7-1. EQUILIBRIUM WATER CONTENT OF METHANE

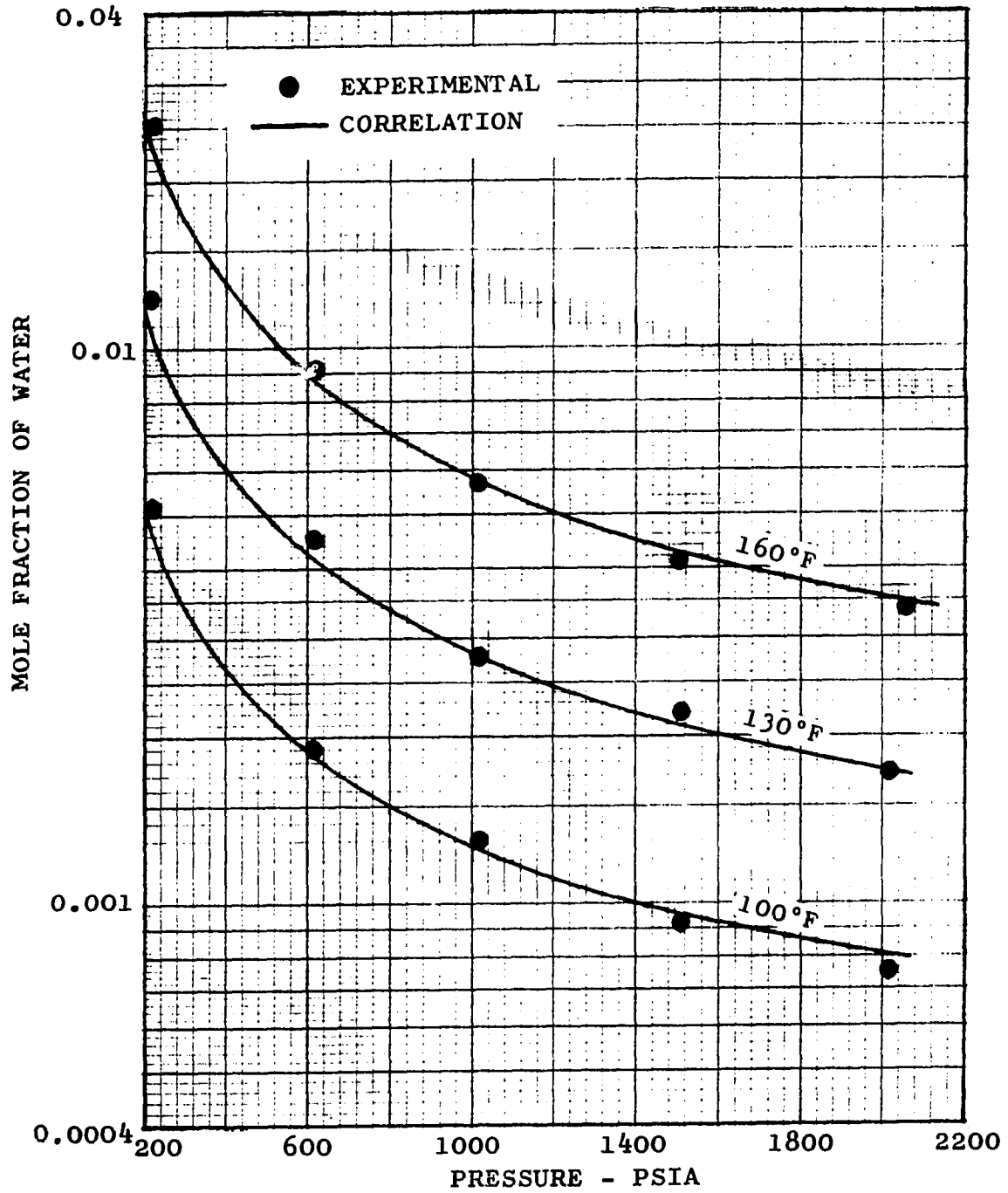


FIGURE 7-2. EQUILIBRIUM WATER CONTENT OF MIXTURE 1

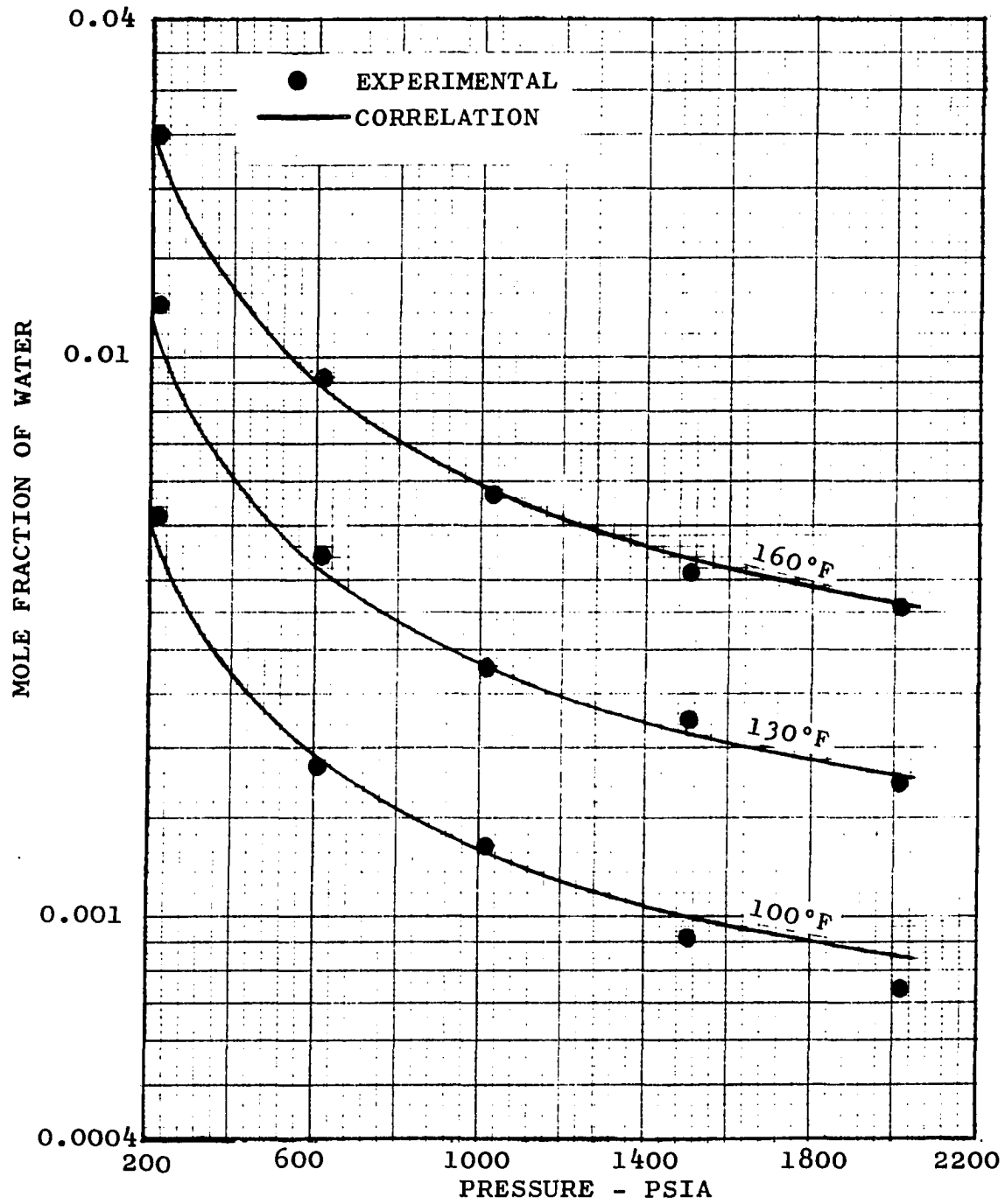


FIGURE 7-3. EQUILIBRIUM WATER CONTENT OF MIXTURE 2

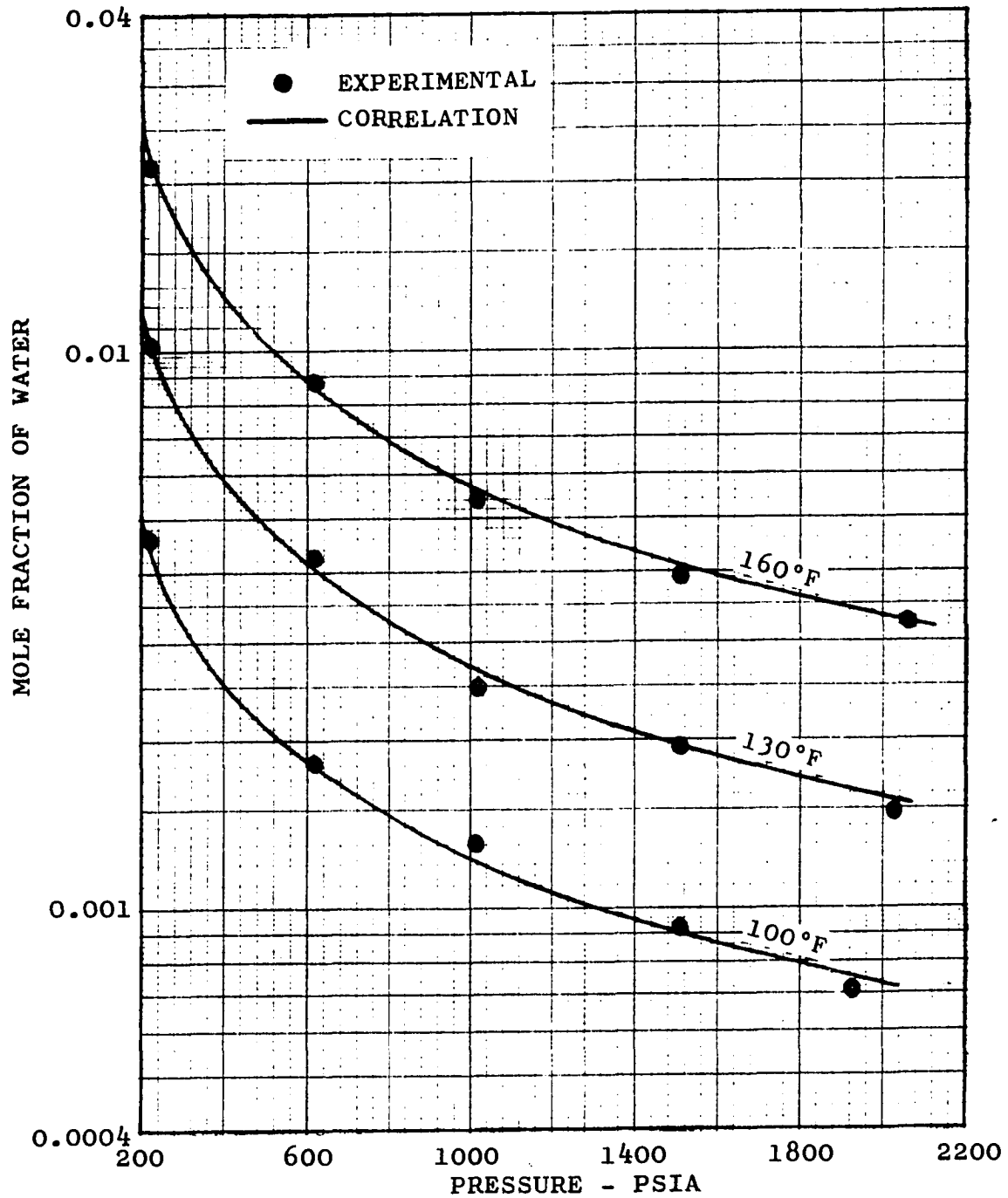


FIGURE 7-4. EQUILIBRIUM WATER CONTENT OF MIXTURE 3

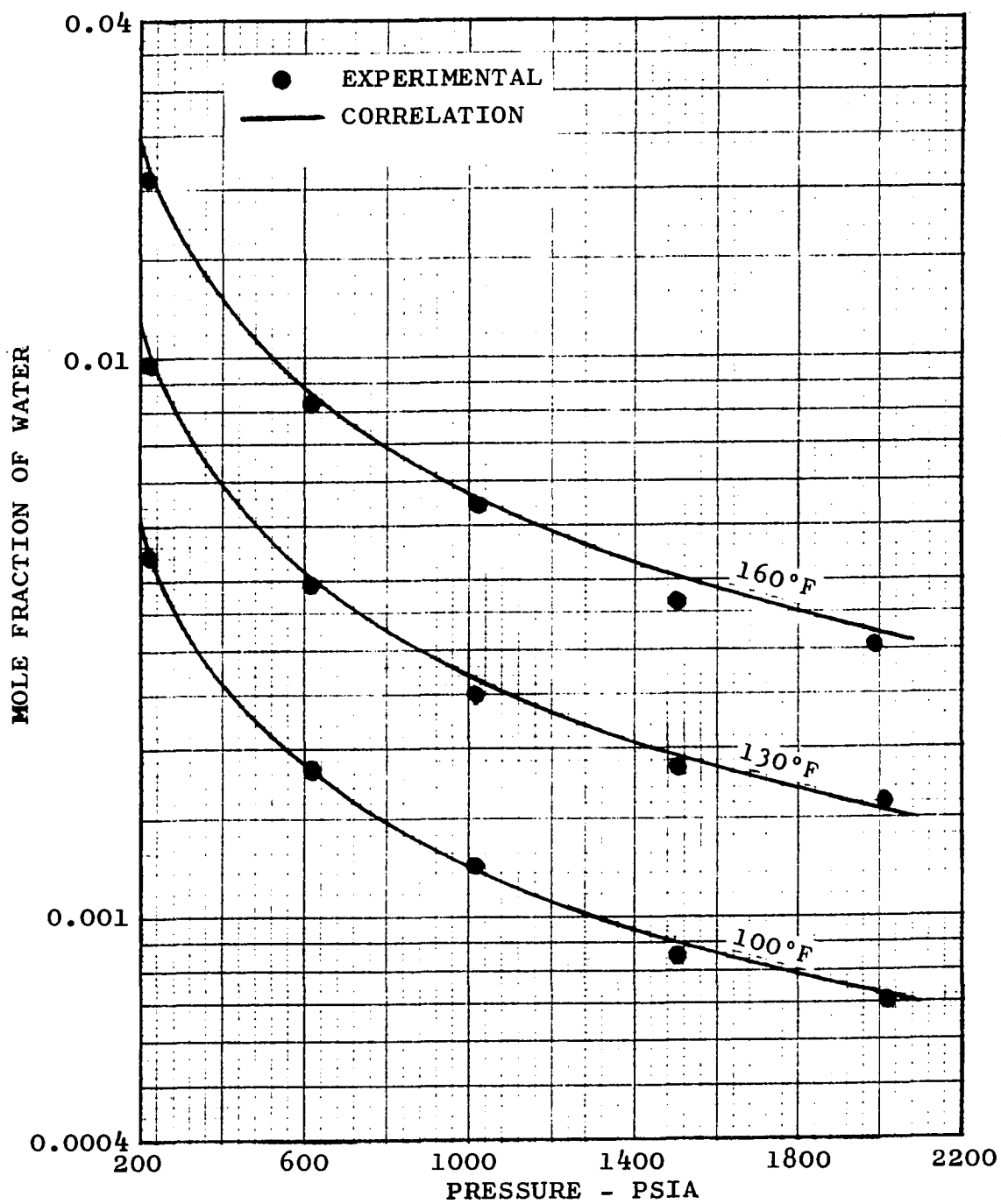


FIGURE 7-5. EQUILIBRIUM WATER CONTENT OF MIXTURE 4

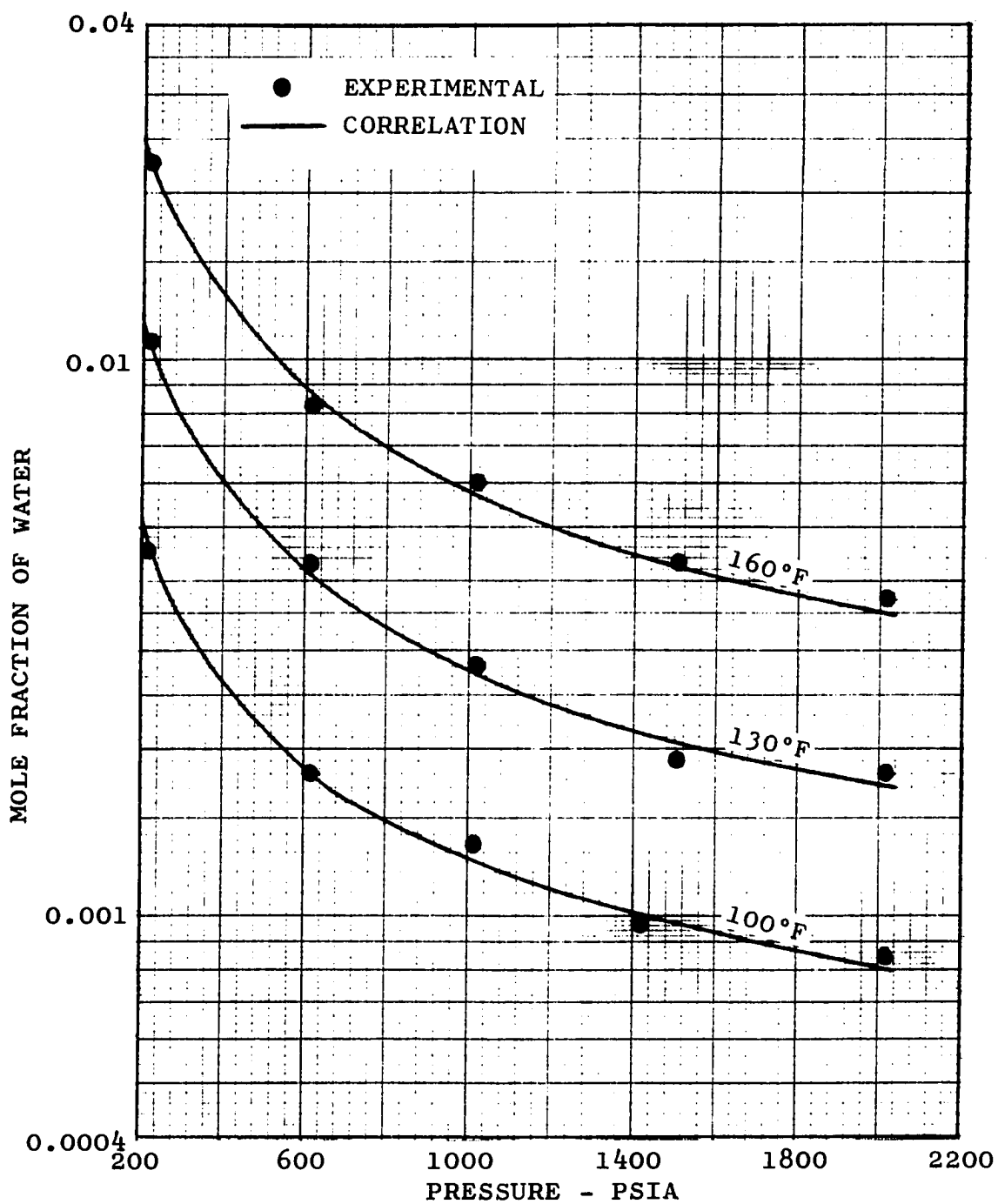


FIGURE 7-6. EQUILIBRIUM WATER CONTENT OF MIXTURE 5

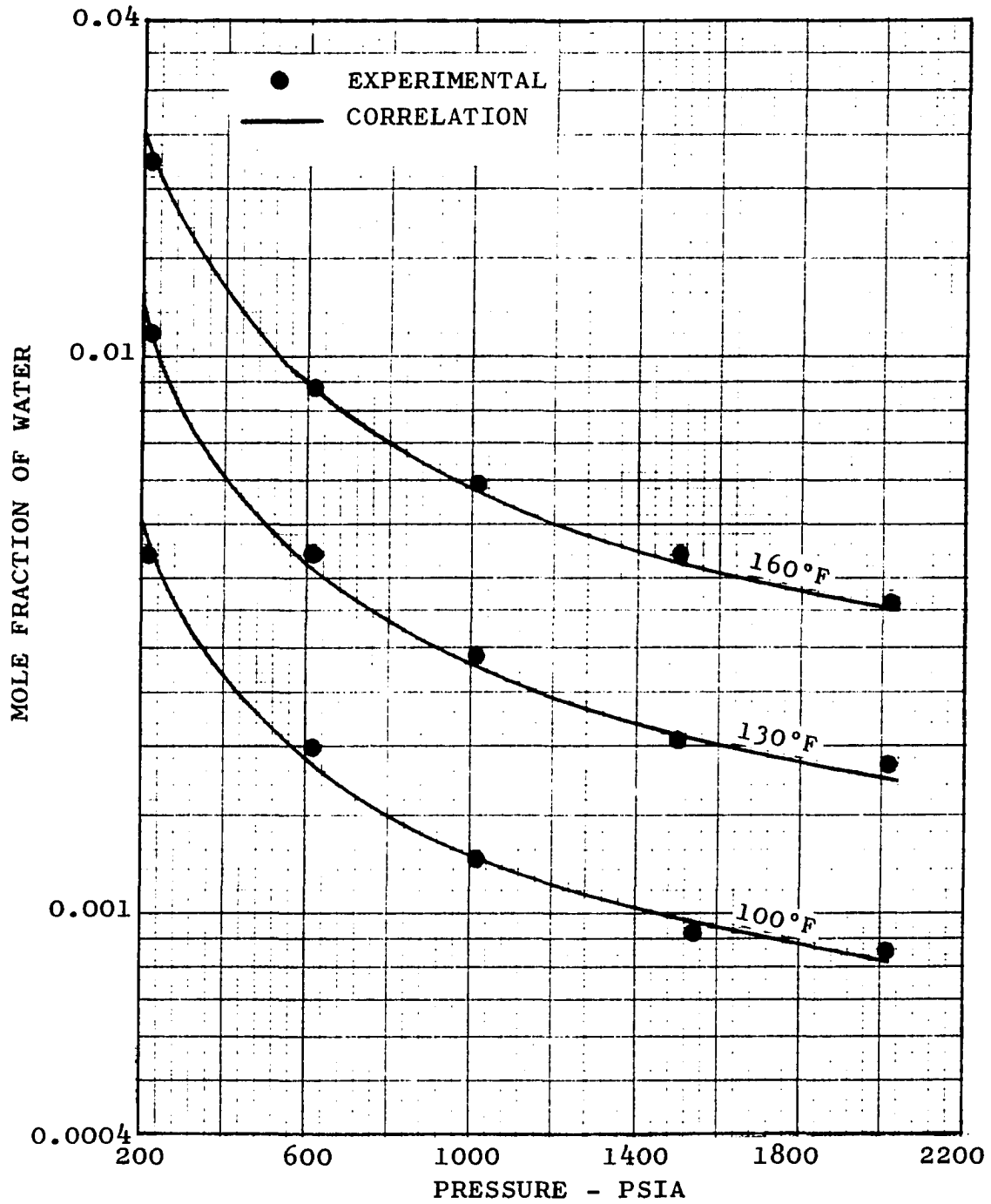


FIGURE 7-7. EQUILIBRIUM WATER CONTENT OF MIXTURE 6

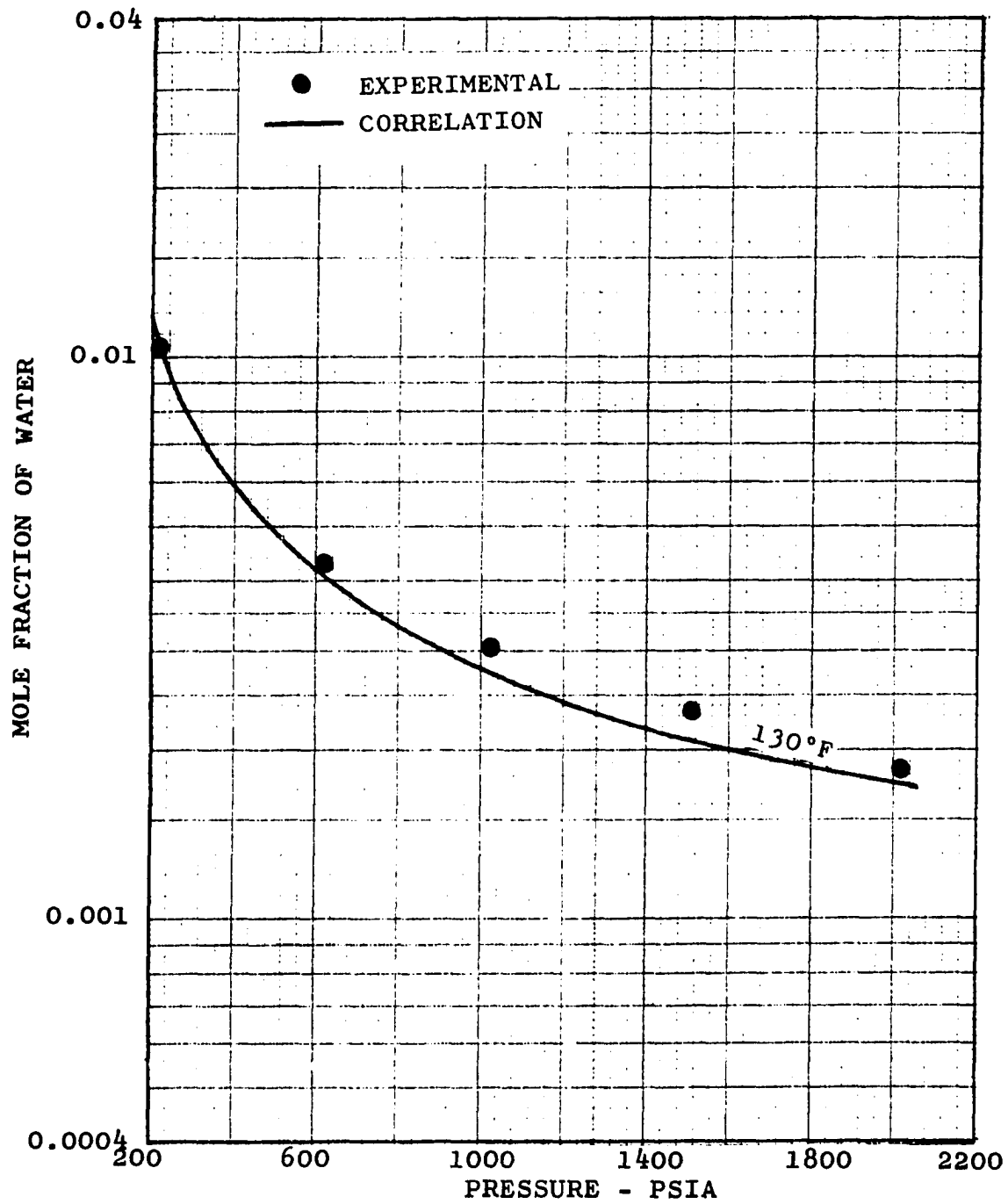


FIGURE 7-8. EQUILIBRIUM WATER CONTENT OF MIXTURE 7

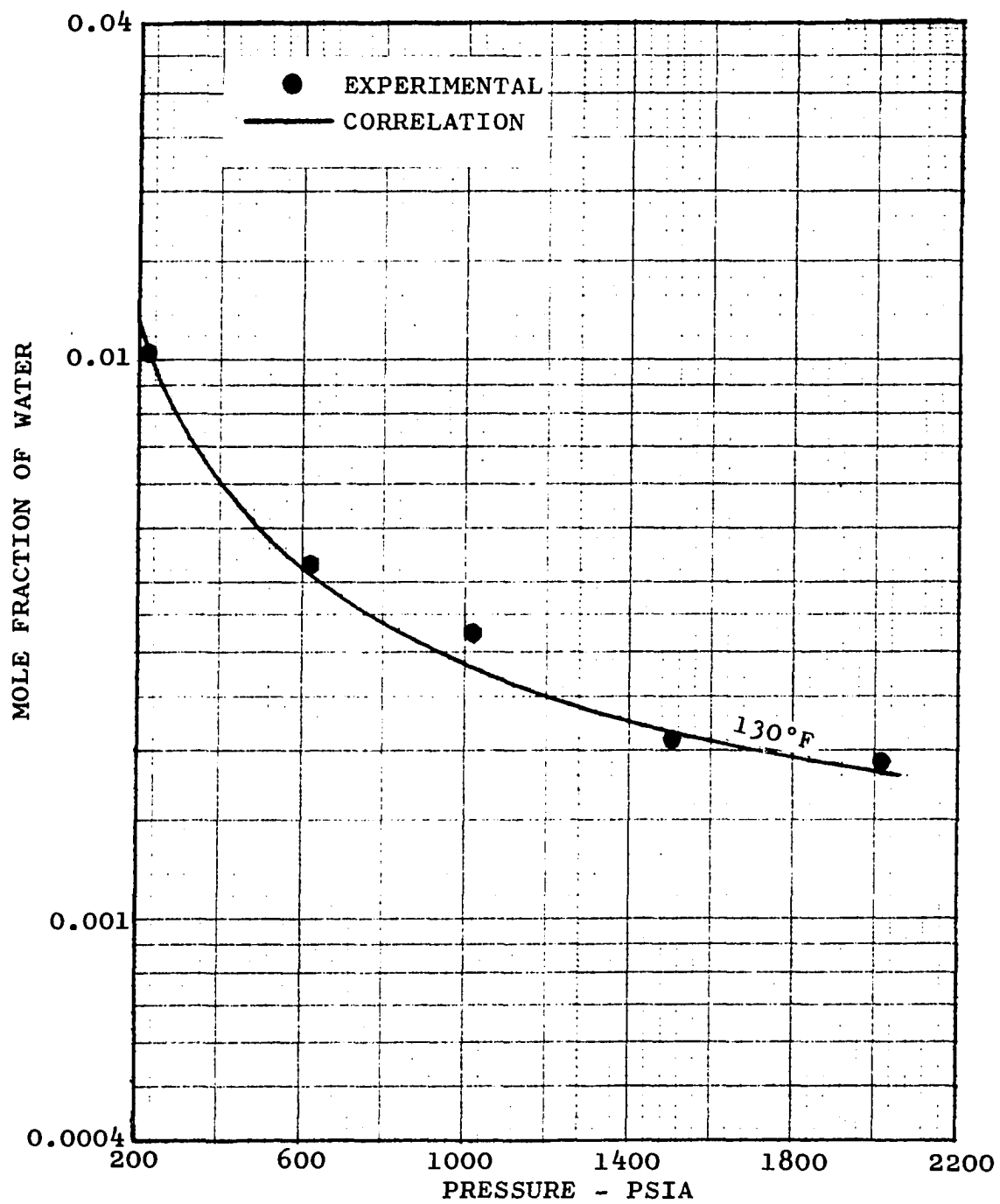


FIGURE 7-9. EQUILIBRIUM WATER CONTENT OF MIXTURE 8

CHAPTER VIII

CONCLUSIONS

This investigation provides an insight into the problem of predicting the equilibrium water content of the vapor phase of a natural gas-water system, which is affected by the system pressure, temperature, non-ideality of pure components, their relative amounts and the interaction between unlike molecules.

A semi-empirical correlation has been developed whereby the equilibrium water content of complex gaseous mixture containing one or more non-hydrocarbons, e.g. N_2 , CO_2 , H_2S may be predicted within ± 6 per cent of experimental data. The pseudo-binary approach followed in the determination of true critical properties of the gaseous mixture adequately accounts for intermolecular forces and molecular structure. Whereas, other factors affecting the equilibrium water content are adequately taken care of by the fugacity pseudo-binary approach, thus making the proposed method the most quantitative yet for predicting the water content of natural gases.

The proposed method has the following advantages over any other method now in use:

1. The accuracy of this method is superior to any other method.

2. This is the only method which can successfully account for non-hydrocarbons, e.g. N_2 , CO_2 , H_2S in a complex gaseous mixture.

3. It can predict quantitatively the change in the equilibrium water content of a gaseous mixture due to the change in system pressure, temperature and composition, all at the same time or each of them taking place separately.

4. Within the operating conditions selected for this study, the results obtained have clearly established this as the most quantitative method yet proposed for predicting the equilibrium water content of natural gases.

5. It is simpler to use than other methods of any comparable accuracy.

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APPENDIX A
NOMENCLATURE

TABLE A-1

NOMENCLATURE

a	= van der Waal intermolecular force correction constant
a'	= Empirically derived constant in Equation (3-9)
A	= Constant in Equation (3-18)
b	= van der Waal volume correction constant
B'	= Experimentally determined constant in Equation (3-18)
B(T)	= Second virial coefficient of the virial equation expressed in the form of power series in specific volume.
B'(T)	= Second virial coefficient of the virial equation expressed in the form of power series in pressure
B ₁₁	= Second virial coefficient between similar molecules
B ₁₂	= Second virial coefficient between dissimilar molecules
C	= Number of components in an equilibrium system
°C	= Degrees Centigrade
C(T)	= Third virial coefficient of the virial equation expressed in the form of power series in specific volume
C'(T)	= Third virial coefficient of the virial equation expressed in the form of power series in pressure
D(T)	= Fourth virial coefficient of the virial equation expressed in the form of power series in specific volume
D'(T)	= Fourth virial coefficient of the virial equation expressed in the form of power series in pressure
e	= Exponential
E	= Maximum energy of interaction

- $(E_o)_i$ = Molal internal energy of pure component "i" at system temperature and zero pressure
 $(E_p)_i$ = Molal internal energy of pure component "i" at temperature and pressure of the system
 f_g = Fugacity of gaseous mixture at system pressure and temperature
 f_i^l = Fugacity of pure component "i" in the liquid state
 $\bar{f}_i^l$ = Partial fugacity of component "i" in the liquid state
 f_i^v = Fugacity of pure component "i" in the vapor state
 $\bar{f}_i^v$ = Partial fugacity of component "i" in the vapor state
 $f_{p_i}^l$ = Fugacity of pure component "i" in liquid state at its vapor pressure and system temperature
 $f_{p_i}^v$ = Fugacity of pure component "i" in vapor state at its vapor pressure and system temperature
 f_p^l = Fugacity of any component in liquid state at system pressure and temperature
 f_w^l = Fugacity of pure water in liquid state at system pressure and temperature
 f_w^v = Fugacity of pure water in vapor state at system pressure and temperature
 $f_{p_w}^o$ = Fugacity of pure water at its vapor pressure and system temperature
 F = Degrees of freedom in an equilibrium system
 F' = Functional notation
 $^{\circ}F$ = Degrees Fahrenheit
 $g(r)$ = Radial distribution function
 k = Boltzmann's constant
 K_i = Equilibrium phase distribution ratio of component "i"

K_{ideal}	= Equilibrium phase distribution ratio of any component under ideal behavior of both phases
K_w	= Equilibrium phase distribution ratio of water
n_1	= Moles of component 1 in a gaseous mixture
n_2	= Moles of component 2 in a gaseous mixture
n_g	= Total moles of a gaseous mixture
N	= Number of molecules in the system
p	= Total pressure exerted by a gas
p_i	= Total pressure exerted by a gas if it were in an ideal state
P	= System pressure
P_b	= Base pressure chosen for gas measurement
P_c	= Critical pressure
p_i^o	= Vapor pressure of pure component "i" at system temperature
p_w^o	= Vapor pressure of pure water at system temperature
p^l	= Total pressure exerted by the liquid phase
p^v	= Total pressure exerted by the vapor phase
p^r	= Reference pressure
P_R	= Reduced pressure
Q	= Partition function
r	= Distance between two molecules
R	= Universal gas constant
oR	= Degrees Rankine
T	= System temperature
T_b	= Base Temperature chosen for gas measurement
T_c	= Critical temperature
T^l	= Temperature of the Liquid phase of a multiphase system
T_R	= Reduced temperature

T^v	= Temperature of the vapor phase of a multiphase system
$U(r)$	= Intermolecular potential function
U_{ii}	= Intermolecular potential energy between molecules of a substance per unit volume of that substance
U_{gg}	= Intermolecular potential energy between molecules of a gas per unit volume of that gas
U_{ww}	= Intermolecular potential energy between water molecules per unit volume of pure water
U_{gw}	= Intermolecular potential energy between a pair composed of a gas and a water molecule per unit volume of the system
V_w^l	= Molal volume of pure water in liquid state at system pressure and temperature
$\bar{V}_w^l$	= Partial molal volume of water in liquid state at system pressure and temperature
V	Total volume of a system
V_g	= Molal volume of the gaseous mixture at system pressure and temperature
V_{lw}	Average specific volume of liquid water at system pressure and temperature
V_w	= Molal volume of pure water at system pressure and temperature
x_i	= Mole fraction of component "i" in the liquid phase
x_w	= Mole fraction of water in the liquid phase
y_i	= Mole fraction of component "i" in vapor phase
y_w	= Mole fraction of water in the vapor phase
y_i^+	Mole fraction of component "i" in the pseudo-binary
y_g	Mole fraction of gaseous mixture in the vapor phase
y_j	Mole fraction of group 2 in McLeod's mixing rule
Z	= Compressibility factor of the gaseous mixture at system pressure and temperature

Z_{av}	= Average compressibility factor of liquid water at log-mean average pressure and system temperature
Z_b	= Compressibility factor of a gas at base conditions chosen for its measurement
cc	= Cubic centimeter
cu. ft.	= Cubic feet
EMR	= Eykman Molecular Refraction
mix	= Mixture
psia, PSIA	= Pounds per square inch absolute
psig	= Pounds per square inch gauge
scf	= Standard cubic feet
β	= Constant of proportionality in Equation (3-5)
γ_w	= Activity coefficient of water in the liquid phase as defined for Equation (3-20)
$\gamma_w^{(P^r)}$	= Liquid phase activity coefficient of water at reference pressure and system temperature
σ	= Collision diameter between two molecules
ϕ	= Number of phases present in an equilibrium system
ϕ_g	= Fugacity coefficient of a gaseous mixture at system pressure and temperature
ϕ_w	= Fugacity coefficient of water in vapor phase at system pressure and temperature
$\phi_{P_w^o}$	= Fugacity coefficient of water in vapor phase at its vapor pressure and system temperature
ϕ'_w, ϕ''_w	= Activity coefficients of water in liquid phase as defined for Equation (3-20)
%	= per cent

APPENDIX B

SURVEY OF EXPERIMENTAL DATA

TABLE B-1

VAPOR PHASE EQUILIBRIUM WATER CONTENT DATA

System	Maximum Temperature °F	Maximum Pressure PSIA	Reference
CH ₄	460 212	10,000 1,470	55 72
C ₂ H ₆	460	10,000	65
C ₃ H ₈	70 187 192 300	120 500 100 3,000	27 59 57 37
C ₄ H ₈	460	10,000	67,70
Natural gas	65 100 220 250 280 280	1,500 2,000 10,000 5,000 6,000 10,000	83 9,17,30 40,74 8 19 46 50
Natural gas-NaCl	250	5,000	19
CO ₂	158 212	735 10,000	61 93,94,95
N ₂	122 212 446	14,700 1,470 4,200	2 72 75
H ₂ S	340	5,200	82
AIR	100	1,500	47
CH ₄ -C ₂ H ₆	140	3,000	91
CH ₄ -nC ₄ H ₁₀	280	3,000	49
CH ₄ -H ₂ S	160	1,400	45

APPENDIX C

PHYSICAL CONSTANTS

TABLE C-1
CRITICAL PROPERTIES AND EMR OF COMPOUNDS

Compound	EMR	Critical Pressure PSIA	Critical Temperature °R
C ₁	13.984	673.10	343.30
C ₂	23.913	708.30	549.77
C ₃	34.316	617.40	665.95
n-C ₄	44.243	550.70	765.31
i-C ₄	44.741	529.10	734.65
n-C ₅	55.267	489.50	845.60
i-C ₅	55.302	483.00	829.80
n-C ₆	65.575	439.70	914.20
n-C ₇	75.875	396.90	972.31
n-C ₈	86.193	362.10	1024.31
N ₂	9.407	492.00	227.20
CO ₂	15.750	1073.00	548.00
O ₂	8.495	730.00	278.00
H ₂ S	19.828	1306.00	672.70
H ₂ O	--	3210.00	1165.00

APPENDIX D

MIXTURE ANALYSES

TABLE D-1

COMPOSITION OF GASEOUS MIXTURES

Compo- nents	Mixture 1	Mixture 2	Mixture 3	Mixture 4	Mixture 5	Mixture 6
O ₂						
N ₂			0.0855	0.1886		
CO ₂					0.1132	0.2022
H ₂ S						
C ₁	0.9173	0.8404	0.9145	0.8114	0.8868	0.7978
C ₂	0.0827	0.1596				
C ₃						
n-C ₄						
i-C ₄						
n-C ₅						
i-C ₅ ⁺						
Compo- nents	Mixture 7	Mixture 8	Mixture ¹ 9	Mixture ¹ 10	Mixture ¹ 11	Mixture ¹ 12
O ₂						
N ₂						
CO ₂						
H ₂ S	0.0830	0.1783	0.16	0.17	0.19	0.21
C ₁	0.9170	0.8217	0.84	0.83	0.81	0.79
C ₂						
C ₃						
n-C ₄						
i-C ₄						
n-C ₅						
i-C ₅ ⁺						

TABLE D-1 (Cont.)

Compo- nents	Mixture ¹ 13	Mixture ¹ 14	Mixture ² 15	Mixture ³ 16	Mixture ⁴ 17
O ₂					0.0020
N ₂				0.0100	
CO ₂				0.0060	0.0060
H ₂ S	0.2750	0.2900			
C ₁	0.7250	0.7100	0.8851	0.9436	0.8530
C ₂			0.0602	0.0264	0.1350
C ₃			0.0318	0.0096	
n-C ₄			--	0.0044	
i-C ₄			0.0046		
n-C ₅			0.0085		
i-C ₅			0.0098		

¹Gas mixtures reported by Lukacs (45).

²Natural gas reported by Dodson and Standing (19).

³Natural gas reported by Russell, et al. (74).

⁴Natural gas reported by Laulhere and Briscoe (40).

APPENDIX E

SAMPLE CALCULATIONS

TABLE E-1

CORRELATION SAMPLE CALCULATION
EQUILIBRIUM WATER CONTENT OF MIXTURE 16
AT 1000 PSIA AND 100°F

$$K_w = 0.00196 \quad (\text{Figure 5-7})$$

$$P_R \text{ for water} = \frac{1000}{3210} = 0.312$$

$$T_R \text{ for water} = \frac{560}{1165} = 0.481$$

$$\phi_w = 0.515 \quad (\text{Figure 5-2})$$

Component	y_i	y_i^*	EMR	$(y_i^*)(\text{EMR})$
N_2	0.0100	0.0104	9.407	0.0980
CO_2	0.0060	0.0063	15.750	0.0934
C_1	0.9436	0.9833	13.984	13.7505
	<u>0.9596</u>	<u>1.0000</u>		<u>13.9419</u>
C_2	0.0264	0.6535	23.913	15.6271
C_3	0.0096	0.2376	34.316	8.1535
C_4^+	0.0044	0.1089	50.004	5.4494
	<u>0.0404</u>	<u>1.0000</u>		<u>29.2300</u>

$$EMR_1 = 13.9419$$

$$EMR_2 = 29.2300$$

$$(T_c/P_c)_1 = 0.515 \quad (\text{Figure 5-4})$$

$$(T_c/P_c)_2 = 0.925 \quad (\text{Figure 5-4})$$

TABLE E-1 (Cont.)

$$\begin{aligned}\frac{T_c}{P_c} &= (0.9596)(0.515) + (0.0404)(0.925) \\ &= 0.5318\end{aligned}$$

$$\begin{aligned}(\text{EMR})_{\text{mix}} &= (0.9596)(13.9419) + (0.0404)(29.2300) \\ &= 14.5651\end{aligned}$$

$$T_c / \sqrt{P_c} = 14.90 \quad (\text{Figure 5-5})$$

$$P_c = 785.1 \text{ PSIA}$$

$$T_c = 417.5^\circ\text{R}$$

$$P = 1000 \text{ PSIA}$$

$$T = 560^\circ\text{R}$$

$$P_R = 1.272$$

$$T_R = 1.341$$

$$\phi_g = 0.850 \quad (\text{Figure 5-2})$$

$$Z = 0.865 \quad (\text{Figure 5-6})$$

$$\begin{aligned}y_w &= 0.00196 \left(\frac{0.515}{0.850} \right)^{0.865} \\ &= 0.001271\end{aligned}$$

TABLE E-2

SAMPLE CALCULATION FOR PREPARING
MIXTURES OF KNOWN COMPOSITION

MIXTURE: Methane (1) and Ethane (2)

Nominal Composition: $y_1 = 0.95$ and $y_2 = 0.05$

Volume of the Mixing Cell, $V = 650$ cc

Temperature of Mixing Cell, $T = 70^\circ\text{F} = 529.69^\circ\text{R}$

Pressure of C_2 filling the cell, $P_2 = 45$ psig = 59.4 psia

Compressibility of C_2 at P_2 and T (from ref. 77), $Z_2 = 0.978$

$$n_2 = \frac{P_2 V}{Z_2 RT} = 2.47 \times 10^{-4} \text{ lb. mole}$$

$$n_1 = n_2 \left(\frac{x_1}{x_2} \right) = 46.93 \times 10^{-4} \text{ lb. mole}$$

$$n_g = n_1 + n_2 = 49.40 \times 10^{-4} \text{ lb. mole}$$

$$P_c' = \sum x_i (P_c)_i = 675.4 \text{ psia}$$

$$T_c' = \sum x_i (T_c)_i = 353.5^\circ\text{R}$$

$$Z = \left(\frac{V}{n_g RT} \right) P_c' P_R = 0.549 P_R$$

Then the method outlined by Sliepcevich, et al. (84) is used to find

$$Z = 0.87$$

and $P_R = 1.57$

$$P = P_c' \cdot P_R = 1,060 \text{ psia}$$

TABLE E-3

SAMPLE CALCULATION OF EQUILIBRIUM WATER CONTENT
OF A GAS FROM EXPERIMENTAL DATA

Equilibrium Water Content of Methane at 2000 psig and 100°F

Weight of tube I + adsorbent = 1.3060 gms.

Weight of tube I + adsorbent + water = 1.3273 "

Amount of water adsorbed = 0.0213 "

Weight of tube II + adsorbent = 0.9770 gm.

Weight of tube II + adsorbent + water = 0.9771 "

Amount of water adsorbed = 0.0001 "

Total amount of water adsorbed = 0.0214 "

Amount of gas passed through the
wet test meter = 1.409 cu. ft.

Temperature = 81°F

Pressure = 730.8 mm of Hg

$$\begin{aligned} \text{SCF of gas passed} &= 1.409 \times \frac{520}{541} \times \frac{730.8}{760} \\ (\text{Assuming } Z &= 1.0) \\ &= 1.3019 \end{aligned}$$

$$\begin{aligned} \text{Moles of water per mole of gas} &= \frac{0.0214}{453.6 \times 18} \times \frac{379}{1.302} \\ &= 0.000763 \end{aligned}$$

$$\begin{aligned} \text{Equilibrium water content of gas} &= \frac{0.000763}{1.0 + 0.000763} \\ &= 0.0007624 \end{aligned}$$

APPENDIX F

CALCULATED EQUILIBRIUM WATER CONTENT
OF GASEOUS MIXTURES

TABLE F-1

CALCULATED WATER CONTENT OF METHANE

Temperature °F	Pressure psia	K_w	ϕ_w	ϕ_g	Z	y_w
100	200	0.00563	0.875	0.972	0.976	0.005080
	400	0.00323	0.770	0.947	0.950	0.002660
	800	0.00214	0.580	0.891	0.899	0.001458
	1,000	0.00196	0.515	0.864	0.874	0.001301
	1,500	0.001659	0.403	0.801	0.820	0.000950
	2,000	0.00150	0.325	0.750	0.790	0.000775
130	200	0.01290	0.890	0.978	0.978	0.011780
	400	0.00725	0.790	0.954	0.955	0.006060
	800	0.00479	0.607	0.910	0.910	0.003305
	1,000	0.00422	0.540	0.888	0.880	0.002730
	1,500	0.00358	0.430	0.834	0.842	0.002045
	2,000	0.00324	0.350	0.791	0.815	0.001663
160	200	0.02730	0.895	0.981	0.980	0.024940
	400	0.01560	0.798	0.961	0.958	0.013070
	800	0.00991	0.620	0.927	0.920	0.006850
	1,000	0.00887	0.555	0.908	0.897	0.005710
	1,500	0.00747	0.442	0.865	0.866	0.004160
	2,000	0.00687	0.360	0.830	0.824	0.003455
220	200	0.0991	0.906	0.989	0.984	0.09099
	400	0.0547	0.822	0.974	0.966	0.04650
	800	0.0342	0.660	0.949	0.935	0.02440
	1,000	0.0310	0.595	0.937	0.921	0.02040
	1,500	0.0260	0.480	0.910	0.890	0.01471
	2,000	0.02365	0.400	0.885	0.875	0.01180

TABLE F-2
CALCULATED WATER CONTENT OF MIXTURE 1

Temperature °F	Pressure psia	ϕ_g	Z	y_w
100	200	0.971	0.972	0.005080
	400	0.938	0.945	0.002681
	800	0.878	0.890	0.001480
	1,000	0.848	0.863	0.001273
	1,500	0.780	0.803	0.000975
	2,000	0.722	0.779	0.000806
130	200	0.976	0.976	0.011780
	400	0.951	0.955	0.006080
	800	0.901	0.904	0.003337
	1,000	0.877	0.883	0.002820
	1,500	0.819	0.830	0.002103
	2,000	0.772	0.804	0.001718
160	200	0.980	0.979	0.02500
	400	0.958	0.957	0.01309
	800	0.915	0.913	0.00695
	1,000	0.897	0.894	0.00579
	1,500	0.848	0.864	0.00425
	2,000	0.808	0.826	0.00353

TABLE F-3
CALCULATED WATER CONTENT OF MIXTURE 2

Temperature °F	Pressure psia	ϕ_g	Z	y_w
100	200	0.969	0.970	0.005100
	400	0.931	0.942	0.002697
	800	0.863	0.880	0.001508
	1,000	0.830	0.846	0.001309
	1,500	0.751	0.784	0.001019
	2,000	0.688	0.765	0.000845
130	200	0.972	0.974	0.01183
	400	0.943	0.950	0.00613
	800	0.890	0.896	0.00338
	1,000	0.860	0.873	0.00282
	1,500	0.798	0.817	0.00216
	2,000	0.745	0.787	0.00179
160	200	0.979	0.978	0.02503
	400	0.951	0.951	0.01311
	800	0.908	0.908	0.00701
	1,000	0.880	0.885	0.00589
	1,500	0.828	0.837	0.00442
	2,000	0.784	0.813	0.00366

TABLE F-4

CALCULATED WATER CONTENT OF MIXTURE 3

Temperature °F	Pressure psia	ϕ_g	Z	y_w
100	200	0.978	0.974	0.005050
	400	0.951	0.955	0.002640
	800	0.903	0.904	0.001434
	1,000	0.880	0.880	0.001222
	1,500	0.824	0.833	0.000922
	2,000	0.778	0.810	0.000739
130	200	0.981	0.976	0.011720
	400	0.960	0.958	0.006010
	800	0.920	0.915	0.003260
	1,000	0.900	0.896	0.002670
	1,500	0.855	0.860	0.001981
	2,000	0.818	0.833	0.001597
160	200	0.983	0.978	0.02492
	400	0.969	0.961	0.01292
	800	0.935	0.924	0.00680
	1,000	0.919	0.908	0.00561
	1,500	0.880	0.874	0.00409
	2,000	0.850	0.854	0.00331

TABLE F-5
CALCULATED WATER CONTENT OF MIXTURE 4

Temperature °F	Pressure psia	ϕ_g	Z	y_w
100	200	0.977	0.970	0.005050
	400	0.952	0.955	0.002640
	800	0.907	0.907	0.001427
	1,000	0.883	0.887	0.001215
	1,500	0.830	0.833	0.000914
	2,000	0.789	0.817	0.000725
130	200	0.981	0.977	0.011710
	400	0.962	0.960	0.006000
	800	0.923	0.920	0.003245
	1,000	0.907	0.897	0.002650
	1,500	0.865	0.863	0.001960
	2,000	0.832	0.845	0.001560
160	200	0.986	0.982	0.02480
	400	0.972	0.963	0.01289
	800	0.942	0.928	0.00673
	1,000	0.928	0.912	0.00555
	1,500	0.892	0.880	0.00404
	2,000	0.865	0.863	0.00323

TABLE F-6
CALCULATED WATER CONTENT OF MIXTURE 5

Temperature °F	Pressure psia	ϕ_g	Z	y_w
100	200	0.972	0.975	0.005080
	400	0.941	0.948	0.002670
	800	0.882	0.892	0.001470
	1,000	0.850	0.865	0.001270
	1,500	0.782	0.808	0.000976
	2,000	0.722	0.777	0.000806
130	200	0.976	0.978	0.011880
	400	0.951	0.954	0.006070
	800	0.903	0.907	0.003300
	1,000	0.879	0.885	0.002745
	1,500	0.822	0.833	0.002085
	2,000	0.772	0.804	0.001715
160	200	0.981	0.980	0.02495
	400	0.961	0.958	0.01308
	800	0.920	0.916	0.00690
	1,000	0.899	0.896	0.00576
	1,500	0.852	0.857	0.00426
	2,000	0.810	0.825	0.00352

TABLE F-7
CALCULATED WATER CONTENT OF MIXTURE 6

Temperature °F	Pressure psia	ϕ_g	Z	y_w
100	200	0.970	0.974	0.005090
	400	0.940	0.947	0.002675
	800	0.879	0.890	0.001480
	1,000	0.848	0.862	0.001274
	1,500	0.773	0.800	0.000993
	2,000	0.713	0.770	0.000819
130	200	0.973	0.975	0.012490
	400	0.950	0.954	0.006070
	800	0.899	0.907	0.003345
	1,000	0.872	0.880	0.002770
	1,500	0.812	0.830	0.002115
	2,000	0.762	0.795	0.001743
160	200	0.979	0.980	0.02500
	400	0.958	0.955	0.01310
	800	0.916	0.913	0.00695
	1,000	0.895	0.892	0.00579
	1,500	0.847	0.850	0.00429
	2,000	0.804	0.820	0.00356

TABLE F-8

CALCULATED WATER CONTENT OF MIXTURE 7

Temperature °F	Pressure psia	ϕ_g	Z	y_w
130	200	0.973	0.978	0.011720
	400	0.949	0.953	0.006060
	800	0.898	0.905	0.003315
	1,000	0.870	0.880	0.002787
	1,500	0.810	0.825	0.002115
	2,000	0.760	0.794	0.001753

TABLE F-9

CALCULATED WATER CONTENT OF MIXTURE 8

Temperature °F	Pressure psia	ϕ_g	Z	y_w
130	200	0.972	0.975	0.011730
	400	0.942	0.948	0.006100
	800	0.885	0.896	0.003365
	1,000	0.855	0.870	0.002845
	1,500	0.788	0.810	0.002185
	2,000	0.731	0.777	0.001829

TABLE F-10

CALCULATED WATER CONTENT OF ETHANE

Temperature °F	Pressure psia	ϕ_g	Z	y_w
100	200	0.892	0.935	0.005240
	400	0.787	0.852	0.003169
	800	0.595	0.670	0.002100
	1,000	0.516	0.615	0.001959
	1,500	0.365	0.595	0.001760
	2,000	0.295	0.648	0.001598
130	200	0.912	0.940	0.012600
	400	0.822	0.877	0.006995
	800	0.658	0.710	0.004500
	1,000	0.580	0.655	0.004030
	1,500	0.438	0.635	0.003535
	2,000	0.352	0.670	0.003235
160	200	0.928	0.943	0.02513
	400	0.855	0.887	0.01466
	800	0.712	0.755	0.00895
	1,000	0.641	0.700	0.00801
	1,500	0.510	0.668	0.00679
	2,000	0.433	0.688	0.00605

TABLE F-11
CALCULATED WATER CONTENT OF CH₄-H₂S MIXTURES
AT 160°F

Mixture No.	Pressure psia	ϕ_g	Z	y_w
9	1,395	0.847	0.855	0.00457
10	1,010	0.880	0.886	0.00587
11	611	0.925	0.930	0.00875
12	358	0.957	0.960	0.01389
13	1,392	0.805	0.825	0.00492
14	925	0.870	0.887	0.00641

TABLE F-12
CALCULATED WATER CONTENT OF MIXTURE 15

Temperature °F	Pressure psia	ϕ_g	Z	y_w
100	500	0.917	0.924	0.002170
	1,000	0.836	0.850	0.001299
	1,500	0.765	0.796	0.000992
	2,000	0.712	0.782	0.000812
150	500	0.940	0.933	0.008450
	1,000	0.878	0.870	0.004640
	1,500	0.825	0.837	0.003435
	2,000	0.788	0.820	0.002825

TABLE F-13
CALCULATED WATER CONTENT OF MIXTURE 16

Temperature °F	Pressure psia	ϕ_g	Z	y_w
80	1,500	0.745	0.780	0.000569
100	1,000	0.850	0.865	0.001271
	1,500	0.782	0.804	0.000971
	2,000	0.723	0.776	0.000806

TABLE F-14
CALCULATED WATER CONTENT OF MIXTURE 17

Temperature °F	Pressure psia	ϕ_g	Z	y_w
110	200	0.971	0.972	0.00654
	500	0.922	0.933	0.00290