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# SOLUBILITY OF LIGHT HYDROCARBONS
# IN WATER UNDER HIGH PRESSURES

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# SOLUBILITY OF LIGHT HYDROCARBONS
# IN WATER UNDER HIGH PRESSURES

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# CHAPTER I

## THE PROBLEM

Quantitative information concerning the behavior of water-hydrocarbon mixtures, under the conditions found in natural reservoirs, is of prime importance to the petroleum engineer. The presence of water in all steps of hydrocarbon gas handling processes points out the need for a thorough understanding of hydrocarbon-water systems.

The reported experimental or theoretical investigations have been more extensive in regard to the formation of gas hydrates and amount of gas water content than the determination of hydrocarbon solubility in water. Solubility of pure light hydrocarbons and natural gas, at wide pressure and temperature ranges, in water have been published. However, the information available concerning the solubility of binary hydrocarbon mixtures is fragmentary and there are few solubility data reported for a ternary hydrocarbon mixture.

At present a reliable theoretical or empirical method, by which solubilities of mixture hydrocarbons in water can be determined, does not exist. The lack of experimental and theoretical information relating to this field has prompted this investigation.

In this work the following experimental data were obtained:

1. Solubility of methane-ethane mixtures in water at temperatures of 100, 130, 160, 190, 220 F and pressures of 700 to 8000 psia.

2. Solubility of methane-propane mixtures in water at a temperature of 220 F and pressures of 700 to 8000 psia.
3. Solubility of ethane-propane mixtures in water at a temperature of 220 F and pressures of 700 to 8000 psia.
4. Solubility of methane-ethane-propane mixtures in water at 160, 190, 220 F and pressures of 700 to 5000 psia.

Since only the solubility of gaseous hydrocarbons in water was desired, the temperatures were chosen such that only two phases would be present. The two phases in equilibrium consisted of: (1) gaseous hydrocarbon mixture and (2) the liquid water with hydrocarbon dissolved in it.

The effect of mixture composition on the solubility has been studied. Based on the experimental data obtained in this work, a correlation has been developed from which solubility of gaseous hydrocarbon mixtures of any composition at any pressure and temperature in water can be determined (provided only two phases are present).

A new method for taking liquid and vapor samples at high pressures has been introduced. Sampling valves of a simple design were used to obtain the samples for chromatographic analysis.

# CHAPTER II

# GENERAL CONSIDERATION OF PHASE EQUILIBRIA AND LITERATURE

For a closed system consisting of a pure component and subject to no external forces other than pressure the criteria of equilibrium is that the change in Gibbs free energy of the system, at constant temperature and pressure, be equal to zero. This is expressed by the following formula:

$$dG_{T,P} = 0 \qquad \text{(II-1)}$$

where G = total Gibbs free energy of the single component system.

Consider a closed system to be constituted of more than one phase and each phase consisting of one or more components. Each individual phase will be an open system whose mass or composition may change. For a complete equilibrium to exist, all phases within the system should be in equilibrium with each other.

If the components are distinguished by means of subscripts and phases by superscripts, the Gibbs free energy of the polyphasic system is

$$G = G^1 + G^2 + \dots \qquad \text{(II-2)}$$

In each phase the variation of the free energy with respect to T, P, and the quantity variables is

$$dG = (\partial G/\partial T)_{P,n_i} dT + (\partial G/\partial P)_{T,n_i} dP + (\partial G/\partial n_i)_{T,P,n_{j\neq i}} dn_i \qquad \text{(II-3)}$$

or $$dG = - SdT + VdP + \sum \mu_i dn_i \qquad \text{(II-4)}$$

in which S is the entropy, V the volume, $n_i$ the moles of component i, and $\mu_i$ is defined as

$$\mu_i^1 = (\partial G^1/\partial n_i^1)_{T,P,n^i_{j\neq i}} \qquad \text{(II-5)}$$

where superscript 1 indicates phase one and $\mu_i^1$ is called the chemical potential of component i in phase one.

Expressions similar to Equation (II-3) can be written for the differential changes of internal energy, U, enthalpy, H, and Helmholtz free energy, A, and it can be shown that

$$\mu_i^1 = (\partial U^1/\partial n_i^1)_{V,S,n_{j\neq i}} = (\partial H^1/\partial n_i^1)_{S,P,n_{j\neq i}} = (\partial A^1/\partial n_i^1)_{T,V,n_{j\neq i}} \qquad \text{(II-6)}$$

From definition of partial molal quantities and Equation (II-5) it is evident that the chemical potential of a component in each phase is the same as the partial molal free energy in that phase, i.e.

$$\mu_i^j = \bar{G}_i^j \qquad \text{(II-7)}$$

Here, $\bar{G}_i^j$ designates the partial molal free energy of component i in phase j.

For a reversible, equilibrium change at constant T and P, in each phase,

$$dG^j = \sum_i \mu_i^j dn_i^j = \sum_i \bar{G}_i^j dn_i^j = 0 \qquad \text{(II-7)}$$

which is the condition for homogeneous equilibrium at constant T and P.

For the heterogeneous equilibrium of the polyphasic system at constant T and P,

$$dG = \sum dG^j = \sum_j (\sum_i \mu_i^j dn_i^j) = 0 \qquad \text{(II-8)}$$

For a reversible change or transfer of components between the phases at constant T and P, Equation (II-8) must be satisfied. If there were no relations between the quantity variations (dn's), the equation would be satisfied only when all $\mu$'s were zero. However, the total number of moles of each component in the closed system remains constant; hence

$$dn_i^1 = - dn_i^2 - dn_i^3 - \ldots \qquad \text{(II-9)}$$

Substituting (II-9) in (II-8) one can show that

$$\mu_i^1 = \mu_i^2 = \mu_i^3 = \ldots \qquad i = 1, 2, 3, \ldots \qquad \text{(II-10)}$$

In thermodynamics the fugacity of a component i at constant temperature is defined as

$$(d\bar{G}_i = RTd\ln\bar{f}_i)_T \qquad \text{(II-11)}$$

where $\bar{f}_i$ is the fugacity of component i in a mixture. Substituting (II-7) in (II-11) gives

$$d\mu_i = RTd\ln\bar{f}_i \qquad \text{(II-12)}$$

Integrating Equation (II-12) between two phases at equilibrium gives

$$\bar{f}_i^1 = \bar{f}_i^2 = \bar{f}_i^3 = \ldots \qquad \text{(II-13)}$$

In general, a multicomponent system would be in equilibrium when the T and P are constants and chemical potentials or fugacities of all components in all phases are the same.

Each phase of the polyphasic system will be completely specified when T, P, and composition of that phase is known. Gibbs' phase rule gives the answer to the following question (7): when the system is in equilibrium, how many intensive variables can be fixed arbitrarily?.

## A. Gibbs Phase Rule

The famous Gibbs phase rule has been described in numerous texts and papers (1, 7, 8, 11) and it can be stated as follows:

$$\text{Degrees of freedom} = (\text{number of independent components}) - (\text{number of phases}) + 2 \qquad (\text{II-14})$$

where degrees of freedom are the number of intensive properties that can be varied without changing the number of phases or the number of components in any phase.

## B. Single Component Systems

For one component the degrees of freedom would depend on the number of phases existing in equilibrium.

A pure substance can exist in a solid, liquid, or gaseous form depending on the temperature and pressure. When a single component exists in one, two, or three different phases, the degrees of freedom would be two, one, and zero, respectively.

The state of equilibrium with two coexisting phases of a one-component system is commonly called the vapor pressure curve of pure substances.

The vapor pressures of pure substances used in this investigation have been reported by numerous investigators. However, in this work the data provided by Hamblin (3) have been used.

### C. Binary Systems

Solubility of a pure hydrocarbon gas in water involves two components, the gas and the water. Addition of another component increases the possible number of phases that could exist in equilibrium. From Equation (II-14) for a zero degree of freedom there would be four phases present in equilibrium.

Since this work was an attempt in determining solubilities of hydrocarbon gases in liquid water, the temperature and pressure would be specified such that only two phases coexist in equilibrium. The degrees of freedom would be two. This would mean that the vapor and liquid compositions at equilibrium would be a function of the temperature and pressure of the system.

Solubilities of pure hydrocarbons in water have been reported by numerous investigators. Frolich, et al., have investigated the solubility of methane in water at 25 C up to pressures of 140 atmospheres. Solubility of methane in water has also been reported by Michels (44) and Culberson (13, 26) at wide temperature and pressure ranges. Olds, Sage, and Lacey (46) have reported the composition of dew point gas for the methane-water system at temperatures to 460 F and pressures to 10,000 psi.

Solubility of ethane in water has been reported by Culberson (13, 25) for temperatures of 100, 160, 220, 280, and 340 F and pressures of up to 10,000 psi. Data on ethane-water system have also been reported by Reamer, et al., (48).

Chaddock (12) has determined the phase equilibria data for the system propane-water in both the two-phase and three-phase regions. The three-phase region was studied over a temperature range, from room temperature to that temperature at which one of the phases disappeared. The two-phase region was studied at various temperatures up to 300 F and pressures up to 3000 psi. The propane-water system was also studied by Kobayashi (14).

Other pure paraffin hydrocarbon-water systems have also been studied. Normal butane-water system has been studied by Reamer, et al., (49) and Scheffer (50, 51) has studied the hexane-water and pentane-water systems up to their respective three-phase critical conditions.

## D. Ternary Systems

In the three-component system each phase will involve two concentration variables. A pressure-temperature curve for a three-component system implies coexistence of four phases since a line corresponds to one degree of freedom. Since coexistence of only two phases is desired in this study, three degrees of freedom will be available. The system will be completely defined when the T, P, and composition of one phase are fixed.

The only solubility data in a ternary system has been reported by McKetta (15). McKetta has determined the phase equilibria data for methane-n-butane-water system in both the two- and three-phase regions. Both phases were studied over a temperature range of 100 to 280 F. The pressure in the three-phase region was varied from 500 psi to the three-phase critical pressure where the liquid and gaseous hydrocarbon phases became identical. The two-phase region was studied only at 2000 and 3000 psi.

## E. Multicomponent Systems

Analysis of vapor-liquid equilibria becomes extremely complicated when more than three components are involved. Experimental data concerning the solubility of three paraffin or unsaturated hydrocarbon mixtures in water are nonexistent. However, solubility of natural gas in water and water content of natural gas have been reported by many investigators. Dodson and Standing (28) have reported the solubility of natural gas in pure and salt water at temperature ranges of 100 to 250 F and pressures of 500 to 5000 psi.

All of the investigations discussed in this chapter have shown that: (a) solubility of hydrocarbons in water increases with increasing pressure; (b) the solubility shows a minimum at a certain temperature, depending on the nature of the hydrocarbon, for a constant pressure; (c) solubility is decreased by the presence of dissolved solids in water; and (d) solubility of unsaturated hydrocarbons is greater than the solubility of paraffin hydrocarbons having the same number of carbons.

# CHAPTER III

## NATURE OF SOLUTIONS

Mixtures of two or more components whether in the gas, liquid, or solid phase have been referred to as solutions. However, Prigogine (7) defines a solution as a condensed phase (liquid or solid) composed of several components. He has stressed that: "even in very dilute solutions, it is incorrect to compare the state of the dissolved components with that of molecules in the gas state. Each dissolved molecule is subject to strong forces exerted on it by the solvent molecules. This point is clearly illustrated by the fact that the heat of solution of a solid is usually very close to the heat of fusion, and differs considerably from heat of vaporization."

Denbigh (1) has stated that solubility is not due to molecular forces, because two gases can mix in all proportions and have infinite mutual solubility. The mixing is due, not to any interaction, but to the motion of molecules and to the fact that a mixed state is more probable than the unmixed one. However, in condensed phases, the molecular forces have a definite influence on the tendency toward mixing.

Any satisfying interpretation of liquids and solutions must be a molecular theory and must involve molecular parameters. However, the oversimplifications necessary in developing the theory of condensed state and evaluation of molecular parameters limits its use. For practical purposes, it is preferred to relate the properties of liquid solutions to those of pure liquids.

Thermodynamic principles are equally applicable to pure components and solutions of fixed composition. Where variations in composition occur, the functional relations for all thermodynamic properties require one additional term for each additional component present.

Solutions can be classified on the basis of their thermodynamic properties. On this basis a distinction can be made between ideal solutions and non-ideal solutions.

## A. Ideal Solutions

The concept of ideal solutions is as valuable in a condensed phase as the concept of ideal gas is in a vapor phase. Even though an ideal solution is as nonexistent as an ideal gas, the laws of ideal solution, similar to ideal gas law for gases, provide a description of actual solutions within certain limits. A solution is considered ideal when the change of volume on mixing is negligibly small. The change of volume on mixing, $\Delta V_{mix}$, can be expressed as

$$\Delta V_{mix} = V_{mixture} - V_{components} \qquad \text{(III-1)}$$

For a mixture of components A and B

$$\Delta V_{mix} = (n_A\bar{V}_A + n_B\bar{V}_B) - (n_A\bar{v}_A + n_B\bar{v}_B) \qquad \text{(III-2)}$$

where $\bar{V}_A = (\partial V/\partial n_A)_{T,P,\text{[illegible]}_B}$ = partial molal volume of component A

$n_A$ = number of moles of component A

$\bar{v}_A$ = specific volume per mole of component A

Equation (III-2) can be rewritten as

$$\Delta V_{mix} = n_A(\bar{V}_A - \bar{v}_A) + n_B(\bar{V}_B - \bar{v}_B) \qquad \text{(III-3)}$$

For an ideal solution, $\Delta V_{mix} = 0$ which means

$$\bar{V}_A - \bar{v}_A = 0; \quad \bar{V}_B - \bar{v}_B = 0$$

or, in general, a required condition for ideal solution is

$$\bar{V}_i - \bar{v}_i = 0 \qquad \text{(III-4)}$$

The fugacity of a component in ideal solution is given as

$$RT\ln(\bar{f}_i/x_i f_i) = \int_0^P(\bar{V}_i - \bar{v}_i)dp \qquad \text{(III-5)}$$

From the definition of ideal solution, $\bar{V}_i - \bar{v}_i = 0$, it follows that

$$\bar{f}_i = x_i f_i \qquad \text{(III-6)}$$

Equation (III-6) is referred to as the Lewis-Randall rule.

The Lewis-Randall rule also implies the following facts:

Enthalpy of mixing = $\Delta H_{mix} = \sum n_i(\bar{H}_i - \bar{h}_i) = 0;$ (III-7a)

Entropy of mixing = $\Delta S_{mix} = - \sum n_i R\ln x_i;$ (III-7b)

and Free energy of mixing = $\Delta G_{mix} = \sum n_i RT\ln x_i$ (III-7c)

For an ideal solution, it can also be shown that the chemical potential of any component "i" in the mixture is

$$\mu_i^l = \mu_i^{*l}(T,P) + RT\ln x_i \qquad \text{(III-8)}$$

where $\mu_i^*(T,P)$ is the chemical potential of pure i at T and P.

Most dilute solutions consisting of molecular species similar in their attractive forces are considered to behave ideally. The familiar Henry and Raoult's laws govern the behavior of such solutions.

### 1. Henry's Law

Assuming an ideal liquid solution in equilibrium with its vapor which behaves as an ideal gas mixture; then according to Equation (II-10)

$$\mu_i^l = \mu_i^g \qquad \text{(III-9)}$$

where superscripts l and g designate liquid and gas phases, respectively.

For an ideal gas mixture, the chemical potential of any component is given as

$$\mu_i^g = \mu_i^{*g}(T) + RT\ln p_i \qquad \text{(III-10)}$$

where $\mu_i^*(T)$ is the chemical potential of pure i at unit pressure, and $p_i$ is the partial pressure of component i in the gas phase. Substituting for $\mu_i^l$ and $\mu_i^g$, according to Equations (III-8) and (III-10), respectively, will give

$$\mu_i^{*l}(T,P) + RT\ln x_i = \mu_i^{*g}(T) + RT\ln p_i \qquad \text{(III-11)}$$

Equation (III-11) can be written in a simple form as

$$p_i = k_i x_i \qquad \text{(III-12)}$$

where $k_i = \exp((\mu_i^{*l} - \mu_i^{*g})/RT)$ (III-13)

Equation (III-12) is known as Henry's law and $k_i$, given by Equation (III-13), is known as the coefficient of Henry's law. The coefficient $k_i$ is not a constant but a function of both T and P. The temperature and pressure dependence of $k_i$ are, respectively,

$$(\partial \ln k_i/\partial T)_P = \frac{h_i^g - \bar{H}_i}{RT^2} \tag{III-14}$$

$$(\partial \ln k_i/\partial P)_T = V_i^l/RT \tag{III-15}$$

For a small change in pressure, $(\partial \ln k_i/\partial P)_T$ is negligible because $V_i^l/RT$ is very small.

### 2. Raoult's Law

For a dilute solution where the mole fraction of the solvent, $x_i$, is nearly unity Equation (III-12) reduces to

$$P_i^o = k_i \tag{III-16}$$

where $P_i^o$ is the vapor pressure of the pure solvent. Substituting for $k_i$ in Equation (III-12) gives

$$p_i = P_i^o x_i \tag{III-17}$$

Equation (III-17) is known as Raoult's law. Raoult's law can also be deduced from the Lewis-Randall rule, Equation (III-6), when $p_i$ and $P_i^o$ are substituted for $\bar{f}_i$ and $f_i$, respectively.

## B. Non-Ideal Solutions

Hildebrand classifies liquid solutions on the basis of molecular structure and intermolecular forces as: ideal, athermal semi-ideal, regular, associated and solvated (4).

### 1. Athermal Semi-Ideal Solutions

For these solutions, the change in volume and enthalpy on mixing is zero, but the entropy of mixing is given as

$$\Delta S_{mix} = - R\sum n_i \ln \phi_i \qquad \text{(III-18)}$$

$$\phi_i = n_i \bar{v}_i^f / \sum n_i \bar{v}_i^f$$

and the free volume, $\bar{v}_i^f$, is defined as the effective space occupied by individual molecules per mole. The entropy of mixing for athermal solutions is always greater than that for ideal solutions. However, the free energy of mixing is smaller than that for ideal solutions. In all cases, athermal solutions show negative deviations from Raoult's law.

### 2. Regular Solutions

These solutions show a positive heat of mixing, zero or negligible volume of mixing and an entropy of mixing equal to that of ideal solutions. Regular solutions show a positive deviation from Raoult's law. Positive enthalpy of mixing would cause the free energy of mixing for regular solutions to be greater than that for ideal solutions.

### 3. Associated and Solvated Solutions

These solutions deviate from ideality with respect to both entropy and heat of solution. Associated solutions show a positive enthalpy of mixing (endothermic) and an entropy of mixing greater than that of ideal behavior.

Solvated solutions are recognized with a negative heat of mixing (exothermic) and an entropy of mixing smaller than that of ideal solutions.

The chemical potential for non-ideal solutions is given as

$$\mu_i = \mu_i^*(T,P) + RT\ln \gamma_i x_i \qquad \text{(III-19)}$$

where $\gamma_i$ is the activity coefficient of component i. The values of $\mu_i^*(T,P)$ and $\gamma_i$ depend on the choice of ideal reference system. Activity coefficients are of particular interest because they enable one to use equations for non-ideal solutions which have the same form as the equations for ideal solutions.

Equation (III-19) as it stands does not provide a complete definition of $\gamma_i$, because $\mu_i^*(T,P)$ is also an unknown. The definition of both $\gamma_i$ and $\mu_i^*$ becomes complete as soon as a reference state is chosen. A reference or standard state specifies the conditions under which $\gamma_i$ becomes equal to unity. For solutions in which all of the components, in their pure states, are liquids at the temperature and pressure of the solution, the activity coefficient is taken as approaching unity as mole fraction approaches unity. Thus,

$$\begin{aligned} &\mu_i = \mu_i^* + RT\ln \gamma_i x_i \\ &\gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 1 \end{aligned} \qquad \text{(III-20)}$$

For solutions in which some of the components are gases or solids at the T and P of the solution, one should distinguish between the solvent and the solutes.

$$\text{Solvent: } \mu_o = \mu_o^* + RT\ln \gamma_o x_o \text{ and } \gamma_o \rightarrow 1 \text{ as } x_o \rightarrow 1$$

$$\text{Solutes: } \mu_i = \mu_i^* + RT\ln \gamma_i x_i \text{ and } \gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 0 \qquad \text{(III-21)}$$

The product of activity coefficient and mole fraction is defined as the activity. Thus,

$$\text{Activity} = a_i \equiv \gamma_i x_i \qquad \text{(III-22)}$$

For ideal solutions where $\gamma_i = 1$, the activity will be the same as the mole fraction. However, for non-ideal solutions the activity will be less than the mole fraction for regular and associated solutions and greater than the mole fraction for the athermal and solvated solutions.

The activity coefficient of any component i in a solution, $\gamma_i$, is a function of T, P, and composition of the solution.

The effect of temperature on the activity coefficient, at constant pressure and composition, is given as

$$(\partial \ln \gamma_i / \partial T)_{P,x_i} = (\bar{h}_i - \bar{H}_i)/RT^2 \text{ for } \gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 1$$

and

$$(\partial \ln \gamma_i / \partial T)_{P,x_i} = (\bar{H}_i^o - \bar{H}_i)/RT^2 \text{ for } \gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 0 \qquad \text{(III-23)}$$

where $\bar{H}_i^o$ is the partial molal enthalpy of component i at infinite dilution.

The effect of pressure on the activity coefficient, at constant T and $x_i$, is given as

$$(\partial \ln \gamma_i/\partial P)_{T,x_i} = (\bar{V}_i - \bar{v}_i)/RT \text{ for } \gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 1$$

and $$(\partial \ln \gamma_i/\partial P)_{T,x_i} = (\bar{V}_i - \bar{V}_i^o)/RT \text{ for } \gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 0$$

(III-24)

where $\bar{V}_i^o$ is the partial molal volume of component i at infinite dilution.

The effect of composition on the activity coefficient, at a constant T and P, is given as

$$\sum x_i(\partial \ln \gamma_i/\partial x_i)_{T,P} = 0 \qquad \text{(III-25)}$$

Equation (III-25) is known as the Gibbs-Duhem equation. For a solution composed of two components A and B, Equation (III-25) reduces to

$$x_A(\partial \ln \gamma_A/\partial x_A)_{T,P} = x_B(\partial \ln \gamma_B/\partial x_B) \qquad \text{(III-26)}$$

knowing that

$$dx_A = - dx_B$$

Consider component A as the solvent whose activity coefficient is already known. The activity coefficient of the solute, component B, can be determined from Equation (III-26).

Solubility of a gas or mixture of gases in a liquid can be determined if the individual activity coefficients can be calculated.

The individual activity coefficients in a general multicomponent system is related to the excess molal free energy as

$$\ln \gamma_i = (\partial n_t G^E_{1-N}/\partial n_i)_{P,T} \qquad \text{(III-27)}$$

where $n_t = n_1 + n_2 + \ldots$

$N$ = number of components

and
$$G^E_{1-N}/RT = \frac{1}{2}\sum_{i=1}^{N}\sum_{i=j}^{N} x_{ij}(B_{ij} + C_{ij}(x_i - x_j) + D_{ij}(x_i - x_j)^2 + \ldots) \tag{III-28}$$

The constants $B_{ij}$, $C_{ij}$, and $D_{ij}$ are known as the Redlich-Kister constants. In the development of Equations (III-27) and (III-28) the ternary and higher constants plus some other correction factors have been neglected.

One can see that determination of solubility as outlined above would be extremely complicated even for a ternary system. Besides the complication involved in applying Equations (III-27) and (III-28), the constants $B_{ij}$, $C_{ij}$, and $D_{ij}$ cannot be determined accurately. Before suggesting correlations for obtaining solubility of hydrocarbon gaseous mixtures in water, a discussion of behavior of gaseous mixtures is in order. The following chapter will contain pertinent information concerning the equations of state governing gaseous mixtures.

# CHAPTER IV

# GASEOUS MIXTURES

## A. Equations of State for Pure Gases:

### 1. Empirical Equations of State

Since the classical work of van der Waals in 1873, a large number of equations of state have appeared in the literature (52). The number of equations of state proposed to date exceeds one hundred. Most of these equations have a theoretical basis, but some are strictly empirical but able to predict P, V, T values in reasonably good agreement with experimental data used to prepare the correlations. Among the numerous equations of state available only a few have found extensive applications. Some of these are given in Table (IV-1). A detailed and comprehensive account of equations of state for pure components has been given by Satter (17) and Shah (52).

### 2. Theorem of Corresponding States

The corresponding state principle was introduced by van der Waals before 1900. Today it is considered one of the most useful by-products of van der Waals equation. According to this principle, all pure fluids have the same compressibility factor at the same reduced pressure and temperature. The reduced conditions of density, pressure, temperature, and volume are defined as

$$\rho_r = \rho/\rho_c,\ P_r = P/P_c,\ T_r = T/T_c,\ \text{and } V_r = V/V_c \qquad \text{(IV-12)}$$

where $\rho_c$, $P_c$, $T_c$, and $V_c$ are the critical density, pressure, temperature, and volume, respectively. According to Equation (IV-11) and the corresponding states principle, the critical compressibility factor for all pure fluids should be the same. However, the $Z_c$ values range from 0.20 to 0.30. Therefore, the principle of corresponding states is only an approximation.

There have been many attempts to refine the prediction of gas compressibility factor by correcting $T_c$ and $P_c$ or introducing third, fourth, and even fifth parameters other than $P_r$ and $T_r$.

Some of the third parameters proposed are Meissner and Seferian's $Z_c$, Pitzer's accentric factor, and Sarem's molecular refraction (16). In a recent work McLeod (16) has suggested using the Eykman molecular refraction as a third parameter rather than the Lorentz-Lorenz molecular relationship used by Sarem.

One of the most recent extensions of corresponding states which contains more than three parameters is given by Stiel (53) as

$$Z = f(kT/\epsilon,\ P\sigma_0^3/\epsilon,\ a/\sigma_0,\ \lambda^2/\epsilon\sigma_0^3,\ hp/\sigma_0(m\epsilon)^{\frac{1}{2}}) \qquad \text{(IV-13)}$$

where the dimensionless group $a/\sigma_0$ represents shape effects, $\lambda^2/\epsilon\sigma_0^3$ the effects of dipole-dipole interactions, and $hp/\sigma_0(m\epsilon)^{\frac{1}{2}}$ quantum effects which are present in certain molecules such as hydrogen and helium at low temperatures. In Equation (IV-13) the symbols $k$, $\epsilon$, $\sigma_0$, $\lambda$, hp, and m designate Boltzmann's constant, maximum energy of interaction, shortest distance between molecular cores when the potential energy is zero, dipole moment of molecule, and Planck's constant, respectively.

Equation (IV-13) would be correct for simple molecules such as argon, krypton, and xenon, when only the first two groups are used. The corresponding potential function in this case would be that of Lennard-Jones. Inclusion of the third and fourth group would make Equation (IV-13) applicable for non-polar gases and polar fluids. Finally, the inclusion of the fifth group would allow for the quantum corrections to the various intermolecular potentials.

A review of the current theory and practice of the corresponding states principle has been presented by Leland and Chappelear (42). They have credited the corresponding states principle as the most powerful tool available for quantitative prediction of the physical properties of pure fluids and their mixtures.

## B. Equations of State for Mixture of Gases:

### 1. Empirical Equations of State

The various equations of state for pure fluids, given in Table (IV-1), may be extended to mixtures of fluids by combination of constants for the separate pure components. It can be shown that Amagat's rule of additive volumes and Dalton's law of additive partial pressures hold exactly for mixture of ideal gases.

For other empirical relations, the pure component constants may be combined in one of the following ways:

$$\text{Linear combination:} \quad K_m = \sum y_i K_i \qquad \text{(IV-14)}$$

where $K_i$ represent the constants in equations of state for pure components, $y_i$ the mole fractions, and $K_m$ the constant in the equation of state for mixture.

$$\text{Square root combination: } K_m = (\sum y_i K_i^{\frac{1}{2}})^2$$

$$\text{Cube root combination: } K_m = (\sum y_i K_i^{1/3})^3 \qquad \text{(IV-15)}$$

$$\text{Lorentz combination: } K_m = (1/8)\sum_i \sum_j y_i y_j (K_i^{1/3} + K_j^{1/3})^3 \qquad \text{(IV-16)}$$

For van der Waals equation of state, the linear combination is used for constant b and the square root rule for constant a. For other equations of state, considerable work has been done to determine the best combining rule for the constants. For example, it appears that for Bendict-Webb-Rubin equation of state, considerable accuracy is achieved by using a linear combination for constant $B_o$, square root combination for constants $A_o$, $C_o$, and $\gamma$, and cube root combination for constants a, b, c, and $\alpha$. The combination rules for different constants are not strict. They may be changed to obtain a better fit to experimental data. Avasthi and Kennedy (19) have developed an equation of state for gaseous hydrocarbon mixtures. The equation predicts molal volumes with an average absolute deviation of less than 1 per cent when applied to 264 natural gas and condensate systems including over 2000 PVT points. In this equation the residual volume, i.e., the difference between the molal volume and a reference volume, is related to P, T, and composition by use of 22 empirical constants. The equation and its constants for a wide T and P range are given in Appendix C.

The pressure or volume explicit form of the virial equation of state may also be used for multicomponent mixtures containing both non-polar and polar components. The second and third virial coefficients for a mixture of N components is given as

$$B_{mix} = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j B_{ij} \tag{IV-17}$$

$$C_{mix} = \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} y_i y_j y_k C_{ijk} \tag{IV-18}$$

where $B_{11}$, $C_{111}$, $B_{22}$, and $C_{222}$ are the second and third virial coefficients of pure components 1 and 2, respectively. The second virial coefficient characterizing the interaction between one i molecule and a j molecule, $B_{ij}$, is directly related to the intermolecular potential $\psi_{ij}$. The third virial coefficient characterizing the interaction between two i molecules and a j molecule, $C_{iij}$, or between one i molecule and two j molecules, $C_{ijj}$, can be calculated from statistical-mechanical formula once the three potential functions $\psi_{11}$, $\psi_{22}$, and $\psi_{12}$ are specified (15).

The compressibility factor equation, Equation (IV-11), for a mixture of real gases may also be written in terms of an average compressibility factor $Z_m$. Thus,

$$P\bar{v} = Z_m RT \tag{IV-19}$$

The average compressibility factor, $Z_m$, is a function of T, P, and composition of the mixture. Where volumes are additive at constant T and P, $Z_m$ is an additive property of compressibility factors of the individual fluids.

### 2. Theorem of Corresponding States

In order to apply the corresponding states principle to a mixture of fluids, a scheme should be devised for calculating the reduced properties of the mixture. The reduced properties of a mixture based on the true critical P, V, and T of the mixture do not give the same functional relations for the compressibility factor as for pure components. There have been many attempts to find pseudocritical constants such that the compressibility factor for the mixture would follow the relationship

$$Z_m = f'_r(T'_r,\ P'_r) \qquad \text{(IV-20)}$$

where $T'_r = T/T'_c$

$P'_r = P/P'_c$

$T'_c$ = pseudocritical temperature

and $P'_c$ = pseudocritical pressure

The pseudocritical constants may be determined by means of empirical rules. One such rule suggested by Kay (37) gives

$$P'_c = \sum y_i P_{ci}$$

$$\text{and} \quad T'_c = \sum y_i T_{ci} \qquad \text{(IV-21)}$$

Since the pioneering work of Kay, many other relationships for predicting $P'_c$ and $T'_c$ have been proposed. Based on the van der Waals equation of state, Joffe (35) proposed the following relationships:

$$T'_c/(P'_c)^{\frac{1}{2}} = \sum_{i=1}^{N} y_i T_{ci}/(P_{ci})^{\frac{1}{2}} \qquad \text{(IV-22)}$$

$$T'_c/P'_c = (1/8)\sum_{i=1}^{N}\ \sum_{j=1}^{N} y_i y_j((T_{ci}/P_{ci})^{1/3} + (T_{cj}/P_{cj})^{1/3})^3$$

(IV-23)

Using statistical mechanics approach, Leland and Mueller (41) arrived at a more lengthy relationship for $T_c'$ and $P_c'$ which depends on empirically evaluated factors.

Pitzer and Hultgren (47) used experimental volumetric data for 12 binary gas mixtures at several compositions to establish values of the $T_c'$, $P_c'$, and accentric factors which permit Pitzer's tables for the compressibility factor to be used for mixtures. For the binary mixtures considered, they found that quadratic terms in the mole fractions were sufficient to relate constants to composition. Recently, Joffe and Zudkevitch (36) have extended Pitzer and Hultgren's rules to multicomponent mixtures as follows:

$$T_c' = \sum_i \sum_j y_i y_j T_{cij} \tag{IV-24}$$

$$P_c' = \sum_i \sum_j y_i y_j P_{cij} \tag{IV-25}$$

$$\omega_m = \sum_i \sum_j y_i y_j \omega_{ij} \tag{IV-26}$$

where $T_{cij}$, $P_{cij}$, and $\omega_{ij}$ $(i \neq j)$ are interaction terms which are determined from the experimental volumetric data for the binary mixture and $\omega_m$ is the accentric factor of the mixture.

Depending on the nature of the gas or gaseous mixture, one should be able to predict its properties by using one of the equations provided in this chapter.

Now that the thermodynamic principles governing the solution and gas in equilibrium with each other has been discussed separately, a correlation by which the solubility of a mixture of gases in a liquid solution can be calculated would be in order. However, since any correlation for determination of solubility of gases needs to be checked against some experimentally determined values, the following chapter will contain the apparatus and technique by which the experimental data of this study were obtained.

## TABLE IV-1

## A LIST OF EQUATIONS OF STATE FOR PURE COMPONENTS

1. Ideal Gas Equation

$$P\bar{v} = RT \qquad \text{(IV-1)}$$

2. van der Waals:

$$(P + a/\bar{v}^2)(\bar{v} - b) = RT \qquad \text{(IV-2)}$$

3. Clasius:

$$(P + a/T(\bar{v} + c)^2)(\bar{v} - b) = RT \qquad \text{(IV-3)}$$

4. Berthelot:

$$(P + a/T\bar{v}^2)(\bar{v} - b) = RT \qquad \text{(IV-4)}$$

5. Dietirici:

$$P(\bar{v} - b)\exp(- a/RT\bar{v}) = RT \qquad \text{(IV-5)}$$

6. Wohl:

$$(P + a/T\bar{v}(\bar{v} - b) - c/T^2\bar{v}^3)(\bar{v} - b) = RT \qquad \text{(IV-6)}$$

7. Redlich-Kwong:

$$(P + a/T^{.5}\bar{v}(\bar{v} + b))(\bar{v} - b) = RT \qquad \text{(IV-7)}$$

8. Beattie-Bridgeman:

$$P = (RT/\bar{v}^2)(1 - c/\bar{v}T^3)(\bar{v} + B_o(1 - b/\bar{v})) - (A_o/\bar{v}^2)$$

$$(1 - a/\bar{v}) \qquad \text{(IV-8)}$$

9. Benedict-Webb-Rubin:

$$P = RT/\bar{v} + (RTB_o - A_o - C_o/T^2)/\bar{v}^2 + (RTb - a)/\bar{v}^3 +$$

TABLE IV-1--*Continued*

$$a\alpha/\bar{v}^6 + (c/\bar{v}^3T^2)(1 + \gamma/\bar{v}^2)\exp(-\gamma/\bar{v}^2) \qquad \text{(IV-9)}$$

10. Virial Equation of State:

A. Pressure Explicit Form

$$P\bar{v}/RT = 1 + B(T)/\bar{v} + C(T)/\bar{v}^2 + \ldots \qquad \text{(IV-10A)}$$

B. Volume Explicit Form

$$P\bar{v}/RT = 1 + B'(T)/P + C'(T)/P^2 + \ldots \qquad \text{(IV-10B)}$$

11. Compressibility Factor Equation:

$$P\bar{v} = ZRT \qquad \text{(IV-11)}$$

# CHAPTER V

# EXPERIMENTAL INVESTIGATION

Solubility of methane-ethane, methane-propane, ethane-propane, and methane-ethane-propane mixtures in pure liquid water was experimentally determined. The reliability of the equipment and the experimental procedure was determined by obtaining the solubility of pure methane in water and comparing it to those reported in the literature. The experimental investigation will be presented in the following order: A. Experimental Apparatus; B. Materials Used; C. Experimental Procedure; D. Possible Sources of Experimental Error; E. Experimental Results; and F. Method of Calculating the Solubility Data from the Measured Values.

## A. Experimental Apparatus

A schematic diagram of the apparatus used in this investigation is given in Figure (V-1). The apparatus consisted of the following main sections:

### I. Equilibrium Cell

The equilibrium cell was made of stainless steel and had a rated test pressure of 37,500 psig and a volume of approximately 75 cc. Since the volume of the cell did not enter into the calculations, no attempt was made to measure its volume closer than 0.5 cc. For reasons that will be mentioned in the procedure section, this pressure cell was of ideal size for the purposes of this investigation.

A circular steel clamp with two extending supports fitted over the cell. The supports were round steel bars which were cradled in a fixed stand. One support was partially drilled to accommodate a handle to rock the cell and was operated from outside the constant temperature air bath.

The cell was equipped with four optically ground quartz glass windows approximately one inch thick. Since no visual observations were necessary and the window glasses developed leaks at pressures higher than 5000 psig, they were replaced by carefully machined stainless steel plugs having the same dimensions as the ground quartz glass.

The cell was equipped such that a thermocouple could be embedded about an inch into its upper outside face. The cell was tapped for connections at the top and the bottom.

## II. Air Bath

A constant temperature air bath was used to house the equilibrium cell, the vapor and the liquid sampling valves. The air bath was a 3' x 3' x 3' box made of plywood. The inside of the box was insulated with 3/4" insulation board and a double layer of aluminum foil which also speeded up the heating process. The box could withstand temperatures up to 300 F. The side of the box facing the operator could be removed with ease and had a double layer of safety glass with an insulating air space in between, to provide visual access to the interior of the bath.

The bath was heated by means of two three-hundred-watt lamps. Constant temperature was maintained with the aid of a thermostat and one of the lamps as the heat source. The air inside the bath was circulated by a small fan to keep the entire bath at a uniform temperature. The temperature inside the bath was measured by a thermocouple close to the back wall and a mercury thermometer next to the observation window. The temperature readings differed by 1 to 2 F with the back wall thermocouple always showing the higher temperature reading.

## III. Sampling Valves

The sampling valves were Autoclave three port valves. The 30V-4074 and 10V-2074 valves were used to obtain liquid and vapor samples, respectively. A detailed drawing of these valves are shown in Figures (V-2) and (V-3).

The valve allows continuous flow through the side ports while the bottom port can be controlled with a two piece stem. The bottom port was plugged using an autoclave plug. The space between the end of the plug and the tip of the stem was used to obtain the liquid or vapor sample. The volumes of the sample space were carefully determined to be .0197 cc and .0246 cc for the 30V-4074 (liquid sampling) valves and the 10V-2074 (vapor sampling) valves, respectively.

These particular valves were chosen because they have the following desired features:

a. they are made of 316 stainless steel. Therefore, they can be used at high pressures and over a wide range of temperatures and a wide variety of components;

b. they are compact, rugged, dependable, and have a low dead volume;

c. they have a reasonably small sample volume so that the whole sample can be injected into the chromatograph without overloading the columns or the chromatograph detector;

d. the two piece stem makes a dependable seal against high pressure fluids and it does not rotate against the valve seat;

e. they allow flow to pass through whether they contain a sample or not. This is important when purging the valve with the mixture to be sampled and for placing it in the carrier gas flow stream;

f. they are machinable. Therefore, the sample space can be made in different sizes in order to get reasonable size samples of a fluid at any pressure;

g. the small quantities required for chromatographic analysis allow many samples to be taken from a high pressure cell before recharging it.

The ability to obtain small samples and analyses by a chromatograph offers a considerable improvement over the methods used in the past. The advantages will be discussed in a later section in this chapter.

## IV. Pressure Pump

A motor driven Ruska mercury pump having a volumetric capacity of 100 cc and calibrated in .01 cc increments was used to pressurize the system. A 25,000 psig Heise pressure gauge with 50 psi divisions was attached to the pump.

Mercury could be admitted to the pump or withdrawn from it by means of a reservoir connected to the pump.

## V. Auxiliary Pressure Cells

Two stainless steel blind cells having a working pressure of 15,000 psig were used for pressurizing the system. The volumes of these cells, numbers 15 and 17 in Figure (V-1), are 500.5 cc and 648.0 cc, respectively.

These cells were used to obtain pressures greater than 1000 psig in the equilibrium cell.

## VI. Chromatograph

An operable chromatograph was constructed from commercially available components. A schematic diagram showing the combined units is given on Figure (V-4). A Model A-650 Varian Aerograph hydrogen generator, capable of generating air and hydrogen, was connected to an Aerograph Model 600-C single-column gas chromatograph which incorporates a hydrogen-flame ionization detector. The Model 600-C contains a separately heated injector tube which permits either flash-vaporized or on-column injections. The oven contains both the column and the detector.

The column was packed with a porous polymer composed of ethylvinyl benzene crosslinked with divinylbenzene to form a uniform structure of a distinct pore size (33). This material is referred to as Porpak. The specific Porpak used is called Porpak R. Porpak R efficiently separates peaks for $C_1$ to $C_4$ hydrocarbons, and this separation is performed at 100 C on a six-foot column made of 1/8 inch stainless steel tubing.

The Model 600-C Aerograph gas chromatograph provided a suitable attenuation of sample signals to a Honeywell Brown Electronik recorder. The recorder has a range of -.05 to +1.05 millivolt.

Pure, dry helium was used as the carrier gas for all analyses. Brooks Instrument "Sho-Rate 150" flow controller was used to control the carrier gas flow.

The hydrogen and air flow rate were controlled by means of a knob and a flow meter in the hydrogen generator unit.

The liquid and gas samples were heated by means of an electric heater before injection into the chromatograph.

## VII. Miscellaneous

### a. Pressure Gauges

The pressure in the equilibrium cell was read by means of three Marsh pressure gauges connected to each other and the equilibrium cell in the manner shown in Figure (V-1).

The pressure gauges used to read the equilibrium cell pressure were all placed outside the air bath so that they will not be subjected to the high temperatures inside the box.

The pressure gauge closest to the box, No. 3 in Figure (V-1), has a range of 10,000 psig and divisions of 200 psi. The pressure gauge in the middle, No. 2 in Figure (V-1), has a range of 5000 psig and divisions of 100 psi. The pressure gauge farthest from the bath, No. 1 in Figure (V-1), has a range of 1000 psig and divisions of 20 psi. Using these pressure gauges in series provided a reading of the pressure in the equilibrium cell within an accuracy of 1 per cent independent of the pressure range.

In order to protect the operator from any mishap, a ½ inch clear lucite sheet was mounted over the pressure gauges.

Another Marsh pressure gauge, No. 7 in Figure (V-1), having a pressure range of 200 psig and divisions of 1 psi was placed inside the air bath. This gauge was used to read the pressure at which the gas samples were obtained.

### b. Safety Equipment

To achieve accurate gas analysis, the gas samples should be obtained at pressures lower than 100 psi. To prevent subjecting the 200 psig range gauge to the high pressure in the equilibrium cell, the following safety precautions were taken:

1. A small amount of the gas coming out of the cell at pressures greater than a few thousand psi could be trapped in a 4-inch-long piece of 1/8 inch o.d. stainless steel tubing connected between two autoclave high pressure valves. The pressure of the gas, when expanded through the rest of the sampling system, reduced to below 70 psig.
2. As an additional safety precaution during the operation, a safety disk, having a maximum rapture pressure of 100 ± 5 psig, was installed in the flow system between the sampling valves and the pressure gauge.
3. The valves, safety disk, and the pressure gauge were all connected securely to a piece of angle iron attached to the equilibrium cell. This made it possible to rock the equilibrium cell without subjecting the fittings and tubing to any extra stress.

### c. Potentiometer and Thermocouples

Two iron-constantan thermocouples were used. One was embedded in the cell wall to measure its temperature and the other was located in the air bath to measure the bath temperature. A highly sensitive Leeds and Northrup Potentiometer having an accuracy of ± .001 millivolts was used to measure the temperatures within ± .05 F.

### d. Valves, Fittings, and Tubing

In this investigation, 1/8 inch o.d. stainless steel tubing capable of withstanding pressures up to 15,000 psig were used. All the valves and fittings were also made of stainless steel, manufactured by Autoclave, and had a working pressure of 15,000 psig.

### B. Materials Used

Gases used in this investigation were Phillips Petroleum Company pure grade (99% minimum purity) methane. The ethane and propane were research grade (99.9% purity).

The water used was obtained from the distilled water supply of the Petroleum Engineering Department. The distilled water was vigorously boiled to expel dissolved air, and was then stored in air-tight volumetric flasks until it was used.

### C. Experimental Procedure

The discussion of the procedure used in obtaining the experimental data can be divided into the following major parts:

#### I. Preliminary Preparations

After the apparatus was assembled as shown in Figure (V-1), the entire system was evacuated before each run for several hours.

The pressure gauges were checked against a dead weight tester and were adjusted by the zero adjuster provided in each gauge.

The thermocouples were calibrated against a standard iron-constantan thermocouple. The discrepancies between the iron-constantan thermocouples used in this work and the standard one were always less than 0.4 F. Since an accuracy of 1 to 2 F could be tolerated, a small deviation of 0.4 F was considered negligible.

The consistency of the chromatograph was tested by analyzing about five identical samples of each of the pure hydrocarbons, while the hydrogen, air, and helium (carrier gas) flow rates, the oven and injection temperatures, the range, and the attenuation of the signal to the recorder were kept constant. Similar tests were run on different dates throughout this investigation. The results of these consistency tests are given in Table (V-1).

The accuracy of the chromatographic analysis was checked by analyzing a standard sample whose composition was known. The standard sample was obtained from a Phillips 66 plant. In addition, mixtures of methane, ethane, and propane at pressures below 50 psig were prepared using the compressibility factor equation for mixtures, i.e., Equation (IV-19). The compressibility factors were obtained from Sage and Lacey (9). There was excellent agreement between the given and measured composition for the standard sample and the gaseous mixtures prepared in the laboratory. This agreement is given in Table (V-2).

Calibration curves showing the amounts of pure methane, ethane, and propane against the area under each peak are shown in Figures (V-5), (V-6), and (V-7), respectively.

In order to make sure that only two phases, liquid phase (water) and vapor phase (hydrocarbon and water mixture), will coexist at equilibrium, it was necessary to calculate the critical temperature of the hydrocarbon mixture. At temperatures above the critical temperature of the gaseous mixture, the absence of hydrocarbon liquid phase can be insured. The critical temperatures for $C_1$-$C_2$, $C_1$-$C_3$, $C_2$-$C_3$, and $C_1$-$C_2$-$C_3$ mixtures were determined using equations developed by Grieves and Thodos (32). The critical temperature of the $C_1$-$C_2$ and $C_1$-$C_3$ mixtures have been plotted against the mole fraction of $C_1$ in the mixture and is shown in Figures (V-8) and (V-9), respectively. The critical temperature of the $C_2$-$C_3$ mixture has been plotted against the mole fraction of $C_2$ and is shown in Figure (V-10). The critical temperature for the $C_1$-$C_2$-$C_3$ mixture has been plotted against the mole fractions of $C_1$, $C_2$, and $C_3$ and is shown in Figure (V-11). The method and computer programs by which the critical temperatures of the different mixtures were calculated is given in Appendix E.

It was decided to obtain the solubility of the hydrocarbon mixtures at temperatures of 100, 160, and 220 F. This decision was based on the fact that most of the pure paraffin solubility data reported in the literature are at the above-mentioned temperatures. Hence, it was hoped that some sort of a simple relationship would be found between the solubility of the pure components and their mixtures.

Once the temperatures for the experimental investigation was set, the composition of the binary and ternary hydrocarbons in the gas had to be chosen such that the predetermined temperatures would be higher than the critical temperature of the mixture.

In order to have a certain composition in the gas phase, some calculations were necessary to determine how much of each component should be injected into the system. A sample of such a calculation is given in Table (V-3)

A study of the time it would take the equilibrium cell to reach 100, 160, and 220 F was undertaken. Approximately $\frac{1}{4}$, 3, and 8 hours were necessary for the equilibrium cell temperature to attain 100, 160, and 220 F, respectively.

The cell temperature was always 4 to 10 F higher than the air bath temperature. This was attributed to heat transfer by radiation from the lamps to the cell and the large mass and heat capacity of the cell. The thermostat was adjusted such that the cell rather than the bath temperature would remain constant.

In order to find the temperature difference between the wall and the contents of the equilibrium cell, one thermocouple was inserted inside the cell to a point where it was immersed in the liquid water contained in the cell while the other thermocouple was embedded in the upper outside wall of the cell. When the cell had been heated for at least an hour, the wall temperature was always about 0.5 to 0.8 F higher than the inside temperature.

## II. Charging the Equilibrium Cell

Before injecting any material into the cell, it was heated to the desired temperature and evacuated as discussed in the previous section. The valves H, G, and E were closed. At pressures below 1000 psig, the valves to the auxiliary cells and the pressure pump, i.e., K and L as shown in Figure (V-1), were closed. The equilibrium cell was charged directly from the hydrocarbon cylinder. The heaviest hydrocarbon was always injected first and the lightest last. The approximate composition of the vapor phase was calculated as shown in Table (V-3). Therefore, the hydrocarbons were injected in order, until the proper pressures were obtained. Then, valves J and N were closed and valve K opened, and pure water was injected into the equilibrium cell. Noting the readings on the pump, enough water was injected until there was 35 cc of water in the cell. The amount of water in the cell is significant. If there is too much water in the cell, the volume of the vapor is small; efficient mixing may not take place between the two phases. If the volume of water is too small, the sampling port may be exposed to the vapor phase and result in poor liquid samples.

Once the water was injected, valve F was closed. The pressure in the pump was reduced to atmospheric pressure, and the liquid sampling valves and valve I were disconnected from the equilibrium cell. If the final pressure in the cell was to be higher than 1000 psig, valve A was closed, and if it was to be higher than 5000 psig, valve B was also closed.

Since the temperature of the cell decreased while the cell was charged, the thermostat was set and the cell heated until the equilibrium temperature was reached. The equilibrium pressure in the cell was established.

When equilibrium pressures higher than 1000 psig were desired depending on the pressure, one or both of the auxiliary cells were also filled with the hydrocarbon mixture. Then, liquid water was pumped into the auxiliary cell or cells and the hydrocarbon mixture displaced into the equilibrium cell. When the pressure in the equilibrium cell was close to the equilibrium pressure desired, valves N and J were closed. Now, enough water was injected through valve K until there was 35 cc of water in the equilibrium cell. Then, the procedure discussed above was followed.

To achieve equilibrium faster, the cell and its contents were rocked by means of a handle extending to the outside of the air bath. Most experimenters in the past have chosen to rock the equilibrium cell, within a maximum of ± 30 degrees from the vertical, for mixing purposes. Most equilibrium cells have a small volume, and the ratio of height to diameter is of the order of 8 to 10. Hence, rocking ± 30 degrees off the vertical would result in only splashing the liquid contents against the walls. The equilibrium cell used in this study was of ideal size because it has a height to diameter ratio of less than 5. Besides, the cell was rocked within approximately ± 180 degrees from the vertical to accomplish as thorough a mixing as possible.

The cell was rocked intermittently every 10 or 15 minutes.

## III. Sample-Taking Technique

Since the liquid and gas samples were obtained in different manners, the discussion in this section will be divided into the following two parts:

### a. Liquid Samples

To obtain liquid samples, the liquid sample valves, i.e., two specially designed Autoclave three-way valves were connected to the valve F of the equilibrium cell. The sampling system was evacuated. The sampling valves were closed and thus trapping only vacuum in the sample space. Valve C was closed. Valve F was barely cracked open to allow the liquid (water plus the dissolved hydrocarbons) to occupy the sampling system.

Valve C was opened slightly to allow a few liquid drops, plus the vapor produced as a result of flashing the liquid, to leave the sampling system.

Valve C was closed and the sampling system was allowed to re-establish temperature equilibrium. Then, the sampling valves were opened momentarily and closed again, and thus the liquid was trapped in the sample space.

The connection at F was broken and the liquid samples were ready to be analyzed.

Two sampling valves were used to check the uniformity of the obtained samples.

To determine whether the system had reached equilibrium or not, three sets of liquid samples at three hour intervals were obtained. It was seldom necessary to wait more than six hours to attain equilibrium. However, the six hour period was after the equilibrium cell and its contents had reached the desired temperature.

The system pressure dropped slightly (approximately 200 psi at 8000 psi system pressure) after each set of liquid samples was obtained.

b. Gas Samples

To obtain gas samples, two specially designed Autoclave three-way valves were used. The sample space in these valves (10V-2074) was slightly larger than the liquid sample space in the 30VM-4074 valves. It thus provided a suitable sample size for chromatographic analysis.

The gas sample was taken as follows. First, valves D and G were closed. Then, valve H was slightly opened and then closed again. Valves E and G were opened and the gas was purged through the sampling system and they were shut again. Valve H was opened and closed to allow some gas to be trapped between valves H and G. Valve G was opened, keeping valve E closed, and the trapped gas was permitted to flow until a pressure of 50 psig was indicated by the pressure gauge (No. 7 in Figure (V-1)). Now, the sampling valves were closed, hence trapping samples of the gaseous mixture at 50 psig. After making sure valves H and G were closed, valve E was opened to release the pressure in the sampling system.

The gas sampling valves were disconnected from the rest of the system and were taken to be analyzed.

Valve D was reopened and the system pressure was read. Since the amount of gas used to obtain the gas samples was very small, the drop in the system pressure was far below the accuracy of the pressure gauges to be noticable.

The cell was usually charged to the highest pressure to be studied at each temperature. After the gas and liquid samples were taken, the cell pressure was reduced to the next pressure level. This was continued until all the necessary data at one temperature and different pressures were obtained. The variation in the gas composition throughout a set of runs at a set temperature was negligibly small.

Two gas samples were taken to test the uniformity of the obtained samples.

The gas samples for all mixtures (binary and ternary) at all temperatures and pressures were taken at 50 psig. However, the liquid samples were obtained at the system pressure.

## IV. Gas and Liquid Analysis

The same technique was used in analyzing both gas and liquid samples. The sampling valves were connected as shown in Figure (V-4). They were heated, using an electric plate heater, until their temperature was higher than 250 F. Hence, it was made sure that the contents would flash into the column in the chromatograph when the valve was opened. The heating process required 10 to 15 minutes. Meanwhile, any excess material in the valves was carried through by the carrier gas.

Each liquid and gas sample was analyzed separately, and the peak height of each component was recorded.

Since the chromatograph was equipped with a flame ionization detector unit, no water peak was observed.

The water vapor carried through the column in the chromatograph served as a cleaning agent.

The amount of water in the gas samples could be neglected at pressures higher than 2000 psig. At lower pressures, they could be calculated by a method recently proposed by Sharma (18).

The mole fraction of water was taken to be the difference between unity and the total mole fractions of the hydrocarbons dissolved in it. The mole fraction of the dissolved hydrocarbons in each liquid sample could be determined from the observed peaks in the analysis of that sample.

### D. Possible Sources of Experimental Error

Temperature, pressure, and composition were the only properties which were measured throughout this investigation. The temperatures were measured to an accuracy of ± .05 F. Since an error of ± 1 F would not affect the results significantly, the temperature measurements could not be considered as a source of considerable error.

The pressure measurement could be considered as a source of experimental error because the errors in the pressure measurements of the system were of the order of 1 per cent regardless of the pressure range. This error could be slightly reduced by using more accurate gauges.

The impurity of the hydrocarbons used could be considered as another possible source of error. Among the hydrocarbons used, methane had a purity of 99%, ethane and propane were 99.9% pure. The gas and liquid compositions were determined by chromatographic analyses. As shown in Tables (V-1) and (V-2), the analyses proved to be both consistent and accurate. However, the gas and liquid analyses could be considered as a third possible source of error.

The ability to obtain liquid samples at the system pressure and its analysis by a chromatograph proved to be a tremendous improvement over the past techniques which made use of chemical trains and employed gravimetric techniques to determine the amount of each component.

Due to all the factors mentioned above, the maximum possible error in the experimental data obtained could not be greater than 2 to 3 per cent.

As was mentioned previously, the reliability of the results obtained in this study was determined by checking the values obtained for the solubility of pure methane with those given by Culberson (13). The comparison at temperatures of 100 and 160 F and pressures up to 5000 psig is presented in Table (V-4). The deviations are insignificant and most probably due to the crude techniques employed in the past.

## E. Experimental Results

In order to determine the effects of temperature, pressure, and composition on the solubility of hydrocarbon mixtures in water, the following systems at different temperatures, pressures, and compositions were investigated: I. Methane-Water; II. Methane-Ethane-Water; III. Methane-Propane-Water; IV. Ethane-Propane-Water; and V. Methane-Ethane-Propane-Water.

A survey of the experimental data is given in Appendix D.

The hydrocarbon-water systems investigated will now be discussed in order.

### I. Methane-Water System

To test the reliability of the experimental measurements obtained in this work, solubility of pure methane at temperatures of 100 and 160 F under pressures of 500, 2000, 3000, and 5000 psi was determined. These values are shown in Figure (V-12). The smoothed values from Figure (V-12) are compared with those given by Culberson (13) in Table (V-4). The agreement seems to be reasonably good.

## II. Methane-Ethane-Water Systems

The effect of temperature on the solubility of $C_1$-$C_2$ mixture was determined by measuring the solubility of a mixture containing 49.90 mole per cent methane and 50.10 mole per cent ethane at temperatures of 100, 130, 160, 190, and 220 F under a pressure of 5000 psia.

The effect of pressure and composition on the solubility of $C_1$-$C_2$ mixture was determined by measuring the solubility of five mixtures at 160 F and five pressures. The compositions, temperatures, pressures, and the total solubility of the different $C_1$-$C_2$ mixtures are given in Table (V-5).

## III. Methane-Propane-Water Systems

Since the solubility of pure or hydrocarbon mixtures in water does not change very much with temperature, the solubility of $C_1$-$C_3$ mixtures was studied only at 220 F. This particular temperature was chosen because it is higher than the critical temperatures of both components.

The pressure and composition effects on the solubility of $C_1$-$C_3$ mixtures were determined by measuring the solubility of five mixtures at five pressures. The compositions, pressures, and the total solubility of the different $C_1$-$C_3$ mixtures are given in Table (V-6).

## IV. Ethane-Propane-Water Systems

Solubility of five mixtures of $C_2$-$C_3$ in water was measured at 220 F and five pressures. The compositions, pressures, and the total solubility of the different $C_2$-$C_3$ mixtures are given in Table (V-7).

### V. Methane-Ethane-Propane-Water Systems

Solubility of a mixture containing 70.15 mole per cent methane, 10.65 mole per cent ethane, and 19.20 mole per cent propane was measured at 160, 190, and 220 F under a pressure of 5000 psia.

To determine the effect of composition and pressure on the solubility of $C_1$-$C_2$-$C_3$ mixtures in water, solubilities of five mixtures under five pressures were measured. The compositions, temperatures, pressures, and the total solubility of the different $C_1$-$C_2$-$C_3$ mixtures are given in Table (V-8).

## F. Method of Calculating Solubility Data from the Measured Values

As was mentioned previously in this chapter, the gas and liquid compositions were measured by chromatographic analysis of each sample. The discussion in this section can be divided into two separate parts: I. Determination of Gas Phase Composition; and II. Determination of Liquid Phase Composition.

### I. Determination of Gas Phase Composition

In this part a sample calculation of the gas phase composition from the measured values will be given. The calculation given below is for a gas sample containing methane, ethane, propane, and water. The calculation method for a gas sample containing a mixture of two hydrocarbons and water or one hydrocarbon and water can be deduced from the following calculation.

The sample calculation given here is for Mixture 20. The sample was obtained at a pressure of 50 psig and a temperature of 220 F. The peak heights for individual components were measured from the recorder chart. From Figures (V-5), (V-6), and (V-7) the number of moles for $C_1$, $C_2$, and $C_3$ were found, respectively, to be

| Components | Measured Peak Height Tenth of Inch | lb moles x $10^9$ | Normalized Mole Per Cent |
|---|---|---|---|
| $C_1$ | 11.4 | 2.048 | 25.94 |
| $C_2$ | 26.0 | 2.760 | 35.58 |
| $C_3$ | 21.8 | 3.082 | 38.48 |
| $H_2O$ | 0 | 0 | 0 |
| Total: | | 7.890 | 100.00 |

The amount of water in the gas phase was considered to be negligible. The mole per cent of each component, on dry basis, was determined by dividing the number of moles of each component by the water-free total number of moles.

## II. Determination of Liquid Phase Composition

As mentioned earlier in this chapter, the liquid sample was obtained at the temperature and pressure of the system. Similar to part I, the sample calculation given below is for the general case where the liquid sample contains methane, ethane, propane, and water. The calculation for the specific cases, such as hydrocarbon-hydrocarbon-water, or hydrocarbon-water samples, can be deduced from the general case.

The sample calculation given here is for Mixture 20 at 220 F and 4000 psi. The peak heights for individual components were measured from the recorder chart. The number of moles of $C_1$, $C_2$, and $C_3$ were obtained from Figures (V-5), (V-6), and (V-7), respectively. The number of moles of water could be calculated if the density of water at the specific temperature and pressure was known. Kobayashi (14) has determined the effects of the dissolved hydrocarbons on the density of water at temperatures ranging from 100 to 250 F and pressures from 1000 to 5000 psi. Using the experimental data provided by Kobayashi, the density of pure water has been plotted against the density of water saturated with hydrocarbons for pressures of 1000,2000, 3000, 4000, and 5000 psi and is shown in Figure (V-13).

The density of pure water at temperatures from 100 to 250 F, and pressures from 1000 to 5000 psi is shown in Figure (V-14).

The density of water saturated with hydrocarbons can be determined in the following way: first, the density of pure water at the specific T and P is read from Figure (V-14); then, the density of water saturated with hydrocarbons is found from Figure (V-13).

The number of moles of water is determined as follows:

Density of pure water at 220 F and 4000 psi = .9615 g/cc

Density of water saturated with hydrocarbons
at 220 F and 4000 psi, from Figure (V-13) = .9660 g/cc

Mass of water in the sample space = (.0197 cc)(.9660 g/cc)

" = .01905 g

$$\text{Gram-moles of water} = \frac{.01905 \text{ g}}{18.016 \text{ g/g-mole}} = 1.057 \times 10^{-3} \text{ g-mole}$$

$$\text{Lb- moles of water} = 1.057 \times 10^{-3} \times \frac{\text{lb-mole}}{453.6 \text{ g-moles}}$$

$$= 2.336 \times 10^{-6} \text{ lb-moles}$$

The mole fraction of individual hydrocarbons can now be determined:

| Components | Peak Height 1/10 inch | Lb-Moles x $10^{9}$ | Mole Fraction of Hydrocarbons in Water x $10^{3}$ |
|---|---|---|---|
| $C_1$ | 26.5 | 3.80 | 1.635 |
| $C_2$ | 28.5 | 3.00 | 1.269 |
| $C_3$ | 9.0 | 1.07 | 0.461 |
| $H_2O$ | 0 | 2336.00 | 996.635 |
| Total: | | 2343.87 | 1000.000 |

The total solubility of $C_1$-$C_2$-$C_3$ mixture in water at 220 F and 4000 psi is

$$\text{Total solubility} = (1.635 + 1.269 + 0.461) \times 10^{-3}$$

$$\text{"} \quad \text{"} \quad = 3.365 \times 10^{-3} \ \frac{\text{lb mole hydrocarbons}}{\text{lb mole water}}$$

Based on the experimental data obtained, correlations by which the total solubility of binary and ternary hydrocarbon mixtures in water can be determined have been developed. These correlations will be discussed in the following chapter. A comparison between the experimental and calculated values of solubilities will also be given in the next chapter.

## TABLE (V-1)

## DETERMINATION OF THE CONSISTENCY IN THE CHROMATOGRAPHIC ANALYSIS OBTAINED UNDER THE FOLLOWING CONDITIONS:

Helium Flow Rate = 22.5 ml/min

Sample Valve = 10V-2074-1

Hydrogen Flow Rate = 22.5 ml/min

Oven Temperature = 100 C

Sample Pressure = 20 psig

Range = 10

Sample Temperature = 80-82 F

Attenuation = 64

Injection Temperature = 145 F

| Date | Hydrocarbon | Peak Height (Tenth of Inch)<br>Sample #1 | Sample #2 | Sample #3 | Sample #4 | Sample #5 |
|---|---|---|---|---|---|---|
| 7-15-68 | Methane | 40.0 | 40.0 | 40.1 | 40.0 | 40.3 |
| " | Ethane | 56.2 | 56.3 | 56.3 | 56.2 | 56.4 |
| " | Propane | 34.2 | 34.2 | 34.1 | 34.0 | 34.3 |
| 7-20-68 | Methane | 40.1 | 40.0 | | | |
| " | Ethane | 56.2 | 56.4 | | | |
| " | Propane | 34.3 | 34.1 | | | |
| 8-14-68 | Methane | 40.2 | 39.9 | | | |
| " | Ethane | 56.2 | 56.1 | | | |
| " | Propane | 34.2 | 34.1 | | | |
| 10-11-68 | Methane | 40.0 | 40.2 | | | |
| " | Ethane | 56.2 | 56.1 | | | |
| " | Propane | 34.2 | 34.1 | | | |
| 1-15-69 | Methane | 39.9 | 40.1 | | | |
| " | Ethane | 56.2 | 56.2 | | | |
| " | Propane | 34.2 | 34.0 | | | |

## TABLE (V-2)

## DETERMINATION OF THE ACCURACY OF THE CHROMATOGRAPHIC ANALYSIS OBTAINED UNDER THE SAME CONDITIONS AS GIVEN IN TABLE (V-1)

| Source of Analysis | Sample | Composition (Per Cent)<br>$C_1$ | $C_2$ | $C_3$ | Others |
|---|---|---|---|---|---|
| Phillips 66 | Standard | 0.7036 | 0.0906 | 0.0593 | 0.1465 |
| Chromatograph | Standard | 0.7030 | 0.0910 | 0.0590 | 0.1465 |
| Calculated | #1 | 0.2590 | 0.3560 | 0.3850 | - |
| Chromatograph | #1 | 0.2590 | 0.3570 | 0.3840 | - |
| Calculated | #2 | 0.6430 | 0.2070 | 0.1500 | - |
| Chromatograph | #2 | 0.6440 | 0.2070 | 0.1490 | - |
| Calculated | #3 | 0.1360 | 0.2440 | 0.6200 | - |
| Chromatograph | #3 | 0.1360 | 0.2430 | 0.6210 | - |

## TABLE (V-3)

## SAMPLE CALCULATION FOR DETERMINATION OF PARTIAL PRESSURES TO OBTAIN A MIXTURE OF SPECIFIC COMPOSITION

The calculations are performed for a ternary mixture. The calculation for binary mixtures can always be deduced from it by setting the mole fraction of the third component equal to zero.

It is desired to prepare a mixture of methane, ethane, and propane to have the following composition:

$x_{C_1}$ = 25.9 mole per cent

$x_{C_2}$ = 35.6 "

$x_{C_3}$ = 38.5 "

$x_i$ = 100.0 "

The mixing cell has a volume of 500 cc and a temperature of 77 F.

The cell is charged with the three hydrocarbons in reverse order of their molecular weights. Hence, first, the propane is injected until the cell pressure is 50 psig. This pressure is chosen arbitrarily. The number of moles of propane is determined using the compressibility factor equation

$$P\bar{v} = ZRT \quad \text{or} \quad PV = nZRT \qquad \text{(IV-11)}$$

where $n = \frac{PV}{ZRT}$

TABLE (V-3)--Continued

$$n = \frac{(50 + 14.7)\ \text{psi} \times (500)\ \text{cc} \times \dfrac{\text{ft}^3}{(30.5)^3\ \text{cc}}}{(0.940)(10.73\ \frac{\text{ft}^3\text{-psi}}{\text{lb mole-R}})(77 + 460)\ \text{R}}$$

The compressibility factor Z for propane was obtained from Sage and Lacey (9).

$$n_{\text{propane}} = \underline{2.11 \times 10^{-4}\ \text{lb moles}}$$

Since $x_{C_3}$, the propane mole fraction, is known, the total number of moles can be calculated as

$$n_{\text{total}} = n_{C_3}/x_{C_3}$$

$$= 2.11 \times 10^{-4}/0.385$$

$$= \underline{5.48 \times 10^{-4}\ \text{lb mole}}$$

The number of moles of ethane and methane can be determined as follows:

$$n_{C_2} = x_{C_2} n_{\text{total}}$$

$$= 0.356 \times 5.48 \times 10^{-4}$$

$$= \underline{1.95 \times 10^{-4}\ \text{lb mole}}$$

and $$n_{C_1} = x_{C_1} n_{\text{total}}$$

$$= 0.259 \times 5.48 \times 10^{-4}$$

TABLE (V-3)--Continued

$= \underline{1.42 \times 10^{-4} \text{ lb mole}}$

The pressure after injecting the ethane is

$$P = (n_{C_3} + n_{C_2})\frac{Z_{mix}RT}{V}$$

where $Z_{mix} = x'_{C_3}Z_{C_3} + x'_{C_2}Z_{C_2}$

$$x'_{C_3} = 2.11 \times 10^{-4}/(2.11 + 1.95) \times 10^{-4}$$

$$x'_{C_3} = 0.520$$

$$x'_{C_2} = 1.000 - 0.520 = 0.480$$

$$Z_{mix} = 0.520 \times 0.940 + 0.480 \times 0.940$$

$$Z_{mix} = 0.940$$

Then, $P = (4.06 \times 10^{-4}) \text{ lb mole} \times 0.94 \times \frac{1}{3.06 \times 10^{-6}} \frac{\text{psi}}{\text{lb mole}}$

$P = \underline{124.7 \text{ psi}}$

The final pressure after injecting the methane is found as

$$P = n_{total}\frac{Z'_{mix}RT}{V}$$

TABLE (V-3)--Continued

where $$Z'_{mix} = x_{C_3}Z_{C_3} + x_{C_2}Z_{C_2} + x_{C_1}Z_{C_1}$$

$$= 0.385 \times 0.940 + 0.356 \times 0.940 + 0.259 \times 0.970$$

$$= 0.696 + 0.251$$

$$= 0.947$$

$$P = (5.48 \times 10^{-4})\ \text{lb mole} \times 0.947 \times \frac{1}{3.06 \times 10^{-6}}\ \frac{\text{psi}}{\text{lb mole}}$$

$$P = \underline{169.7\ \text{psi}}$$

Hence, to obtain a mixture composed of 0.259, 0.356, and 0.385 mole per cent methane, ethane, and propane, respectively, the propane is injected until the cell pressure is 64.7 psi; then ethane is injected until the pressure in the cell reaches 124.7 psi, and finally, methane is injected until the pressure reaches 169.7 psi.

To obtain higher final pressures, the propane can be injected until a higher initial pressure is obtained. However, the initial pressure will be limited by the vapor pressure of propane at the room temperature.

## TABLE (V-4)

## SOLUBILITY OF METHANE IN WATER: COMPARISON OF GRAPHICALLY SMOOTHED DATA OF THIS STUDY WITH THOSE GIVEN BY CULBERSON (13)

| Pressure Psia | Mole Fraction of Methane in the Water-Rich Phase | | | |
|---|---|---|---|---|
| | 100 F | | 160 F | |
| | This Study | Culberson | This Study | Culberson |
| 600 | 0.000759 | 0.000760 | 0.000602 | 0.000599 |
| 2000 | 0.001956 | 0.001953 | 0.001612 | 0.001608 |
| 3000 | 0.002519 | 0.002530 | 0.002150 | 0.002094 |
| 5000 | 0.003350 | 0.003360 | 0.002800 | 0.002888 |

## TABLE (V-5)

## COMPOSITION, TEMPERATURE, PRESSURE, AND SOLUBILITY OF METHANE-ETHANE MIXTURES

|  |  |  | Mole Fraction of Hydrocarbon in the Water-Free Gas Phase |  | Mole Fraction of Hydrocarbon in Water x $10^3$ |  |  |
|---|---|---|---|---|---|---|---|
| Mixture | T(F) | P(Psi) | $Y_{C_1}$ | $Y_{C_2}$ | $X_{C_1}$ | $X_{C_2}$ | $X_{C_1} + X_{C_2}$ |
| #1 | 160 | 665 | 0.1996 | 0.8004 | 0.450 | 0.696 | 1.146 |
|  | " | 2065 | " | " | 0.798 | 1.243 | 2.041 |
|  | " | 3065 | " | " | 0.954 | 1.486 | 2.440 |
|  | " | 4965 | " | " | 1.158 | 1.802 | 2.960 |
|  | " | 7915 | " | " | 1.564 | 2.439 | 4.003 |
| #2 | 160 | 665 | 0.4050 | 0.5950 | 0.779 | 0.636 | 1.415 |
|  | " | 2065 | " | " | 1.382 | 1.128 | 2.510 |
|  | " | 3065 | " | " | 1.648 | 1.345 | 2.993 |
|  | " | 4965 | " | " | 1.988 | 1.624 | 3.612 |
|  | " | 7915 | " | " | 2.648 | 2.158 | 4.806 |
| #3 | 100 | 5000 | 0.4990 | 0.5010 | 2.260 | 1.637 | 3.897 |
|  | 130 | " | " | " | 2.150 | 1.561 | 3.711 |
|  | 160 | " | " | " | 2.080 | 1.506 | 3.586 |

TABLE (V-5)--Continued

| | | | Mole Fraction of Hydrocarbon in the Water-Free Gas Phase | | Mole Fraction of Hydrocarbon in Water x $10^3$ | | |
|---|---|---|---|---|---|---|---|
| Mixture | T(F) | P(Psi) | $Y_{C_1}$ | $Y_{C_2}$ | $X_{C_1}$ | $X_{C_2}$ | $X_{C_1} + X_{C_2}$ |
| #3 | 190 | 5000 | 0.4990 | 0.5010 | 2.190 | 1.590 | 3.780 |
| | 220 | " | " | " | 2.432 | 1.768 | 4.200 |
| | 160 | 665 | " | " | 0.819 | 0.593 | 1.412 |
| | " | 2065 | " | " | 1.455 | 1.057 | 2.512 |
| | " | 3065 | " | " | 1.800 | 1.302 | 3.102 |
| | " | 4965 | " | " | 2.081 | 1.508 | 3.589 |
| | " | 7915 | " | " | 2.804 | 2.036 | 4.840 |
| #4 | 160 | 665 | 0.7100 | 0.2900 | 0.875 | 0.452 | 1.327 |
| | " | 2065 | " | " | 1.598 | 0.822 | 2.420 |
| | " | 3065 | " | " | 1.848 | 0.952 | 2.800 |
| | " | 4965 | " | " | 2.322 | 1.197 | 3.519 |
| | " | 7915 | " | " | 3.170 | 1.637 | 4.807 |
| #5 | 160 | 665 | 0.8536 | 0.1464 | 0.840 | 0.232 | 1.072 |
| | " | 2065 | " | " | 1.605 | 0.445 | 2.050 |

TABLE (V-5)--Continued

| | | | Mole Fraction of Hydrocarbon in the Water-Free Gas Phase | | Mole Fraction of Hydrocarbon in Water x $10^3$ | | |
|---|---|---|---|---|---|---|---|
| Mixture | T(F) | P(Psi) | $Y_{C_1}$ | $Y_{C_2}$ | $X_{C_1}$ | $X_{C_2}$ | $X_{C_1} + X_{C_2}$ |
| #5 | 160 | 3065 | 0.8536 | 0.1464 | 2.008 | 0.556 | 2.564 |
| | " | 4965 | " | " | 2.554 | 0.706 | 3.260 |
| | " | 7915 | " | " | 3.366 | 0.934 | 4.300 |

TABLE (V-6)

COMPOSITION, TEMPERATURE, PRESSURE, AND SOLUBILITY OF METHANE-PROPANE MIXTJRES

| Mixture | T(F) | P(Psi) | Mole Fraction of Hydrocarbon in the Water-Free Gas Phase | | Mole Fraction of Hydrocarbon in Water x $10^3$ | | |
|---|---|---|---|---|---|---|---|
| | | | $Y_{C_1}$ | $Y_{C_3}$ | $X_{C_1}$ | $X_{C_3}$ | $X_{C_1} + X_{C_3}$ |
| #6 | 220 | 715 | 0.2040 | 0.7960 | 0.862 | 0.898 | 1.760 |
| | " | 2065 | " | " | 1.274 | 1.327 | 2.601 |
| | " | 3015 | " | " | 1.449 | 1.510 | 2.959 |
| | " | 5015 | " | " | 1.616 | 1.686 | 3.302 |
| | " | 8015 | " | " | 1.787 | 1.863 | 3.650 |
| #7 | 220 | 715 | 0.3967 | 0.6033 | 1.460 | 0.731 | 2.191 |
| | " | 2065 | " | " | 1.925 | 0.962 | 2.887 |
| | " | 3015 | " | " | 2.198 | 1.098 | 3.296 |
| | " | 5015 | " | " | 2.468 | 1.234 | 3.702 |
| | " | 8015 | " | " | 2.792 | 1.398 | 4.190 |
| #8 | 220 | 715 | 0.5015 | 0.4985 | 1.525 | 0.646 | 2.171 |
| | " | 2065 | " | " | 2.016 | 0.855 | 2.871 |
| | " | 3015 | " | " | 2.282 | 0.970 | 3.250 |

TABLE (V-6)--Continued

| | | | Mole Fraction of Hydrocarbon in the Water-Free Gas Phase | | Mole Fraction of Hydrocarbon in Water x $10^3$ | | |
|---|---|---|---|---|---|---|---|
| Mixture | T(F) | P(Psi) | $Y_{C_1}$ | $Y_{C_3}$ | $X_{C_1}$ | $X_{C_3}$ | $X_{C_1} + X_{C_3}$ |
| #8 | 220 | 5015 | 0.5015 | 0.4985 | 2.642 | 1.120 | 3.762 |
| | " | 8015 | " | " | 2.928 | 1.242 | 4.170 |
| #9 | 220 | 715 | 0.7280 | 0.2720 | 1.326 | 0.425 | 1.751 |
| | " | 2065 | " | " | 1.895 | 0.605 | 2.500 |
| | " | 3015 | " | " | 2.196 | 0.705 | 2.901 |
| | " | 5015 | " | " | 2.690 | 0.861 | 3.551 |
| | " | 8015 | " | " | 3.184 | 1.023 | 4.207 |
| #10 | 220 | 715 | 0.8645 | 0.1355 | 1.130 | 0.150 | 1.280 |
| | " | 2065 | " | " | 1.860 | 0.249 | 2.109 |
| | " | 3015 | " | " | 2.250 | 0.314 | 2.550 |
| | " | 5015 | " | " | 2.912 | 0.384 | 3.306 |
| | " | 8015 | " | " | 3.702 | 0.498 | 4.200 |

## TABLE (V-7)

## COMPOSITION, TEMPERATURE, PRESSURE, AND SOLUBILITY OF ETHANE-PROPANE MIXTURES

| | | | Mole Fraction of Hydrocarbon in the Water-Free Gas Phase | | Mole Fraction of Hydrocarbon in Water x $10^3$ | | |
|---|---|---|---|---|---|---|---|
| Mixture | T(F) | P(Psi) | $Y_{C_2}$ | $Y_{C_3}$ | $X_{C_2}$ | $X_{C_3}$ | $X_{C_2} + X_{C_3}$ |
| #11 | 220 | 665 | 0.2214 | 0.7786 | 0.208 | 0.352 | 0.560 |
| | " | 2015 | " | " | 0.301 | 0.510 | 0.811 |
| | " | 3015 | " | " | 0.316 | 0.534 | 0.850 |
| | " | 4965 | " | " | 0.336 | 0.570 | 0.906 |
| | " | 8015 | " | " | 0.365 | 0.618 | 0.983 |
| #12 | 220 | 665 | 0.4059 | 0.5941 | 0.294 | 0.331 | 0.625 |
| | " | 2015 | " | " | 0.447 | 0.503 | 0.950 |
| | " | 3015 | " | " | 0.481 | 0.539 | 1.020 |
| | " | 4965 | " | " | 0.515 | 0.579 | 1.094 |
| | " | 8015 | " | " | 0.556 | 0.625 | 1.181 |
| #13 | 220 | 665 | 0.5640 | 0.4360 | 0.318 | 0.317 | 0.635 |
| | " | 2015 | " | " | 0.509 | 0.505 | 1.014 |
| | " | 3015 | " | " | 0.545 | 0.541 | 1.086 |

TABLE (V-7)--Continued

| Mixture | T(F) | P(Psi) | Mole Fraction of Hydrocarbon in the Water-Free Gas Phase $Y_{C_2}$ | $Y_{C_3}$ | Mole Fraction of Hydrocarbon in Water x $10^3$ $X_{C_2}$ | $X_{C_3}$ | $X_{C_2} + X_{C_3}$ |
|---|---|---|---|---|---|---|---|
| #13 | 220 | 4965 | 0.5640 | 0.4360 | 0.582 | 0.584 | 1.166 |
| | " | 8015 | " | " | 0.648 | 0.642 | 1.290 |
| #14 | 220 | 665 | 0.7005 | 0.2995 | 0.367 | 0.256 | 0.623 |
| | " | 2015 | " | " | 0.595 | 0.415 | 1.010 |
| | " | 3015 | " | " | 0.653 | 0.457 | 1.110 |
| | " | 4965 | " | " | 0.707 | 0.493 | 1.200 |
| | " | 8015 | " | " | 0.798 | 0.559 | 1.357 |
| #15 | 220 | 665 | 0.8151 | 0.1849 | 0.377 | 0.188 | 0.565 |
| | " | 2015 | " | " | 0.672 | 0.332 | 1.004 |
| | " | 3015 | " | " | 0.744 | 0.369 | 1.113 |
| | " | 4965 | " | " | 0.812 | 0.402 | 1.214 |
| | " | 8015 | " | " | 0.929 | 0.461 | 1.390 |

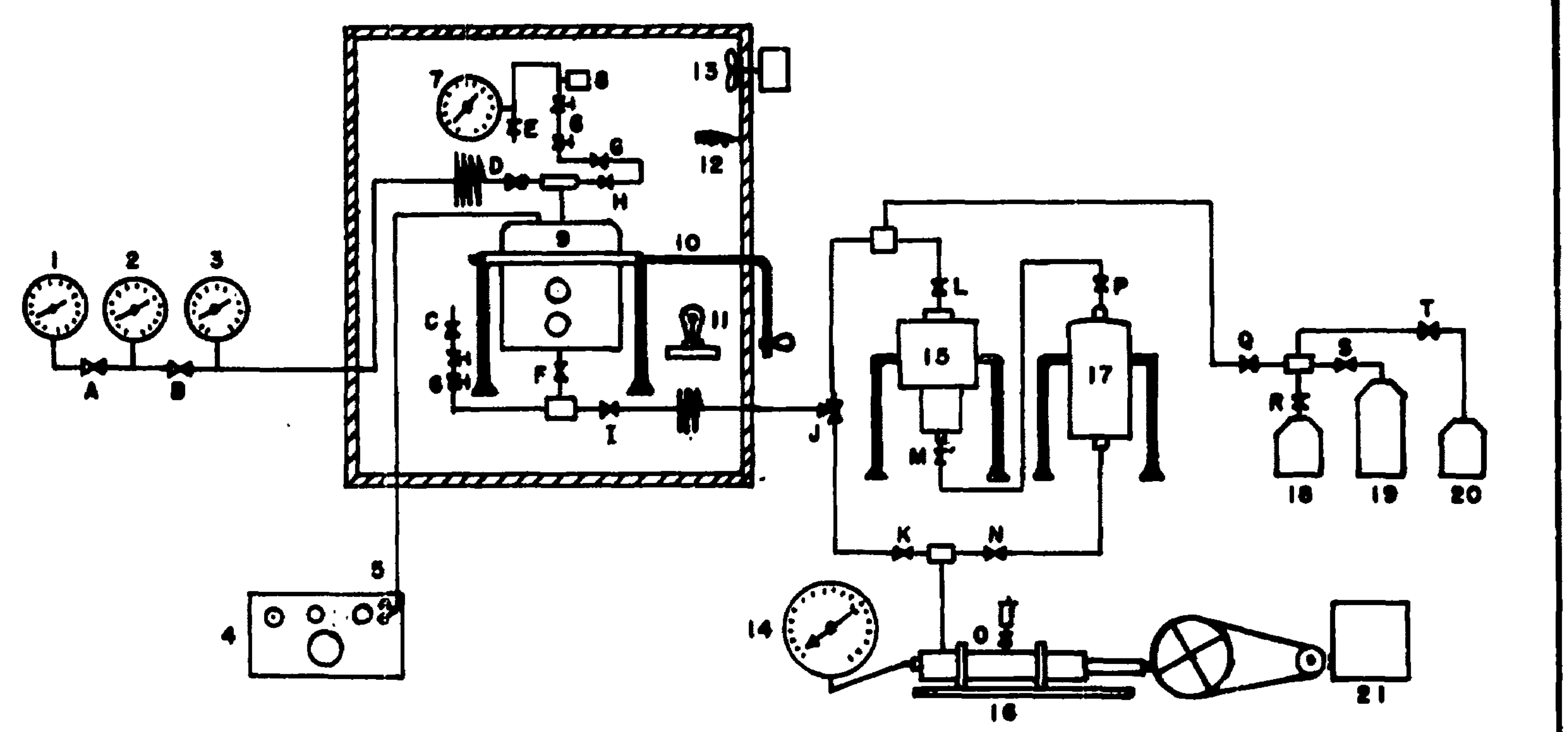
## TABLE (V-8)

## COMPOSITION, TEMPERATURE, PRESSURE, AND SOLUBILITY OF METHANE-ETHANE-PROPANE MIXTURES

|  |  |  | Mole Fraction of Hydrocarbon in the Water-Free Gas Phase |  |  | Mole Fraction of Hydrocarbon in Water x $10^3$ |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
| Mixture | T(F) | P(Psi) | $Y_{C_1}$ | $Y_{C_2}$ | $Y_{C_3}$ | $X_{C_1}$ | $X_{C_2}$ | $X_{C_3}$ | $X_{C_1} + X_{C_2} + X_{C_3}$ |
| #16 | 220 | 665 | 0.5023 | 0.2527 | 0.2450 | 1.178 | 0.398 | 0.019 | 1.595 |
|  | " | 2065 | " | " | " | 2.068 | 0.700 | 0.032 | 2.800 |
|  | " | 3015 | " | " | " | 2.370 | 0.803 | 0.041 | 3.214 |
|  | " | 4015 | " | " | " | 2.676 | 0.906 | 0.042 | 3.624 |
|  | " | 5015 | " | " | " | 2.942 | 0.998 | 0.039 | 3.986 |
| #17 | 220 | 665 | 0.6110 | 0.1780 | 0.2110 | 1.276 | 0.271 | 0.048 | 1.595 |
|  | " | 2065 | " | " | " | 2.244 | 0.476 | 0.086 | 2.806 |
|  | " | 3015 | " | " | " | 2.570 | 0.546 | 0.102 | 3.218 |
|  | " | 4015 | " | " | " | 2.882 | 0.613 | 0.111 | 3.606 |
|  | " | 5015 | " | " | " | 3.162 | 0.672 | 0.123 | 3.957 |
| #18 | 160 | 5000 | 0.7015 | 0.1065 | 0.1920 | 2.780 | 0.323 | 0.198 | 3.301 |
|  | 190 | " | " | " | " | 2.830 | 0.329 | 0.206 | 3.365 |
|  | 220 | " | " | " | " | 3.158 | 0.367 | 0.225 | 3.750 |
|  | " | 665 | " | " | " | 1.175 | 0.137 | 0.083 | 1.395 |

TABLE (V-8)--Continued

| | | | Mole Fraction of Hydrocarbon in the Water-Free Gas Phase | | | Mole Fraction of Hydrocarbon in Water x $10^3$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| Mixture | T(F) | P(Psi) | $Y_{C_1}$ | $Y_{C_2}$ | $Y_{C_3}$ | $X_{C_1}$ | $X_{C_2}$ | $X_{C_3}$ | $X_{C_1} + X_{C_2} + X_{C_3}$ |
| #18 | 220 | 2065 | 0.7015 | 0.1065 | 0.1920 | 2.234 | 0.260 | 0.161 | 2.655 |
| | " | 3015 | " | " | " | 2.614 | 0.304 | 0.187 | 3.105 |
| | " | 4015 | " | " | " | 2.822 | 0.328 | 0.205 | 3.355 |
| #19 | 220 | 665 | 0.8218 | 0.0945 | 0.0837 | 1.230 | 0.119 | 0.040 | 1.389 |
| | " | 2065 | " | " | " | 2.000 | 0.194 | 0.056 | 2.250 |
| | " | 3015 | " | " | " | 2.668 | 0.258 | 0.079 | 3.005 |
| | " | 4015 | " | " | " | 2.842 | 0.275 | 0.087 | 3.204 |
| | " | 5015 | " | " | " | 3.276 | 0.317 | 0.099 | 3.692 |
| #20 | 220 | 665 | 0.2594 | 0.3558 | 0.3848 | 0.768 | 0.596 | 0.216 | 1.580 |
| | " | 2065 | " | " | " | 1.305 | 1.002 | 0.348 | 2.655 |
| | " | 3015 | " | " | " | 1.508 | 1.170 | 0.427 | 3.105 |
| | " | 4015 | " | " | " | 1.635 | 1.269 | 0.461 | 3.365 |
| | " | 5015 | " | " | " | 1.800 | 1.396 | 0.607 | 3.703 |



1 - PRESSURE GAUGE 0 - 1000 PSI
2 - PRESSURE GAUGE 0 - 5000 PSI
3 - PRESSURE GAUGE 0 - 10,000 PSI
4 - POTENTIOMETER
5 - THERMOCOUPLE
6 - SAMPLE VALVES
7 - PRESSURE GAUGE 0 - 200 PSI
8 - SAFETY DISK
9 - EQUILIBRIUM CELL
10 - MIXING HANDLE
11 - 300 W LAMP
12 - THERMOSTAT
13 - FAN
14 - HEISE GAUGE
15 - AUXILIARY CELL
16 - MERCURY PUMP
17 - AUXILIARY CELL
18 - PROPANE CYLINDER
19 - METHANE CYLINDER
20 - ETHANE CYLINDER
21 - MOTOR

FIGURE V-1 SCHEMATIC DIAGRAM OF EXPERIMENTAL APPARATUS

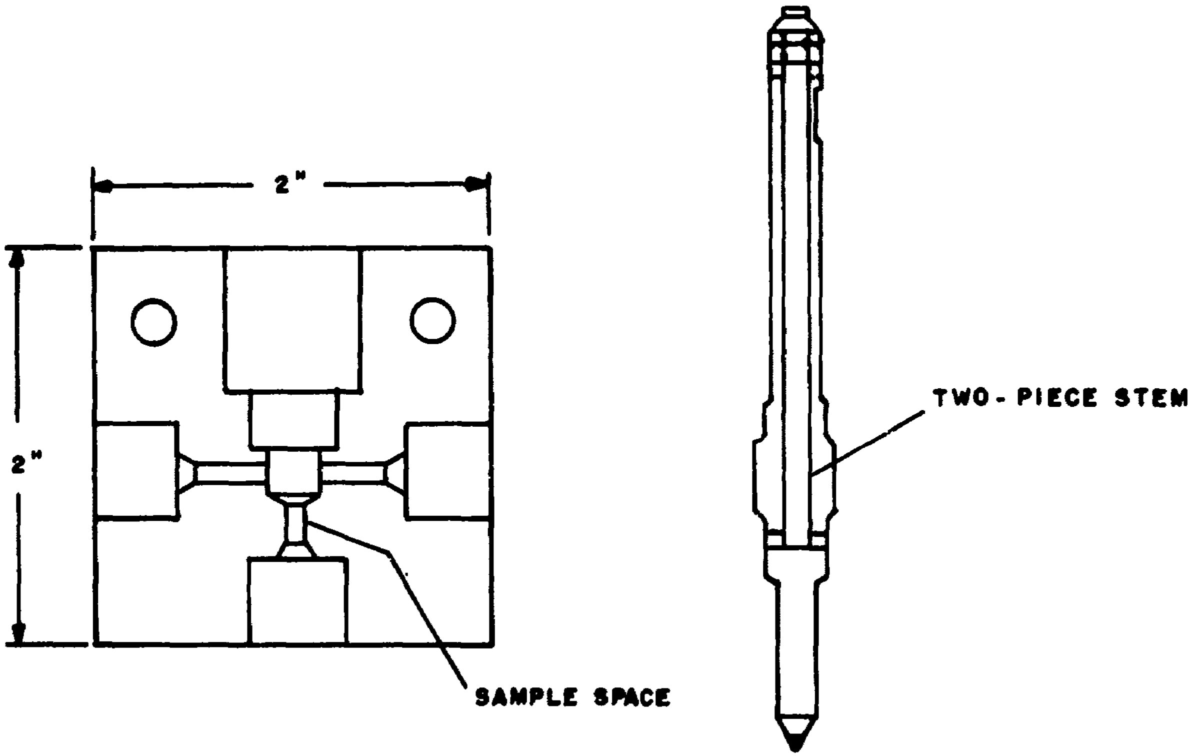


FIGURE V-2 DRAWING OF LIQUID SAMPLING VALVE (AUTOCLAVE 30VM-4074).
VOLUME OF THE SAMPLE SPACE IS 0.0197 cc.

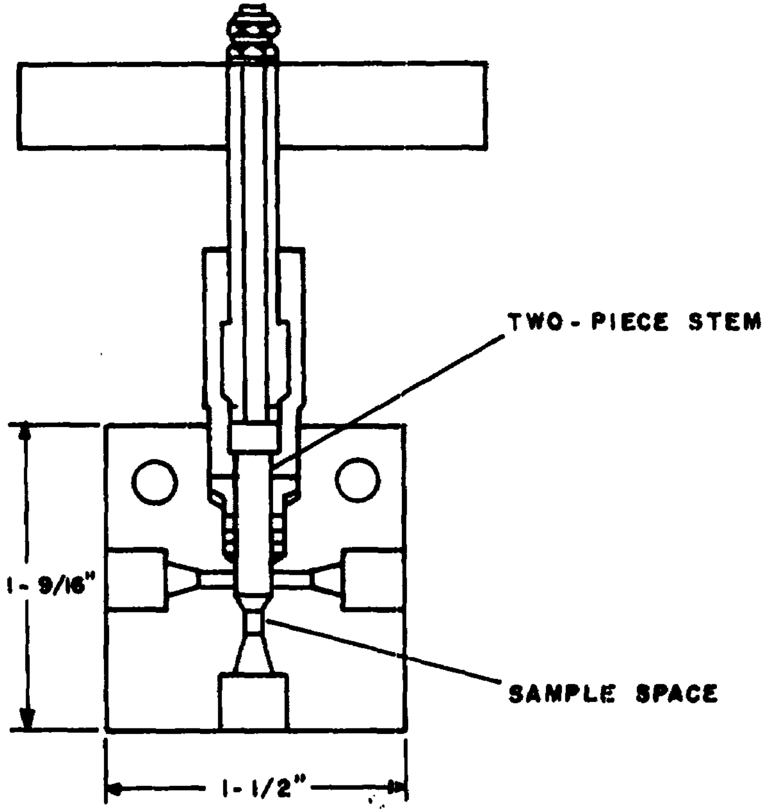


FIGURE V-3 DRAWING OF GAS SAMPLING VALVE (AUTOCLAVE 10VM-2074). VOLUME OF THE SAMPLE SPACE IS .0246 cc.

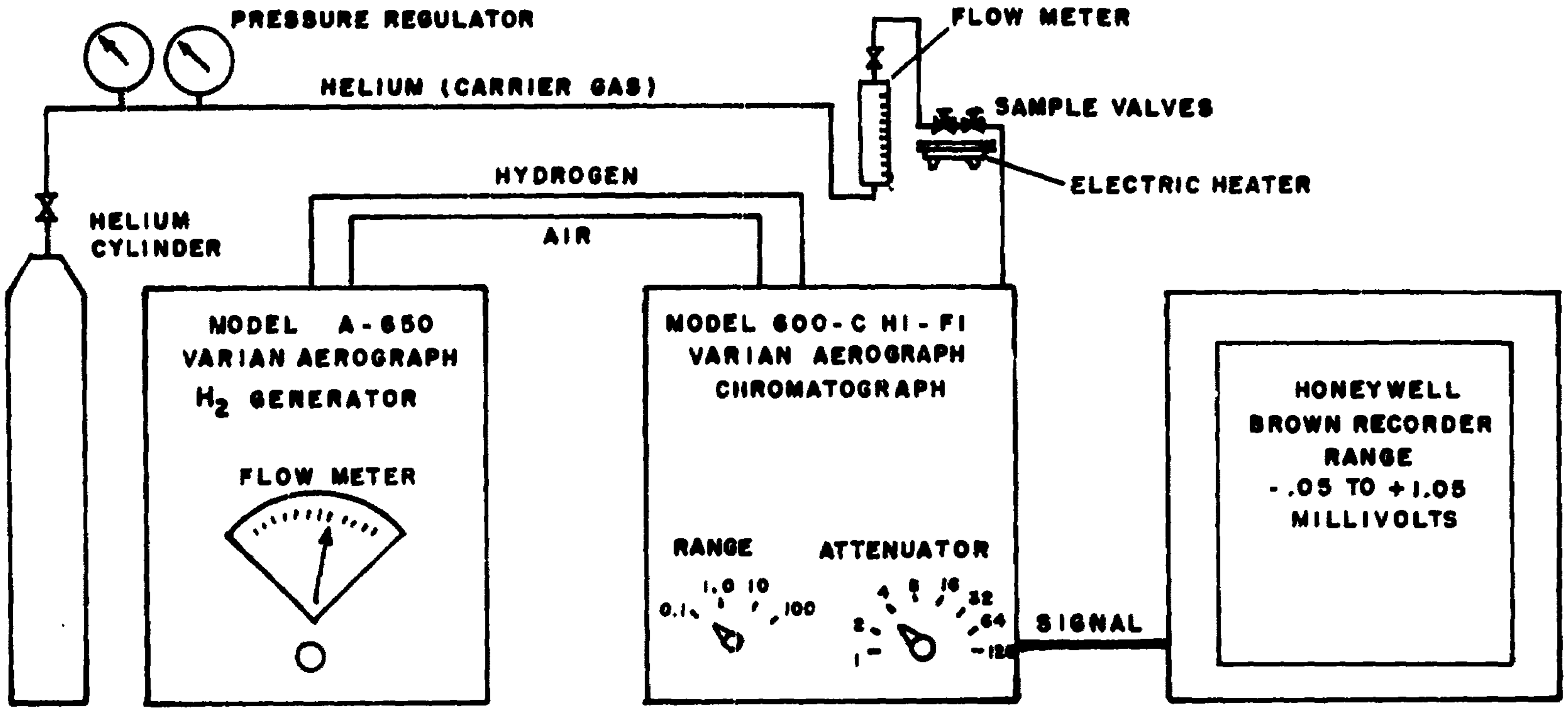


FIGURE V-4 SCHEMATIC DIAGRAM OF GAS CHROMATOGRAPH COMPOSED OF SEPARATE PARTS

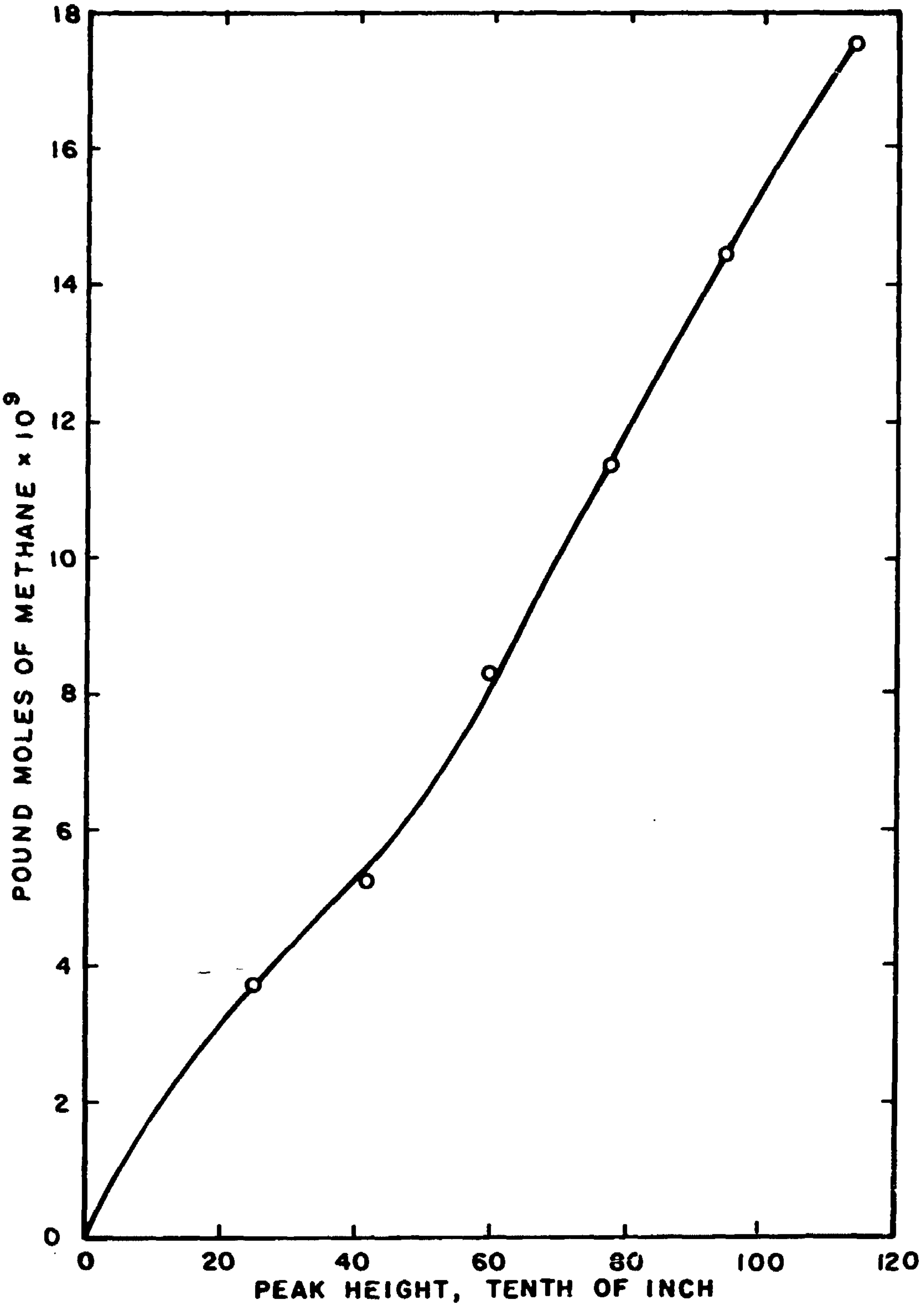


FIGURE V-5 POUND MOLES OF METHANE VS PEAK HEIGHT AT HE = $H_2$ FLOW RATE OF 22.5 ML./MIN., OVEN TEMP. = 100°C., INJECTION TEMP. = 145°F., RANGE = 10, AND ATTENUATION = 64.

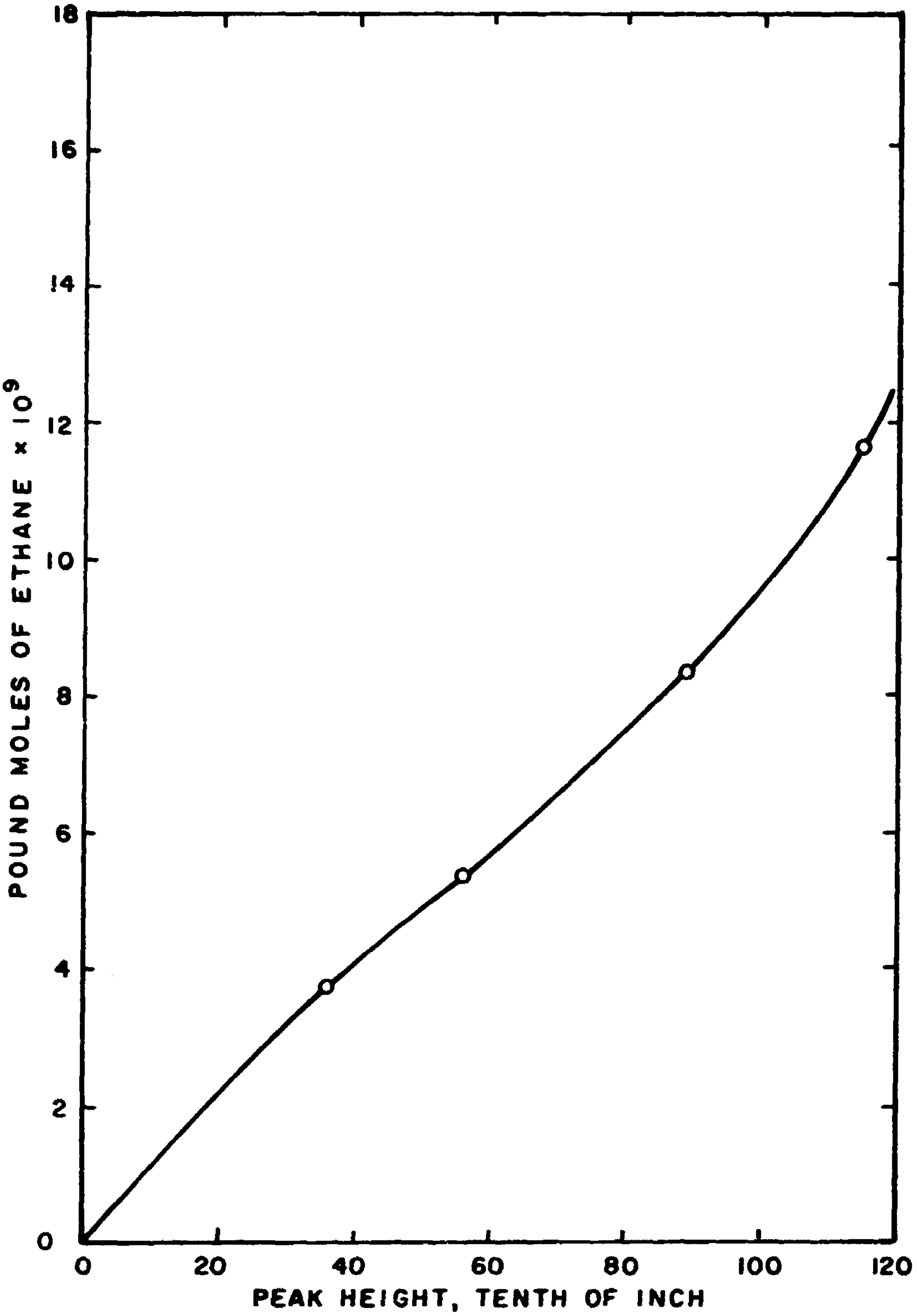


FIGURE V-6 POUND MOLES OF ETHANE VS PEAK HEIGHT AT HE = $H_2$ FLOW RATE OF 22.5 ML./MIN., OVEN TEMP. = 100° C., INJECTION TEMP. = 145° F., RANGE = 10, AND ATTENUATION = 64.

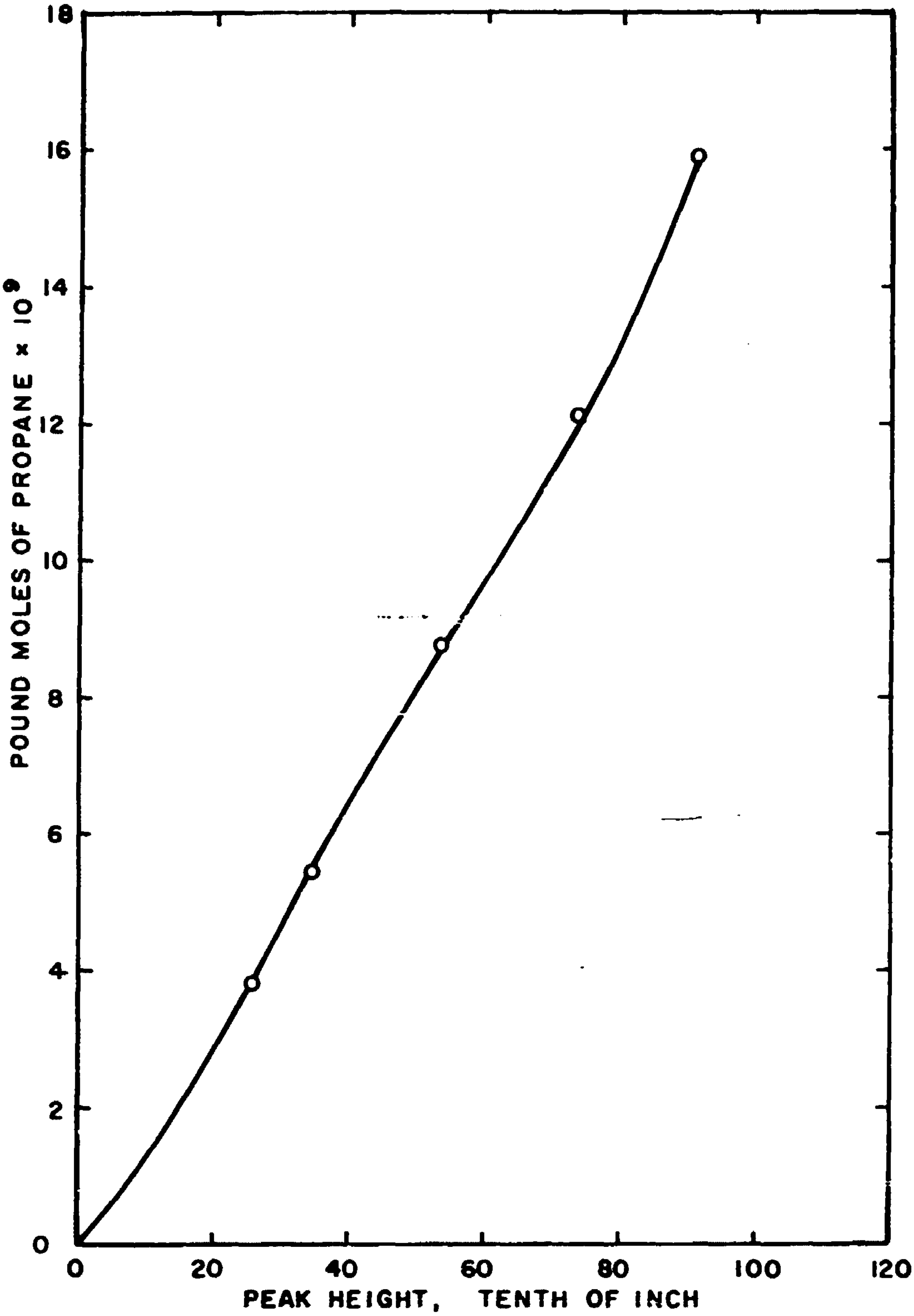


FIGURE V-7 POUND-MOLES OF PROPANE VS PEAK HEIGHT AT HE = $H_2$ FLOW RATE OF 22.5 ML./MIN., OVEN TEMP. = 100° C., INJECTION TEMP. = 145° F., R = 10 AND ATTENUATION = 64.

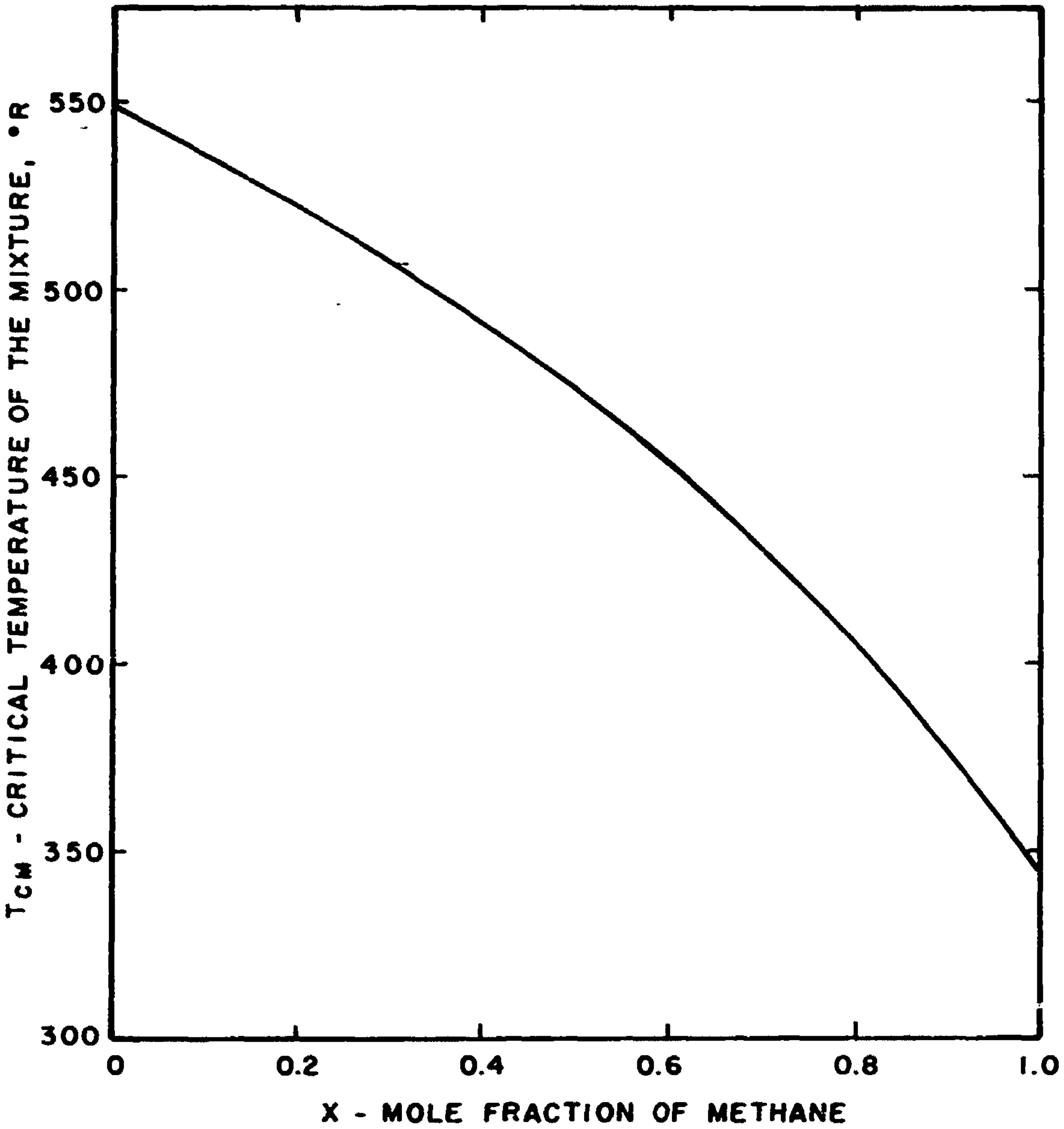


FIGURE V-8 CRITICAL TEMPERATURE OF METHANE-ETHANE MIXTURE USING GRIEVES-THODOS' EQUATION

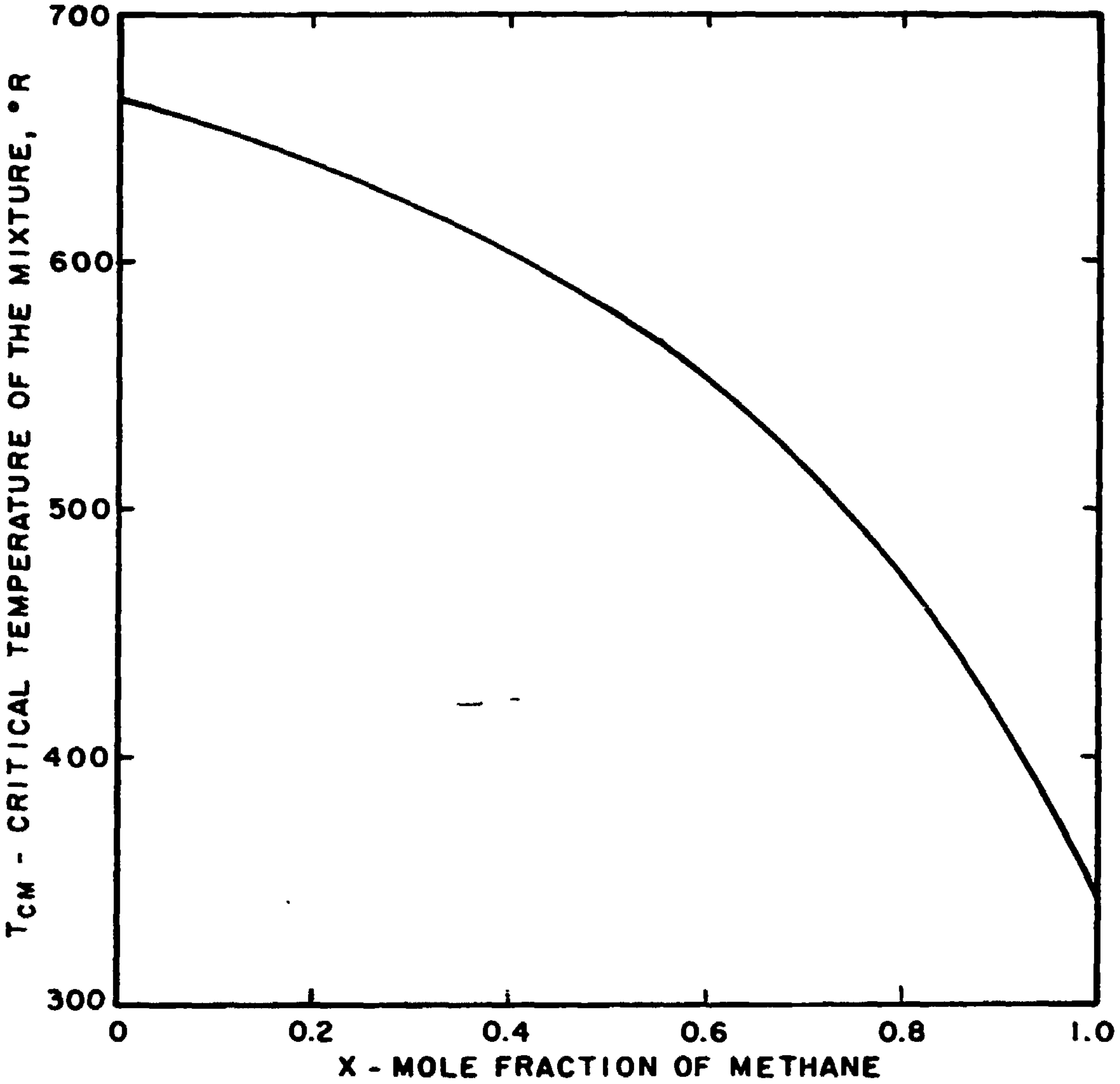


FIGURE V-9 CRITICAL TEMPERATURE OF METHANE-PROPANE MIXTURE USING GRIEVES-THOROS' EQUATION

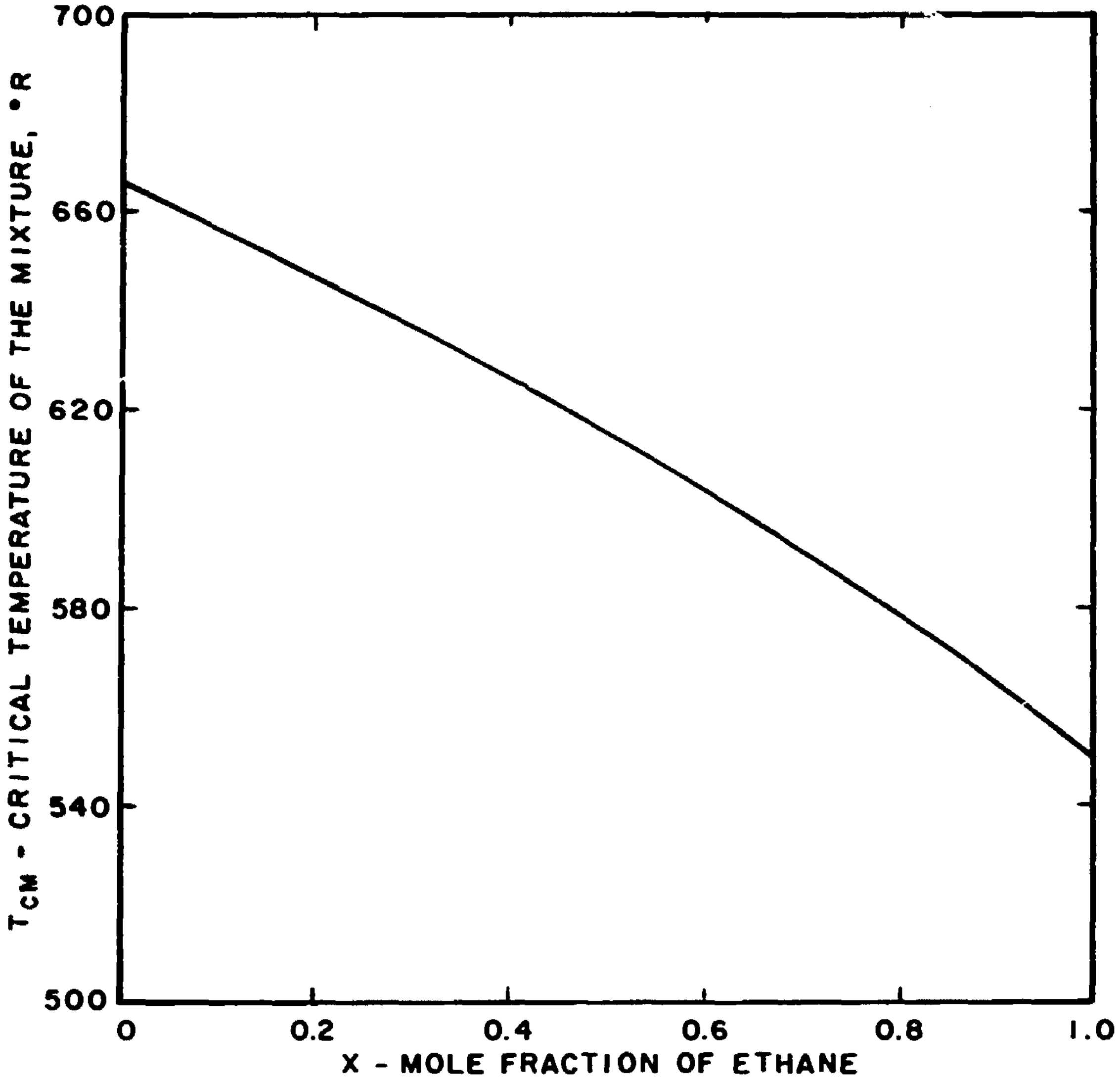


FIGURE V-10 CRITICAL TEMPERATURE OF ETHANE-PROPANE MIXTURE USING GRIEVES-THOROS' EQUATION

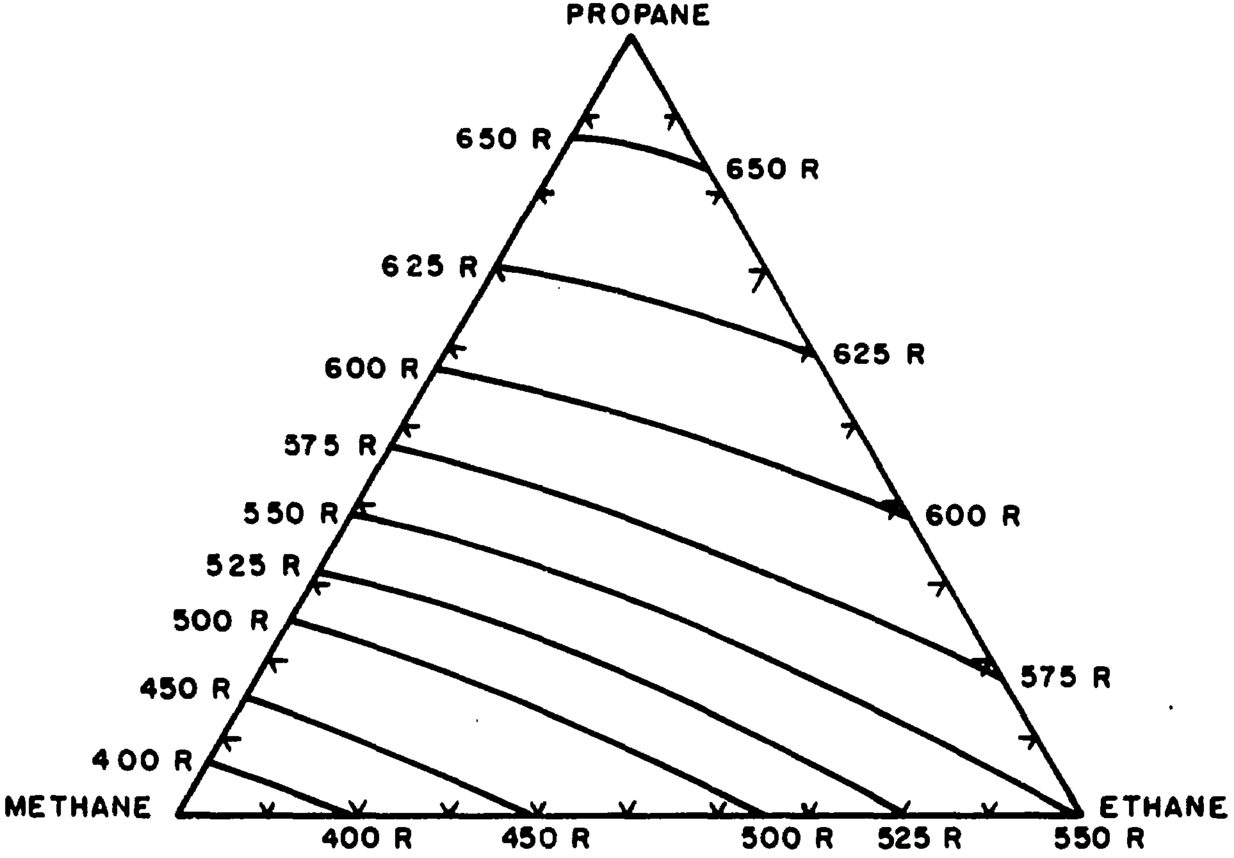


FIGURE V-11 CRITICAL TEMPERATURE OF METHANE - ETHANE - PROPANE MIXTURE USING GRIEVES - THOROS' EQUATION

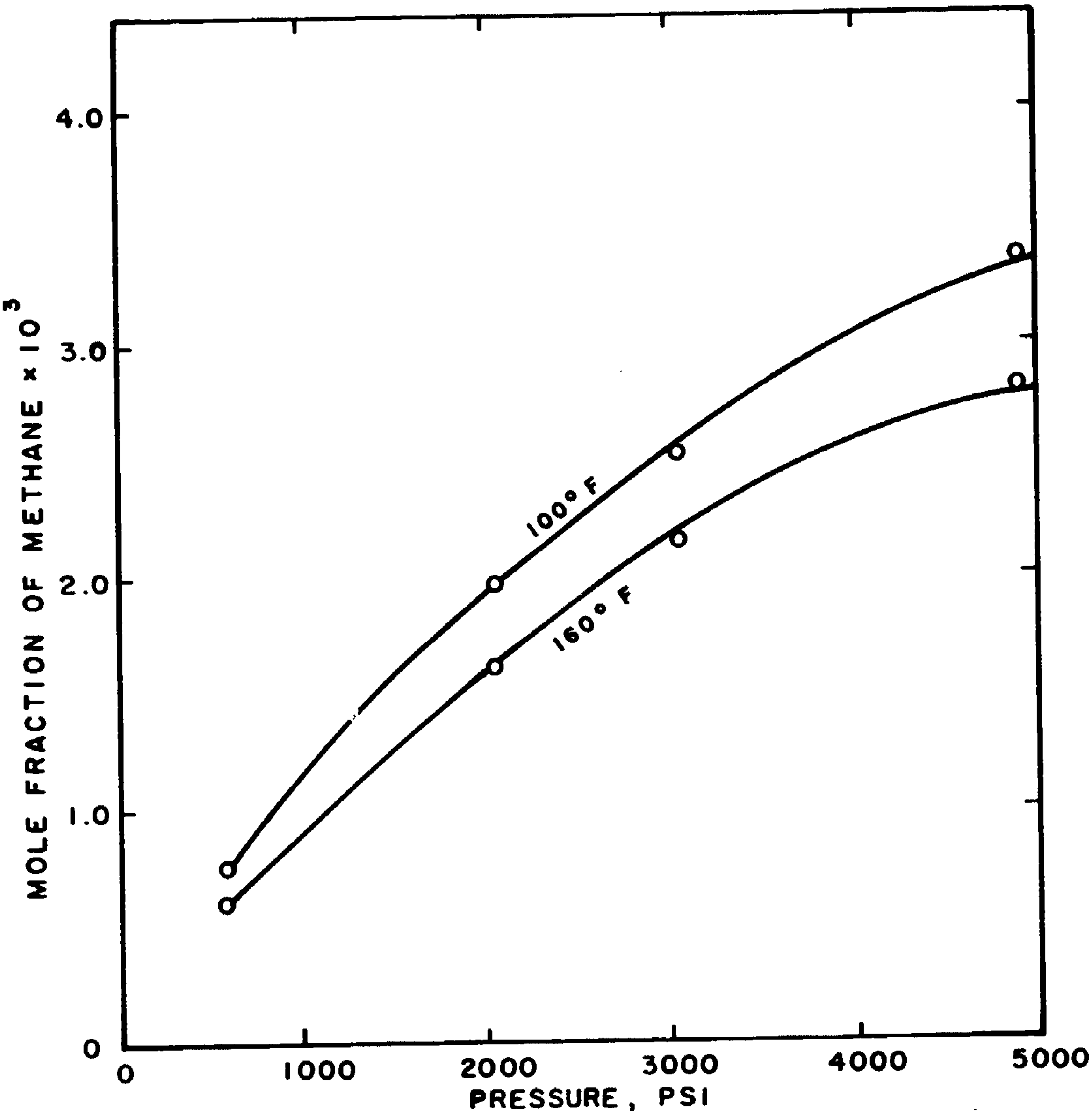


FIGURE V-12 MOLE FRACTION OF METHANE IN WATER RICH LIQUID PHASE AT 100° AND 160° F.

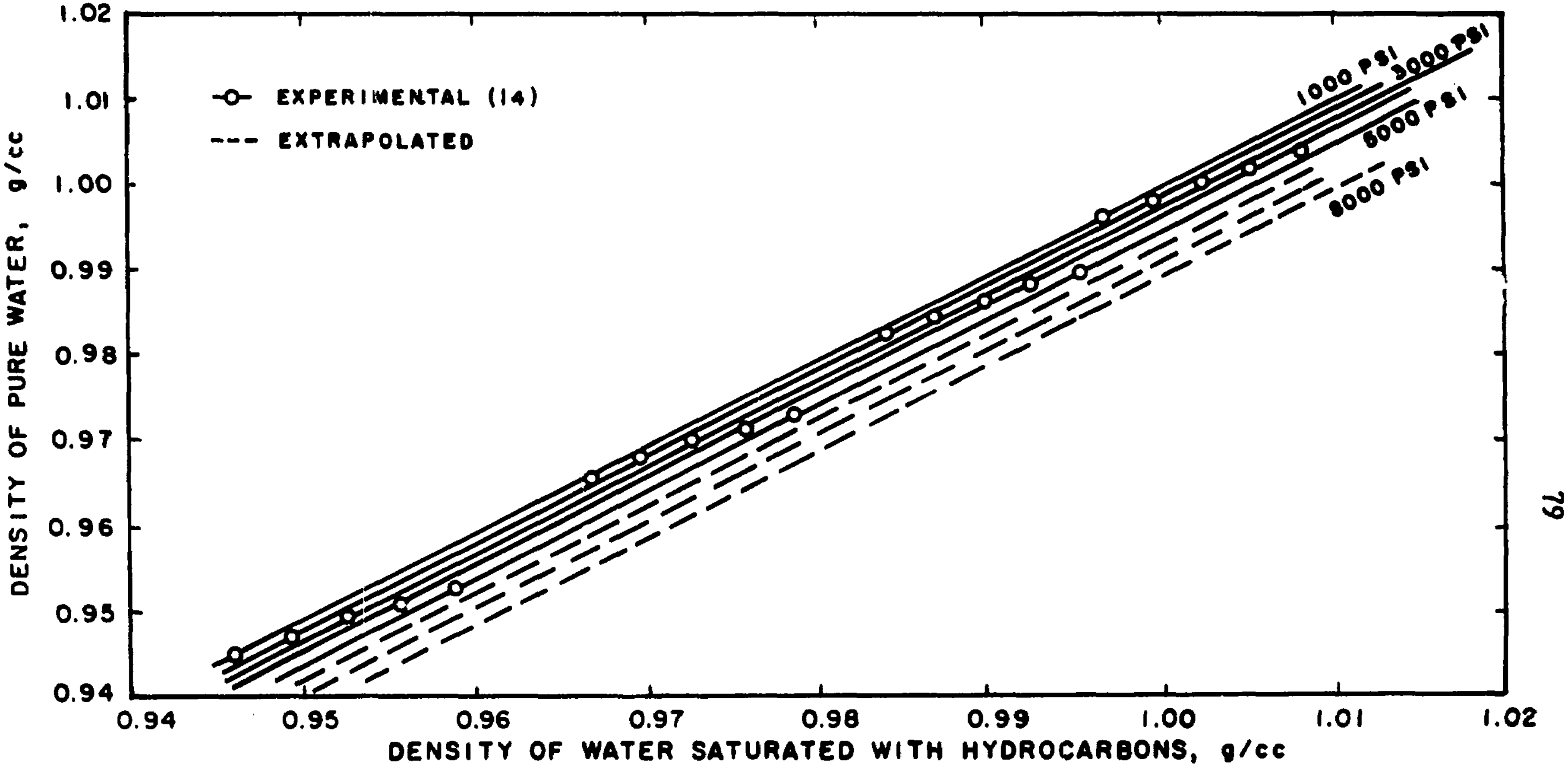


FIGURE V-13 A PLOT OF DENSITY OF PURE WATER VS DENSITY OF WATER SATURATED WITH HYDROCARBONS AT TEMPERATURES OF 100° TO 250° F AND PRESSURES OF 1000 TO 5000 PSI.

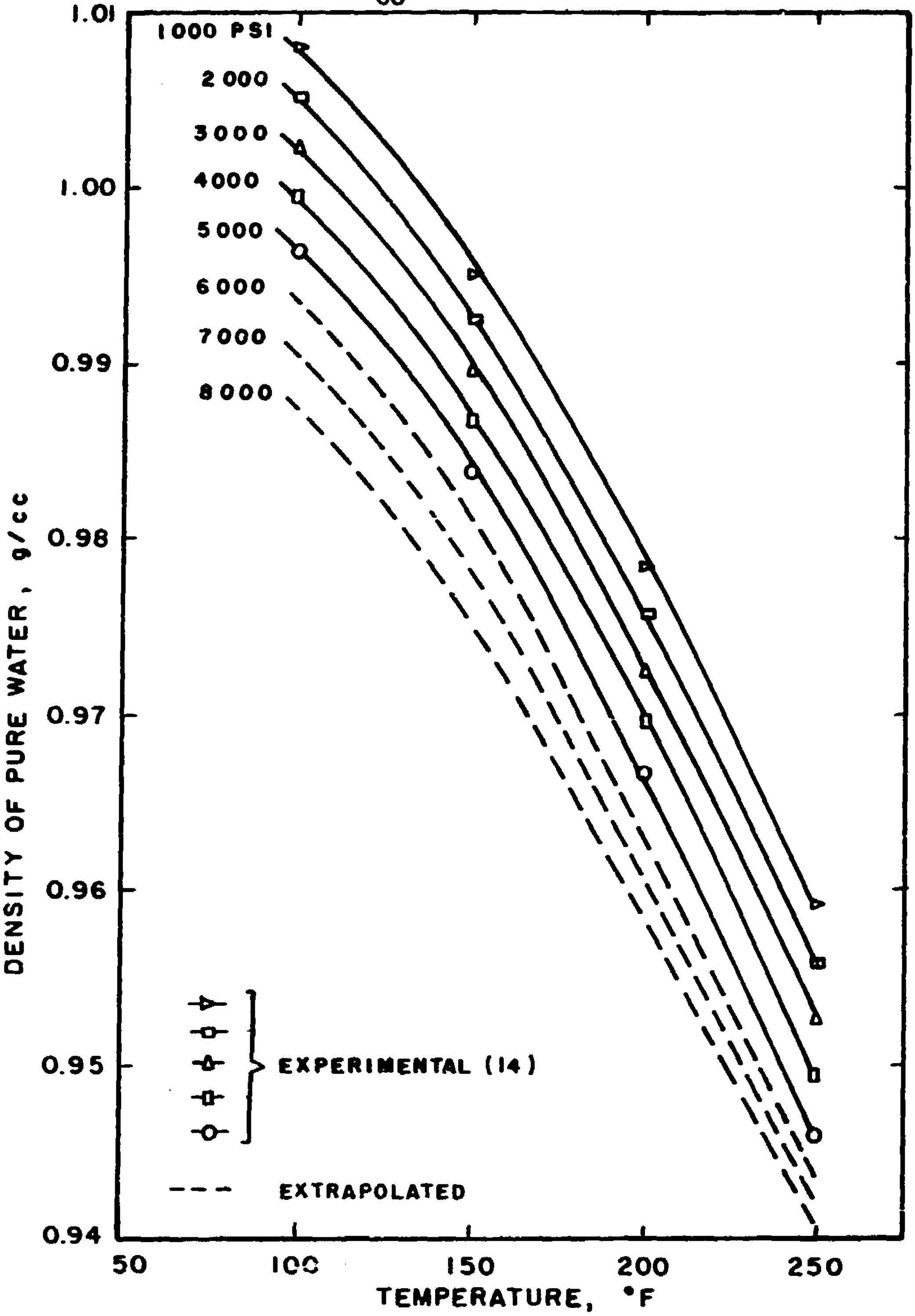


FIGURE V-14 DENSITY OF PURE LIQUID WATER AT TEMPERATURES OF 100° TO 250° F AND PRESSURES OF 1000 TO 5000 P

# CHAPTER VI

## CORRELATION AND DISCUSSION OF THE EXPERIMENTAL DATA

### A. Existing Correlations

As mentioned earlier, little work has been reported concerning the solubility of hydrocarbon mixtures in water. McKetta (15) has obtained experimental data for solubility of methane-n-butane in water. There is, however, at present no relationship available which can be used to determine the solubility of binary, ternary, or higher hydrocarbon mixtures in water.

Experimental data for solubility of pure methane, ethane, propane, n-butane, pentane, and hexane in water are available (13, 26, 25, 48, 12, 14, 49, 51, 50). If dilute hydrocarbon-water solution could be considered an ideal solution, the solubility of the hydrocarbon in water can be calculated from Henry's law:

$p_i = k_i x_i$ where gas behaves ideally

or $\bar{f}_i = k_i x_i$ " " " nonideally (III-12)

Krichevski and Kasarnovski (39) have derived a more rigorous relationship, based on thermodynamic principles, for the solubility of nonpolar gases in liquids:

$$\ln\frac{\bar{f}_i}{x_i} = \ln k_i + \frac{\bar{V}_i}{RT}(P-p_s) \qquad \text{(VI-1)}$$

where $p_s$ = the saturation pressure of pure water

$k_i$ = the Henry's law constant evaluated at $P = p_s$

$\bar{V}_i$ = partial molal volume

Kobayashi (14, 38) has calculated $\bar{V}_i$ for different hydrocarbons by applying Equation (VI-1) to water-rich phase of hydrocarbon-water binaries, and found that $\bar{V}_i$ cannot be assumed independent of pressure. Kobayashi has also shown that the solubilities of pure hydrocarbons, determined by using Equation (VI-1), are in excellent agreement with experimental data obtained by other investigators.

The application of Equation (VI-1) to hydrocarbon mixtures is hampered by the lack of partial-molal-volume and partial-fugacity data for mixtures.

Since there are ample information available concerning the solubility of pure components in water, a correlation which would make use of the data for pure components to predict the solubility of hydrocarbon mixtures in water would be of great importance. Based on the experimental data obtained in this work, such a correlation has been developed. The proposed correlation will be discussed in the next section.

## B. Proposed Correlation

In order to predict the solubility of binary hydrocarbon mixtures such as methane-ethane, methane-propane, or ethane-propane in water, the following empirical relationship is proposed:

$$x_t = y_1x_1^* + y_2x_2^* + y_1y_2\left(\frac{x_1^*x_2^*}{y_1x_1^* + y_2x_2^*}\right)\left(\frac{P_{c_1} + P_{c_2}}{0.5\ P}\right)^{0.125}\left(\frac{MW_2}{MW_1}\right)^{2.52} \qquad \text{(VI-2)}$$

where $x_t$ = total mole fraction of the hydrocarbons in water-rich phase

$y_1$, $y_2$ = mole fractions of components 1 and 2 in the water-free gas phase

$x_1^*$, $x_2^*$ = mole fraction of the pure components 1 and 2 in the water-rich phase at the same temperature and pressure as the mixture

$P_{c_1}$, $P_{c_2}$ = critical pressures of components 1 and 2

$MW_1$, $MW_2$ = molecular weights of components 1 and 2

and $P$ = pressure in psi

This particular equation was proposed on the following grounds:

1. The third term was added because the total solubility ($x_t$), obtained experimentally, was always larger than the sum of the first two terms. The sum of the first two terms, i.e., $y_1x_1^* + y_2x_2^*$, is a result of Kay's mixing rule.
2. The third term reduces to zero when either $y_1$ or $y_2$ equals to unity, and Equation (VI-2) reduces to

$$x_t = x_i^*$$

3. The relationship is dimensionally correct.
4. The effect of pressure on solubility is accounted for not only through $x_i^*$ terms (which are also functions of P) but also through the

$(\frac{P_{c_1} + P_{c_2}}{0.5\ P})^{.125}$ term.

5. It was observed that the greater the difference in the molecular size of the individual components the greater the difference between $x_t$ and $(y_1 x_1^* + y_2 x_2^*)$. Hence, the term $(MW_2/MW_1)^{2.52}$ was supplemented to account for the difference in the size of the various molecules composing the mixture.

The pure component solubilities, $x_1^*$, for $C_1$, $C_2$, $C_3$, and n-$C_4$ were obtained from Culberson (13), Kobayashi (14), and Reamer (49). The experimental values of $x_1^*$ at different T and P are shown in Figures (VI-1 to VI-3) and given in Tables (VI-1 to VI-3).

The total solubilities for $C_1$-$C_2$, $C_1$-$C_3$, and $C_2$-$C_3$ mixtures, calculated from Equation (VI-2), are compared with those obtained experimentally in Tables (VI-4), (VI-5), and (VI-6), respectively. The deviations between the experimental and calculated values are generally below 2 per cent. However, two or three samples were off as high as 3.91 per cent. Considering the precision of the experimental apparatus plus the fact that the pure component solubilities were obtained from different sources and they in turn contained some error, the agreement between the experimental and calculated values is excellent.

The correlation proposed here was also used to predict the total solubility of the methane-n-butane mixture at 100, 160, and 220 F under 2000 and 3000 psi. These values are compared with the experimental data obtained by McKetta (15) at the same T and P conditions and given in Table (VI-7). The deviations between the experimental and calculated values are less than 10 per cent with the exception of a single point which was off as high as 26.9 per cent. No sound reason can be given for the high discrepancy except a remote chance that the particular experimental value could be in error. From the total solubility values for $C_1$-$C_2$, $C_1$-$C_3$, and $C_2$-$C_3$ mixtures, given in Tables (V-5), (V-6), and (V-7), respectively, it can be observed that the total solubility increases slightly with an increase in the mole fraction of the more soluble component in the gas phase. Looking at the rest of McKetta's data, the gas phase composition seems to have little or no effect on the total solubility with the exception of the point in question. Considering the total solubilities of two mixtures at 220 F and 3000 psi having the following gas phase composition:

Mixture A: $y_{C_1} = 0.098$, $(x_t)_{exp.} = 2.460$, $(x_t)_{calc.} = 2.509$

Mixture B: $y_{C_1} = 0.4915$, $(x_t)_{exp.} = 2.320$, $(x_t)_{calc.} = 3.043$

it is seen that the total solubility, experimental values, decreases with an increase in the mole fraction of the more soluble component (methane compared to n-butane). This could be given as a reason for the large deviation. Altogether, a reasonable agreement is observed between the experimental values of McKetta and those calculated from the proposed correlation.

The solubility of individual components in the mixture can be determined as

$$x_i = Y_i^* x_t \qquad \text{(VI-3)}$$

where $Y_i^*$ is a corrected mole fraction of component i in the water-free gas phase. The corrected mole fractions, $Y_i^*$, are a function of the $y_i$, mole fractions in the gas. A plot of the $Y_i^*/y_i$ against $y_i$ for $C_1$-$C_2$, $C_1$-$C_3$, $C_1$-n-$C_4$, and $C_2$-$C_3$ is shown in Figure (VI-4). The curves in Figure (VI-4) are based on the experimental results obtained in this work and by McKetta.

The proposed correlation was extended to apply to ternary hydrocarbon mixtures as follows:

let $$\text{KMR} = y_1x_1^* + y_2x_2^* + y_3x_3^*$$

then $$x_t = \text{KMR} + y_1y_2(x_1^*x_2^*/\text{KMR})((P_{C_1} + P_{C_2})/0.5P)^{0.125}(MW_2/MW_1)^{2.52} +$$
$$y_1y_3(x_1^*x_3^*/\text{KMR})((P_{C_1} + P_{C_3})/0.5P)^{0.125}(MW_3/MW_1)^{2.52} + y_2y_3$$
$$(x_2^*x_3^*/\text{KMR})((P_{C_2} + P_{C_3})/0.5P)^{0.125}(MW_3/MW_2)^{2.52} + y_1y_2y_3$$
$$(x_1^*x_2^*x_3^*/\text{KMR})((P_{C_1} + P_{C_2} + P_{C_3})/0.5P)^{0.125}((MW_2 + MW_3)/$$
$$(MW_1 + MW_2))^{2.52} \qquad \text{(VI-4)}$$

As mentioned earlier in this chapter, the term KMR represents Kay's mixing rule and other terms in Equation (VI-4) can be considered as correction terms due to binary and ternary interactions. It can be shown that, for light hydrocarbons, the ternary term is negligible compared to the other terms in Equation (VI-4) and it may be dropped out. For simplicity the following terms may be defined:

$$\text{PCR}(12) \equiv ((P_{C_1} + P_{C_2})/0.5P)^{0.125} \qquad \text{(VI-5A)}$$

$$\text{PCR}(13) \equiv ((P_{C_1} + P_{C_3})/0.5P)^{0.125} \qquad \text{(VI-5B)}$$

$$\text{PCR}(23) \equiv ((P_{C_2} + P_{C_3})/0.5P)^{0.125} \qquad \text{(VI-5C)}$$

$$\text{MWCR}(12) \equiv (MW_2/MW_1)^{2.52} \qquad \text{(VI-5D)}$$

$$MWCR(13) \equiv (MW_3/MW_1)^{2.52} \qquad (VI\text{-}5E)$$

$$MWCR(23) \equiv (MW_3/MW_2)^{2.52} \qquad (VI\text{-}5F)$$

Dropping the ternary term and substituting Equations (VI-5A) through (VI-5F) in Equation (VI-4) will give

$$x_t = KMR + y_1y_2(x_1^*x_2^*/KMR)(PCR\ 12)(MWCR\ 12) + y_1y_3(x_1^*x_3^*/KMR)$$
$$(PCR\ 13)(MWCR\ 13) + y_2y_3(x_2^*x_3^*/KMR)(PCR\ 23)(MWCR\ 23) \qquad (VI\text{-}5)$$

The total solubilities for methane-ethane-propane mixtures at 220 F and 665-5015 psig were calculated according to Equation (VI-5) and are compared with the experimental data in Table (VI-8). The maximum difference between the calculated and experimental values is 6.37 per cent.

The individual solubilities can be determined from

$$x_i = Y_i^*x_t \qquad (VI\text{-}3)$$

where a plot of $Y_i^*/y_i$ against $y_i$ for $C_1$-$C_2$-$C_3$ mixtures is shown in Figure (VI-4A).

Considering the excellent agreement between the proposed correlation for calculating the solubility of binary and ternary hydrocarbon mixtures in water, one can suggest the following equation for multicomponent hydrocarbon mixtures:

$$x_t = \sum_i y_ix_i^* + \sum_i \sum_j (y_iy_j(x_i^*x_j^*/\sum_i y_ix_i^*)PCR(ij)MWCR(ij)) \qquad (VI\text{-}6)$$

where $PCR(ij) = ((P_{C_i} + P_{C_j})/0.5P)^{0.125}$

and $\quad MWCR(ij) = (MW(j)/MW(i))^{2.52}, \quad j > i$

It should be noted that in Equation (VI-6) the ternary and higher terms have been neglected.

## C. Discussion of the Experimental Results

The experimental values of total solubility of methane-ethane mixtures given in Table (V-5) have been plotted against pressure in Figure (VI-5) and against composition in Figure (VI-6). As seen from these figures, the total solubility of the mixture increases with increase in pressure and shows a maximum when the mole fraction of methane is 45 to 50 per cent.

The experimental total solubilities for a methane-ethane mixture, having a composition of 49.90 mole per cent methane, at 5000 psi and 100 to 220 F are plotted against temperature. The mixture shows a definite minimum at 160 F. This is in agreement with Culberson's data on pure methane and ethane (13).

The experimental values of total solubilities of methane-propane mixtures at 220 F have been plotted against pressure and methane mole fraction and are shown in Figures (VI-8) and (VI-9), respectively. The total solubility of the mixture increases with an increase in pressure and shows a maximum at $y_{CH_4} = .40$ to $.70$ for all pressures. It should be noted that the total solubility of methane-ethane or methane-propane mixtures is greater than the solubility of pure methane, at the same temperature and pressure, when the methane mole fraction is greater than 20 per cent. This is in agreement with the findings of other investigators including Culberson (25, 26). Culberson noticed that the solubilities of natural gas in pure water, determined by Dodson and Standing (28), were greater than the solubility of pure methane at the same pressure and temperature up to 5000 psi. As can be seen from Figures (VI-6) and (VI-9), the total mixture solubilities are greater than the solubility of pure methane at lower pressures and approach the solubility of pure methane at higher pressures.

The experimental values of total solubility for ethane-propane mixtures at 220 F have been plotted against pressure and ethane composition and are shown in Figures (VI-10) and (VI-11), respectively. The total solubility increases with an increase in pressure and shows a maximum at $y_{C_2H_6} = .50$ to $y_{C_2H_6} = .70$, for all pressures. The total solubility of the mixtures is greater than the solubility of pure ethane, at the same T and P, for mixtures that have more than 20-55 mole per cent ethane at pressures lower than 3000 psi. At pressures higher than 3000 psi, the total solubility of the mixture is less than the solubility of pure ethane.

It is seen that the hydrocarbon-water solutions are non-ideal. They show a positive deviation from Raoult's law. If the degree of deviation from Raoult's law could be considered as a measure of non-ideality, then, methane-ethane-water solutions are more non-ideal than methane-propane-water which in turn are more non-ideal than ethane-propane-water solutions.

The experimental total solubility values for methane-ethane-propane mixtures at 220 F have been plotted against pressure and are shown in Figure (VI-12). The total solubility increases with an increase in pressure.

The total solubility seems to be fairly constant and independent of the compositions as seen in Figure (VI-14).

The experimental total solubility of $C_1$-$C_2$-$C_3$ was also obtained at 5000 psi and 160, 190, and 220 F. A plot of total solubility of a $C_1$-$C_2$-$C_3$ mixture containing 70.15 per cent methane and 10.65 per cent ethane against temperature is shown in Figure (VI-13). The total solubility increases exponentially with temperature from 160 to 220 F and it indicates a possible minimum in the neighborhood of 140 to 160 F.

The total solubility of methane-ethane-propane mixtures in water is greater than the solubility of pure methane at the same temperature and pressures up to 5000 psi. However, the difference between the solubility of the mixture and pure methane decreases as the pressure increases.

## TABLE (VI-1)

## SOLUBILITY OF METHANE, ETHANE, PROPANE, AND n-BUTANE IN WATER AT 100 F AND PRESSURES UP TO 10,000 PSIA

| Pressure Psia | $10^3$ x Mole Fraction of Hydrocarbon in Water | | | |
|---|---|---|---|---|
| | $CH_4$ (13) | $C_2H_6$ (13) | $C_3H_8$ (14) | $nC_4$-$H_{10}$ (49) |
| 200 | 0.273 | 0.328 | 0.204 | 0.062 |
| 400 | 0.528 | 0.534 | 0.208 | 0.063 |
| 600 | 0.760 | 0.667 | 0.211 | 0.064 |
| 800 | 0.986 | 0.749 | 0.214 | 0.064 |
| 1000 | 1.199 | 0.793 | 0.217 | 0.065 |
| 1250 | 1.425 | 0.822 | - | - |
| 1500 | 1.620 | 0.849 | 0.222 | 0.066 |
| 2000 | 1.953 | 0.888 | 0.226 | 0.068 |
| 2500 | 2.247 | 0.915 | 0.229 | - |
| 3000 | 2.503 | 0.933 | 0.230 | 0.071 |
| 3500 | 2.738 | 0.959 | - | - |
| 4000 | 2.962 | 0.982 | 0.235* | 0.073 |
| 5000 | 3.360 | 1.032 | - | 0.075 |
| 6000 | 3.701 | 1.080 | 0.242* | 0.076 |
| 7000 | 3.987 | 1.112 | - | - |
| 8000 | 4.236 | 1.126 | 0.246* | 0.078 |
| 9000 | 4.461 | 1.129 | - | - |
| 10,000 | 4.671 | 1.133 | 0.248* | 0.080 |

---

* Thermodynanically smoothed values.

## TABLE (VI-2)

## SOLUBILITY OF METHANE, ETHANE, PROPANE, AND n-BUTANE IN WATER AT 160 F AND PRESSURES UP TO 10,000 PSIA

| Pressure Psia | $10^3$ x Mole Fraction of Hydrocarbon in Water | | | |
|---|---|---|---|---|
| | $CH_4$ (13) | $C_2H_6$ (13) | $C_3H_8$ (14) | $nC_4$-$H_{10}$ (49) |
| 200 | 0.203 | 0.173 | 0.130 | 0.088 |
| 400 | 0.407 | 0.348 | 0.214 | 0.088 |
| 600 | 0.599 | 0.478 | 0.226 | 0.089 |
| 800 | 0.780 | 0.569 | 0.232 | 0.089 |
| 1000 | 0.945 | 0.628 | 0.236 | 0.090 |
| 1250 | 1.133 | 0.683 | - | - |
| 1500 | 1.308 | 0.729 | 0.242 | 0.091 |
| 2000 | 1.608 | 0.788 | 0.246 | 0.092 |
| 2500 | 1.861 | 0.831 | 0.251 | - |
| 3000 | 2.094 | 0.873 | 0.254 | 0.094 |
| 3500 | 2.309 | 0.913 | - | - |
| 4000 | 2.516 | 0.951 | 0.261* | 0.096 |
| 5000 | 2.888 | 1.014 | - | 0.098 |
| 6000 | 3.221 | 1.060 | 0.269* | 0.099 |
| 7000 | 3.519 | 1.098 | - | - |
| 8000 | 3.782 | 1.142 | 0.273* | 0.101 |
| 9000 | 4.007 | 1.187 | - | - |
| 10,000 | 4.211 | 1.228 | 0.274* | 0.103 |

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* Thermodynamically smoothed values.

## TABLE (VI-3)

## SOLUBILITY OF METHANE, ETHANE, PROPANE, AND n-BUTANE IN WATER AT 220 F AND PRESSURES UP TO 10,000 PSIA

| Pressure Psia | $10^3$ x Mole Fraction of Hydrocarbon in Water | | | |
|---|---|---|---|---|
| | $CH_4$ (13) | $C_2H_6$ (13) | $C_3H_8$ (14) | $nC_4$-$H_{10}$ (49) |
| 200 | 0.188 | 0.144 | 0.118 | 0.113 |
| 400 | 0.383 | 0.299 | 0.217 | 0.140 |
| 600 | 0.572 | 0.449 | 0.280 | 0.142 |
| 800 | 0.752 | 0.559 | 0.305 | 0.143 |
| 1000 | 0.930 | 0.647 | 0.316 | 0.143 |
| 1250 | 1.148 | 0.742 | - | 0.143 |
| 1500 | 1.339 | 0.823 | 0.326 | 0.144 |
| 2000 | 1.662 | 0.955 | 0.336 | 0.145 |
| 2500 | 1.961 | 1.038 | 0.345 | 0.146 |
| 3000 | 2.233 | 1.073 | 0.353 | 0.148 |
| 3500 | 2.478 | 1.121 | - | - |
| 4000 | 2.701 | 1.163 | 0.366* | 0.150 |
| 5000 | 3.100 | 1.222 | - | - |
| 6000 | 3.447 | 1.287 | 0.385* | 0.155 |
| 7000 | 3.757 | 1.350 | - | 0.158 |
| 8000 | 4.034 | 1.412 | 0.397* | 0.161 |
| 9000 | 4.296 | 1.464 | - | 0.163 |
| 10,000 | 4.538 | 1.500 | 0.403* | 0.165 |

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* Thermodynamically smoothed values.

## TABLE (VI-4)

## TOTAL SOLUBILITY OF METHANE-ETHANE MIXTURES IN WATER: COMPARISON OF EXPERIMENTAL DATA WITH THOSE CALCULATED ACCORDING TO THE CORRELATION PROPOSED IN THIS WORK

| Mixture | T(F) | P(Psi) | Total Solubility of the Mixture x $10^3$ | | Maximum Deviation |
|---|---|---|---|---|---|
| | | | Exptl. | Calcd. | |
| #1 | 160 | 665 | 1.146 | 1.126 | + 1.78 % |
| | " | 2065 | 2.041 | 2.049 | - 0.39 |
| | " | 3065 | 2.440 | 2.412 | + 1.16 |
| | " | 4965 | 2.960 | 2.904 | + 1.86 |
| | " | 7915 | 4.003 | 3.933 | + 1.02 |
| #2 | 160 | 665 | 1.415 | 1.405 | + 0.71 |
| | " | 2065 | 2.510 | 2.525 | - 0.60 |
| | " | 3065 | 2.993 | 2.963 | + 1.01 |
| | " | 4965 | 3.612 | 3.562 | + 1.41 |
| | " | 7915 | 4.806 | 4.831 | - 0.52 |
| #3 | 100 | 5000 | 3.897 | 3.977 | - 2.06 |
| | 130 | " | 3.711 | 3.731 | - 0.54 |
| | 160 | " | 3.586 | 3.646 | - 1.69 |
| | 190 | " | 3.780 | 3.800 | - 0.54 |
| | 220 | " | 4.200 | 4.138 | + 1.50 |
| | 160 | 665 | 1.412 | 1.428 | - 1.14 |
| | " | 2065 | 2.512 | 2.562 | - 2.00 |
| | " | 3065 | 3.102 | 3.012 | + 3.00 |
| | " | 4965 | 3.589 | 3.637 | - 1.34 |
| | " | 7915 | 4.840 | 4.932 | - 1.90 |

TABLE (VI-4)--Continued

| Mixture | T(F) | P(Psi) | Total Solubility of the Mixture x $10^3$ Exptl. | Total Solubility of the Mixture x $10^3$ Calcd. | Maximum Deviation |
|---|---|---|---|---|---|
| #4 | 160 | 665 | 1.327 | 1.277 | + 3.91 % |
| | " | 2065 | 2.420 | 2.360 | + 2.54 |
| | " | 3065 | 2.800 | 2.822 | - 0.79 |
| | " | 4965 | 3.519 | 3.497 | + 0.63 |
| | " | 7915 | 4.807 | 4.717 | + 1.91 |
| #5 | 160 | 665 | 1.072 | 1.032 | + 3.87 |
| | " | 2065 | 2.050 | 2.055 | - 0.24 |
| | " | 3065 | 2.564 | 2.524 | + 1.59 |
| | " | 4965 | 3.260 | 3.238 | + 1.30 |
| | " | 7915 | 4.300 | 4.324 | - 0.56 |

## TABLE (VI-5)

## TOTAL SOLUBILITY OF METHANE-PROPANE MIXTURES IN WATER: COMPARISON OF EXPERIMENTAL DATA WITH THOSE CALCULATED ACCORDING TO THE CORRELATION PROPOSED IN THIS WORK

| Mixture | T(F) | P(Psi) | Total Solubility of the Mixture x $10^3$ | | Maximum Deviation |
|---|---|---|---|---|---|
| | | | Exptl. | Calcd. | |
| #6 | 220 | 715 | 1.760 | 1.800 | - 2.28 % |
| | " | 2065 | 2.601 | 2.611 | - 0.39 |
| | " | 3015 | 2.959 | 2.939 | + 0.68 |
| | " | 5015 | 3.302 | 3.342 | - 1.21 |
| | " | 8015 | 3.650 | 3.698 | + 1.31 |
| #7 | 220 | 715 | 2.191 | 2.207 | - 0.73 |
| | " | 2065 | 2.887 | 2.957 | - 2.02 |
| | " | 3015 | 3.296 | 3.282 | + 0.43 |
| | " | 5015 | 3.702 | 3.732 | - 0.81 |
| | " | 8015 | 4.190 | 4.180 | + 0.24 |
| #8 | 220 | 715 | 2.171 | 2.181 | - 0.46 |
| | " | 2065 | 2.871 | 2.889 | - 0.63 |
| | " | 3015 | 3.250 | 3.230 | + 0.62 |
| | " | 5015 | 3.762 | 3.730 | + 0.86 |
| | " | 8015 | 4.170 | 4.250 | - 1.92 |
| #9 | 220 | 715 | 1.751 | 1.731 | + 1.16 |
| | " | 2065 | 2.500 | 2.448 | + 2.12 |
| | " | 3015 | 2.901 | 2.871 | + 1.05 |
| | " | 5015 | 3.551 | 3.523 | + 0.80 |
| | " | 8015 | 4.207 | 4.229 | - 0.52 |

TABLE (VI-5)--Continued

| Mixture | T(F) | P(Psi) | Total Solubility of the Mixture x $10^3$ Exptl. | Total Solubility of the Mixture x $10^3$ Calcd. | Maximum Deviation |
|---|---|---|---|---|---|
| #10 | 220 | 715 | 1.280 | 1.274 | + 0.47 % |
| | " | 2065 | 2.109 | 2.069 | + 1.93 |
| | " | 3015 | 2.550 | 2.564 | - 0.55 |
| | " | 5015 | 3.306 | 3.326 | - 0.61 |
| | " | 8015 | 4.200 | 4.156 | + 1.06 |

## TABLE (VI-6)

## TOTAL SOLUBILITY OF ETHANE-PROPANE MIXTURES IN WATER: COMPARISON OF EXPERIMENTAL DATA WITH THOSE CALCULATED ACCORDING TO THE CORRELATION PROPOSED IN THIS WORK

| Mixture | T(F) | P(psi) | Total Solubility of the Mixture x $10^3$ |  | Maximum Deviation |
|---|---|---|---|---|---|
|  |  |  | Exptl. | Calcd. |  |
| #11 | 220 | 665 | 0.560 | 0.541 | + 3.51 % |
|  | " | 2015 | 0.811 | 0.801 | + 1.25 |
|  | " | 3015 | 0.850 | 0.844 | + 0.71 |
|  | " | 4965 | 0.906 | 0.900 | + 0.67 |
|  | " | 8015 | 0.983 | 0.975 | + 0.82 |
| #12 | 220 | 665 | 0.625 | 0.632 | - 1.12 |
|  | " | 2015 | 0.950 | 0.957 | - 0.74 |
|  | " | 3015 | 1.020 | 1.014 | + 0.59 |
|  | " | 4965 | 1.094 | 1.088 | + 0.55 |
|  | " | 8015 | 1.181 | 1.189 | - 0.68 |
| #13 | 220 | 665 | 0.635 | 0.645 | - 1.57 |
|  | " | 2015 | 1.014 | 1.009 | + 0.50 |
|  | " | 3015 | 1.086 | 1.080 | + 0.56 |
|  | " | 4965 | 1.166 | 1.170 | - 0.34 |
|  | " | 8015 | 1.290 | 1.294 | - 0.31 |
| #14 | 220 | 665 | 0.623 | 0.617 | + 0.97 |
|  | " | 2015 | 1.010 | 1.018 | - 0.79 |
|  | " | 3015 | 1.110 | 1.102 | + 0.73 |
|  | " | 4965 | 1.200 | 1.206 | - 0.50 |
|  | " | 8015 | 1.357 | 1.353 | + 0.30 |

TABLE (VI-6)--Continued

| Mixture | T(F) | P(Psi) | Total Solubility of the Mixture x $10^3$ Exptl. | Total Solubility of the Mixture x $10^3$ Calcd. | Maximum Deviation |
|---|---|---|---|---|---|
| #15 | 220 | 665 | 0.565 | 0.571 | - 1.06 % |
| | " | 2015 | 1.004 | 1.006 | - 0.20 |
| | " | 3015 | 1.113 | 1.103 | + 0.91 |
| | " | 4965 | 1.214 | 1.220 | - 0.50 |
| | " | 8015 | 1.390 | 1.386 | + 0.29 |

TABLE (VI-7)

COMPARISON OF THE TOTAL SOLUBILITY OF METHANE-n-BUTANE MIXTURE IN WATER, IN THE TWO-PHASE REGION, BETWEEN CALCULATED VALUES FROM THE CORRELATION PROPOSED IN THIS STUDY AND EXPERIMENTAL DATA GIVEN BY McKETTA (15)

| Temperature F | Pressure Psia | Composition of the Gas Phase Mole Fraction of Methane | Mole Fraction of n-Butane | Total Solubility x $10^3$ This Study | McKetta's Data | Average Deviation |
|---|---|---|---|---|---|---|
| 100 | 2996 | 0.7325 | 0.2675 | 2.331 | 2.500 | 7.00 % |
| 100 | 1998 | 0.7310 | 0.2690 | 1.927 | 1.900 | 1.41 |
| 160 | 1988 | 0.7996 | 0.2004 | 1.788 | 1.750 | 2.15 |
| 160 | 1990 | 0.1874 | 0.8126 | 1.952 | 1.750 | 10.90 |
| 160 | 2048 | 0.6302 | 0.3698 | 1.927 | 1.750 | 9.66 |
| 160 | 2948 | 0.7995 | 0.2005 | 2.166 | 2.220 | 2.47 |
| 160 | 2998 | 0.1905 | 0.8095 | 2.100 | 2.220 | 5.56 |
| 160 | 3018 | 0.6300 | 0.3700 | 2.215 | 2.207 | 0.36 |
| 220 | 2996 | 0.0908 | 0.9192 | 2.509 | 2.460 | 1.98 |
| 220 | 2998 | 0.4915 | 0.5085 | 3.043 | 2.320 | 26.90 |

## TABLE (VI-8)

## TOTAL SOLUBILITY OF METHANE-ETHANE-PROPANE MIXTURES IN WATER: COMPARISON OF EXPERIMENTAL DATA WITH THOSE CALCULATED ACCORDING TO THE CORRELATION PROPOSED IN THIS WORK

| | | | Total Solubility of the Mixture x $10^3$ | | Maximum |
|---|---|---|---|---|---|
| Mixture | T(F) | P(Psi) | Exptl. | Calcd. | Deviation |
| #16 | 220 | 665 | 1.595 | 1.668 | - 4.58 % |
| | " | 2065 | 2.800 | 2.907 | - 3.82 |
| | " | 3015 | 3.214 | 3.296 | - 2.56 |
| | " | 4015 | 3.624 | 3.690 | - 1.82 |
| | " | 5015 | 3.986 | 4.047 | - 1.53 |
| #17 | 220 | 665 | 1.595 | 1.590 | + 0.31 |
| | " | 2065 | 2.806 | 2.750 | + 2.04 |
| | " | 3015 | 3.218 | 3.230 | - 0.37 |
| | " | 4015 | 3.606 | 3.580 | + 0.73 |
| | " | 5015 | 3.957 | 3.934 | + 0.59 |
| #18 | 160 | 5000 | 3.301 | 3.206 | + 2.97 |
| | 190 | " | 3.365 | 3.341 | + 0.72 |
| | 220 | " | 3.750 | 3.749 | + 0.03 |
| | " | 665 | 1.395 | 1.484 | - 6.37 |
| | " | 2065 | 2.655 | 2.554 | + 3.96 |
| | " | 3015 | 3.105 | 3.038 | + 2.22 |
| | " | 4015 | 3.355 | 3.400 | - 1.27 |
| #19 | 220 | 665 | 1.389 | 1.459 | - 5.04 |
| | " | 2065 | 2.250 | 2.259 | - 0.40 |

TABLE (VI-8)--Continued

| Mixture | T(F) | P(Psi) | Total Solubility of the Mixture x $10^3$ Exptl. | Total Solubility of the Mixture x $10^3$ Calcd. | Maximum Deviation |
|---|---|---|---|---|---|
| #19 | 220 | 3015 | 3.005 | 2.888 | + 3.91 % |
|  | " | 4015 | 3.204 | 3.194 | + 0.31 |
|  | " | 5015 | 3.692 | 3.682 | + 0.28 |
| #20 | 220 | 665 | 1.580 | 1.565 | + 0.96 |
|  | " | 2065 | 2.655 | 2.688 | - 1.24 |
|  | " | 3015 | 3.105 | 3.117 | - 0.39 |
|  | " | 4015 | 3.365 | 3.379 | - 0.42 |
|  | " | 5015 | 3.703 | 3.698 | + 0.14 |

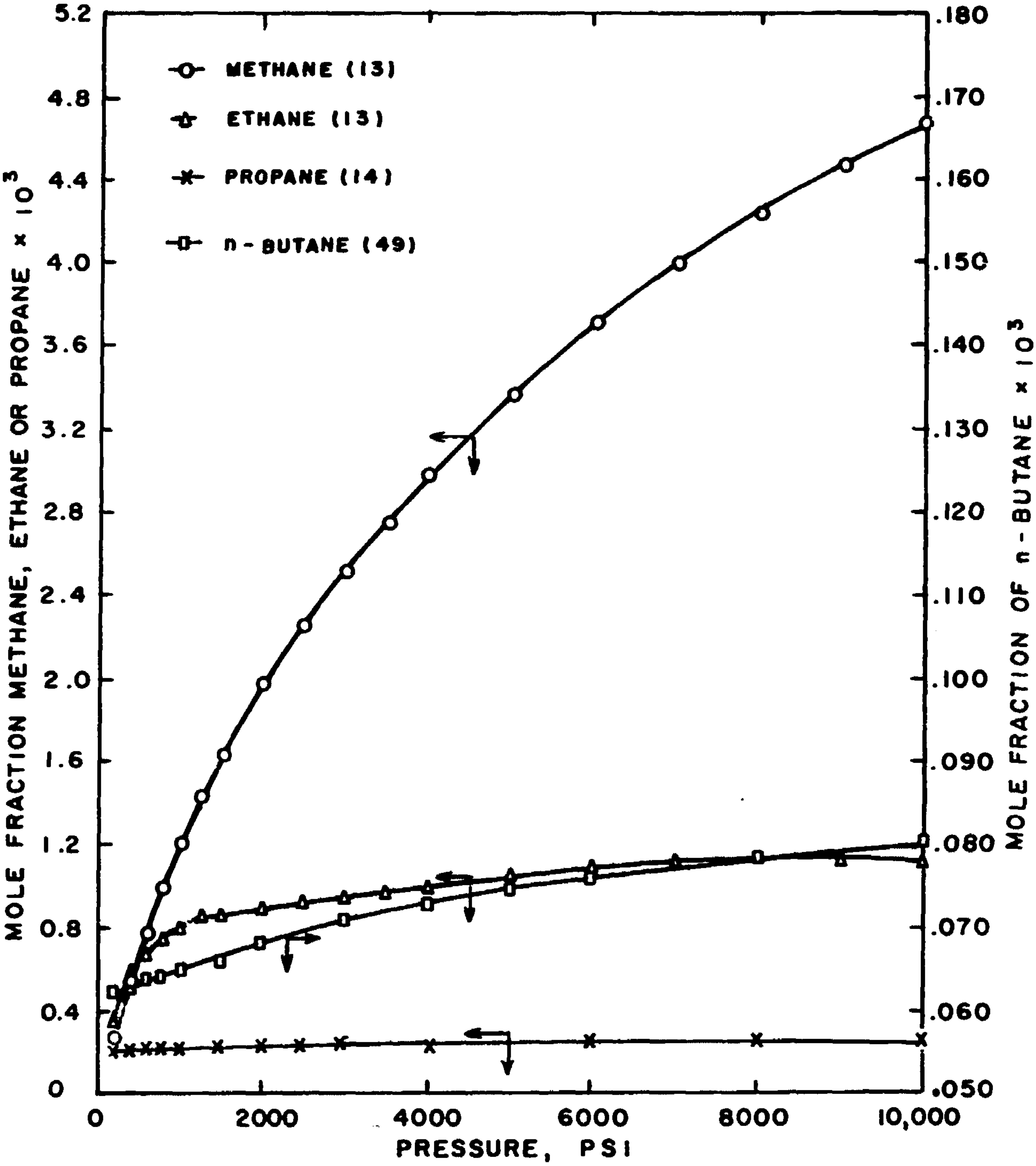

FIGURE VI-1 MOLE FRACTION OF METHANE, ETHANE, PROPAN AND n-BUTANE IN WATER-RICH LIQUID PHASE AT 100° F.

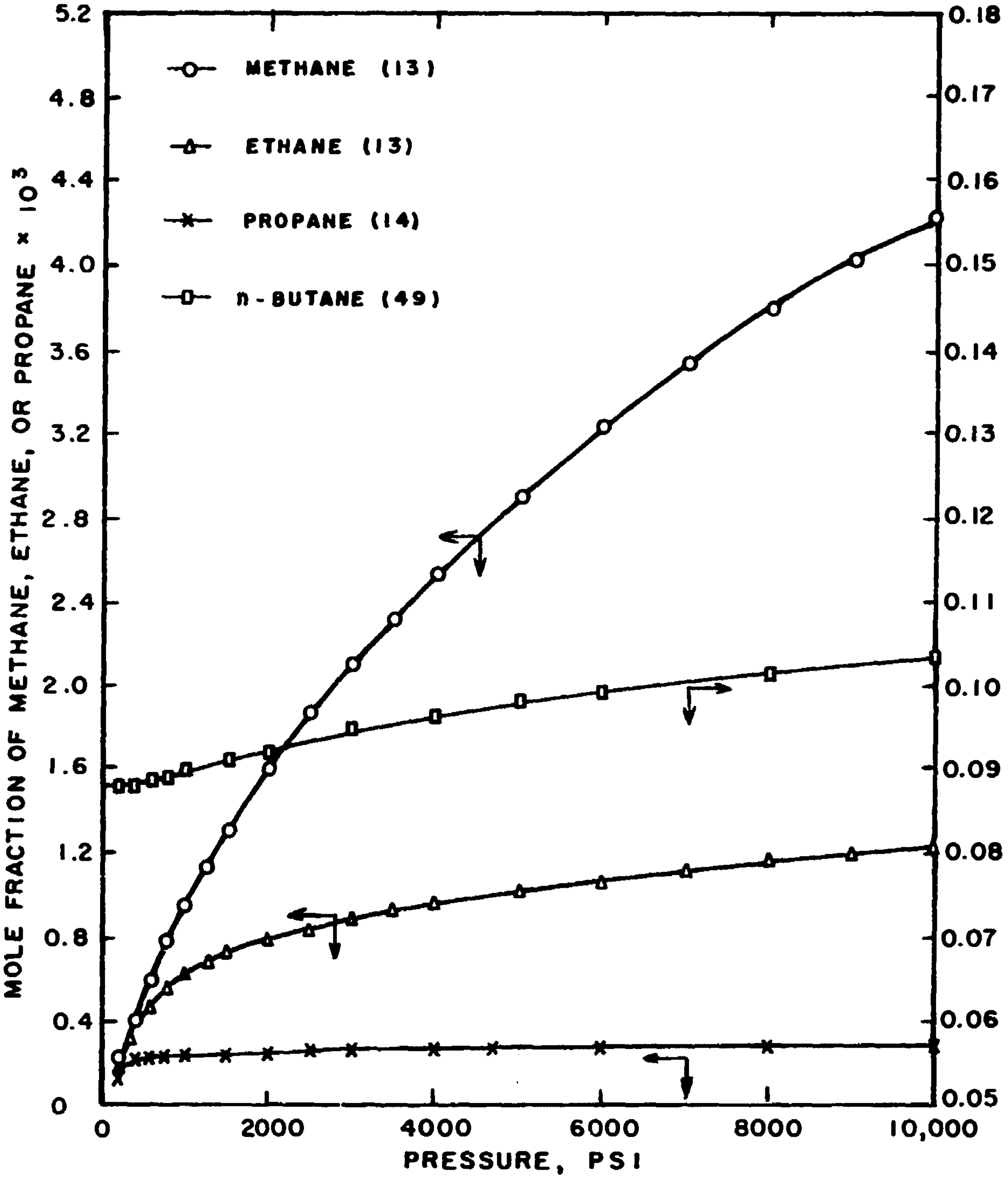

FIGURE VI-2 MOLE FRACTION OF METHANE, ETHANE, PROPANE AND n-BUTANE IN WATER-RICH LIQUID PHASE AT 160° F.

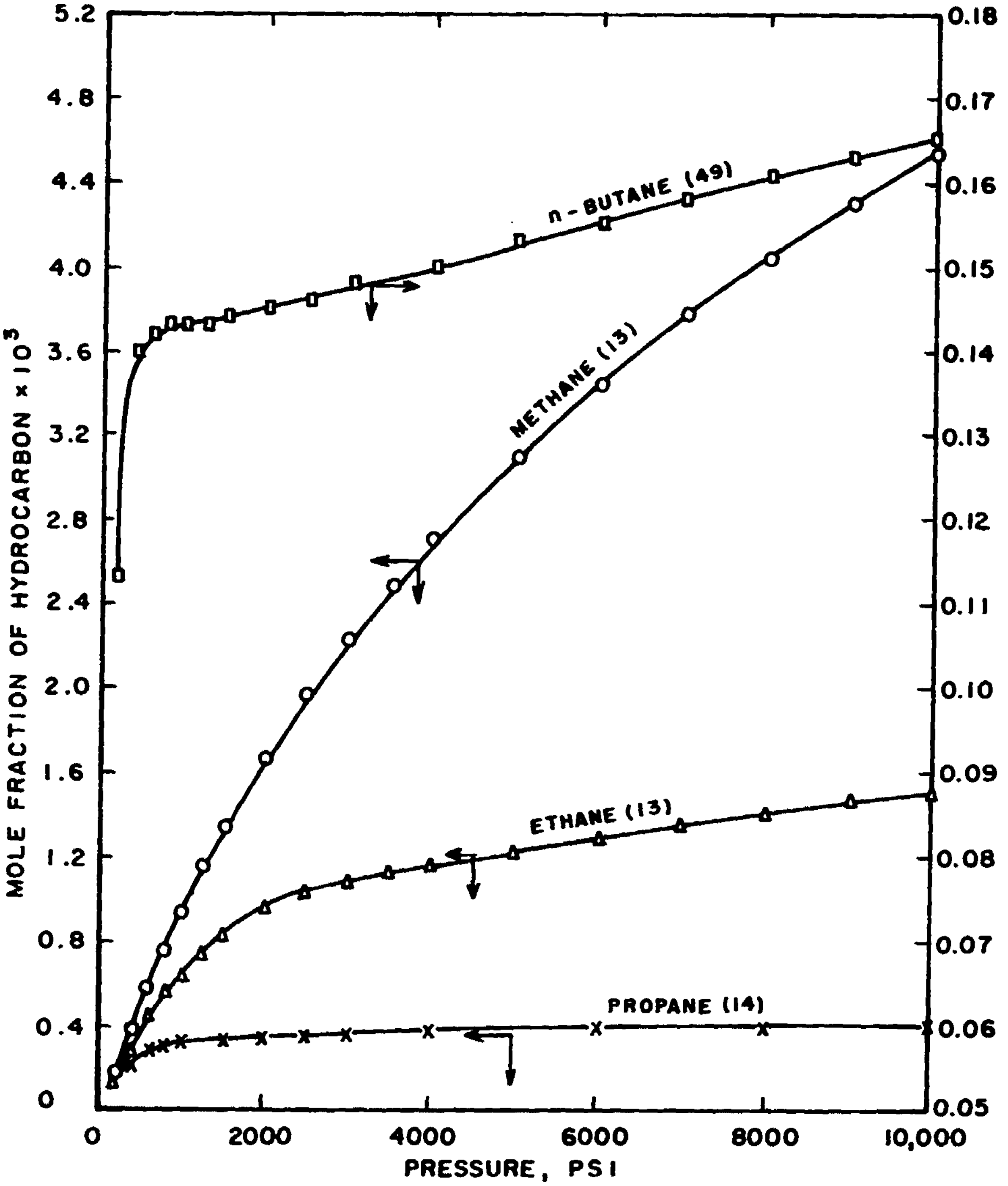

FIGURE VI-3 MOLE FRACTION OF METHANE, ETHANE, PROPANE AND n-BUTANE IN WATER-RICH LIQUID PHASE AT 220° F.

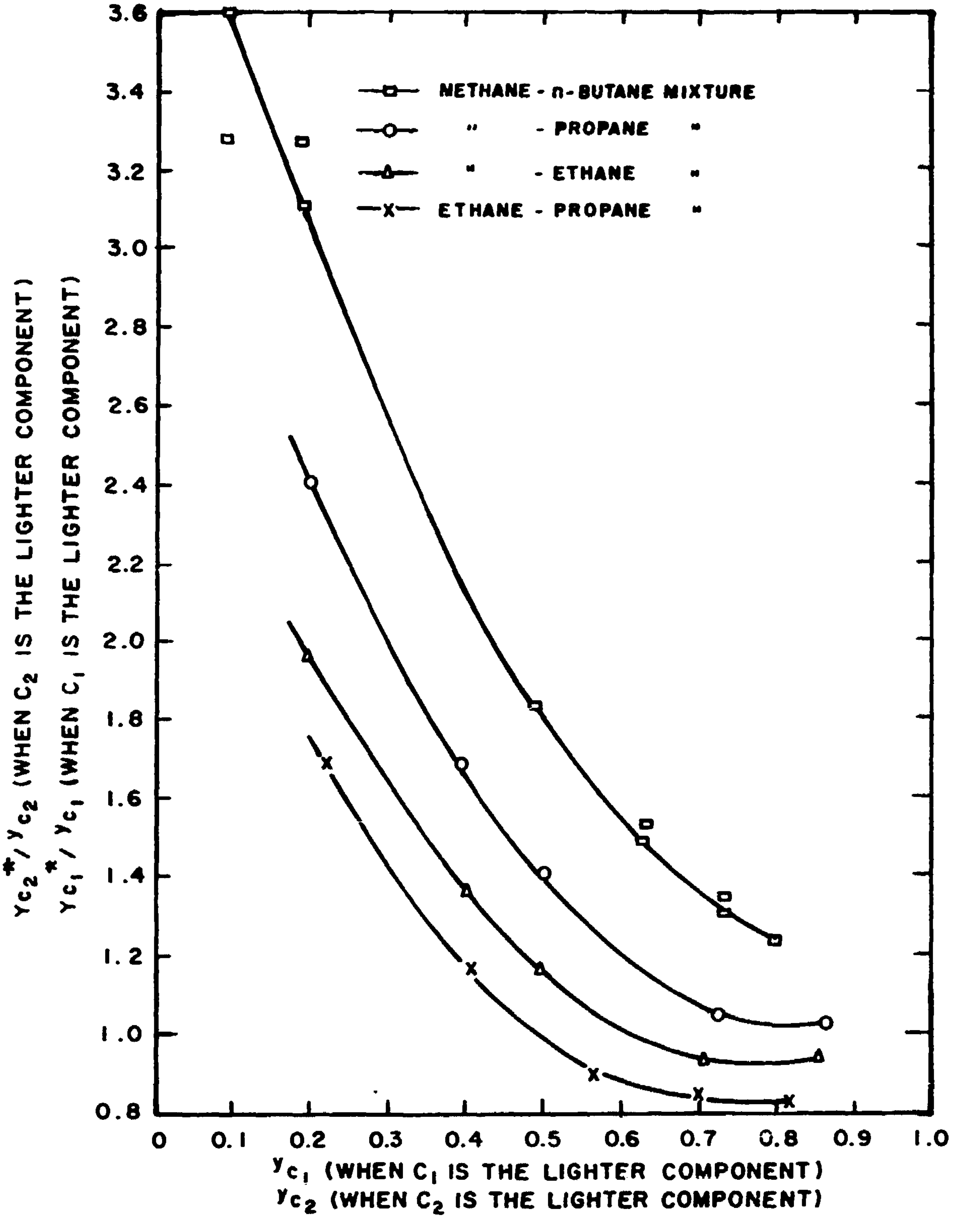

FIGURE VI-4 RATIO OF CORRECTED MOLE FRACTION TO THE TRUE MOLE FRACTION VS TRUE MOLE FRACTION FOR $C_1$-n-$C_4$, $C_1$-$C_3$, $C_1$-$C_2$, AND $C_2$-$C_3$ MIXTURES.

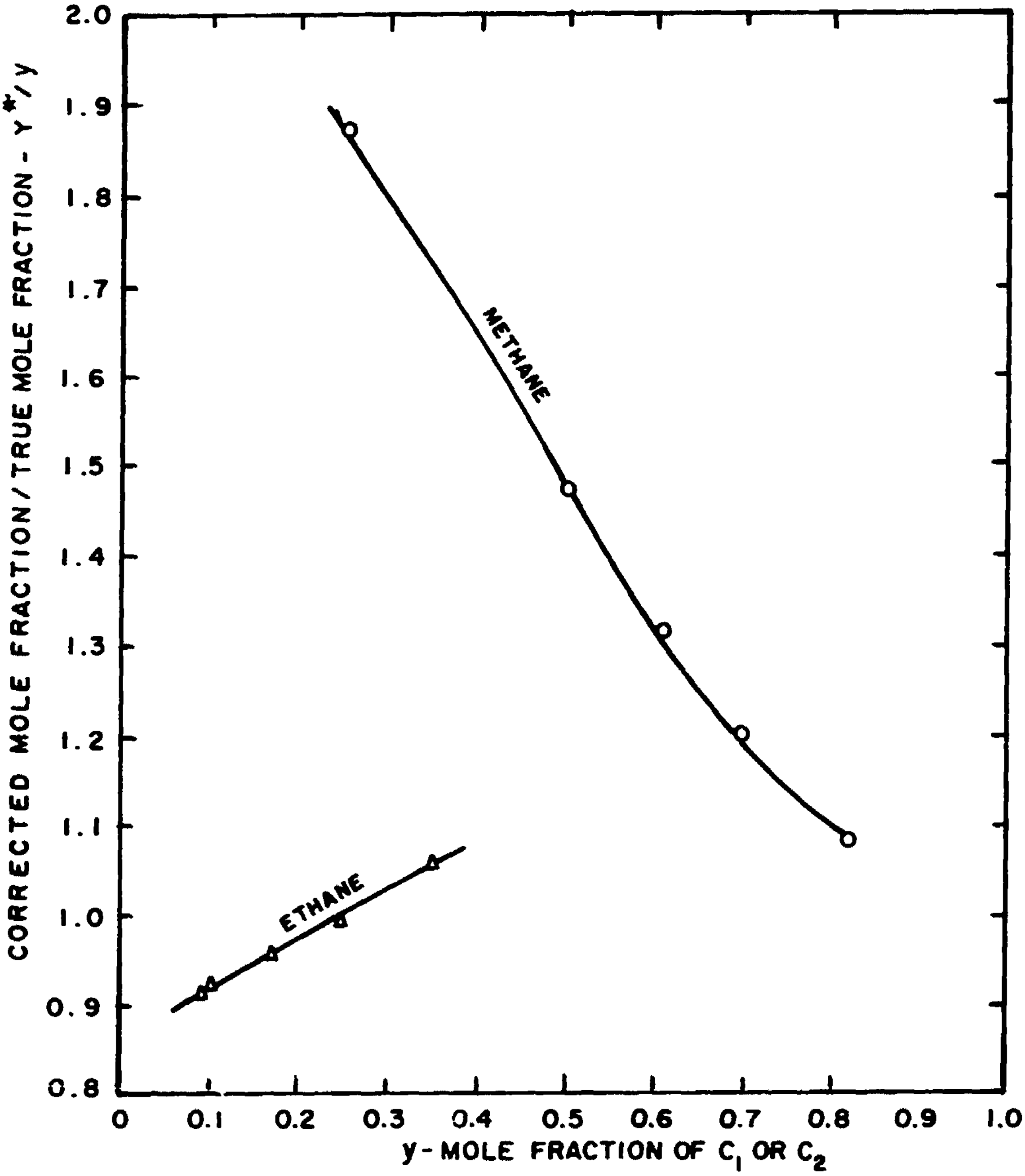

FIGURE VI-4A RATIO OF THE CORRECTED MOLE FRACTION OF THE TRUE MOLE FRACTION VS TRUE MOLE FRACTION FOR METHANE-ETHANE - PROPANE MIXTURES.

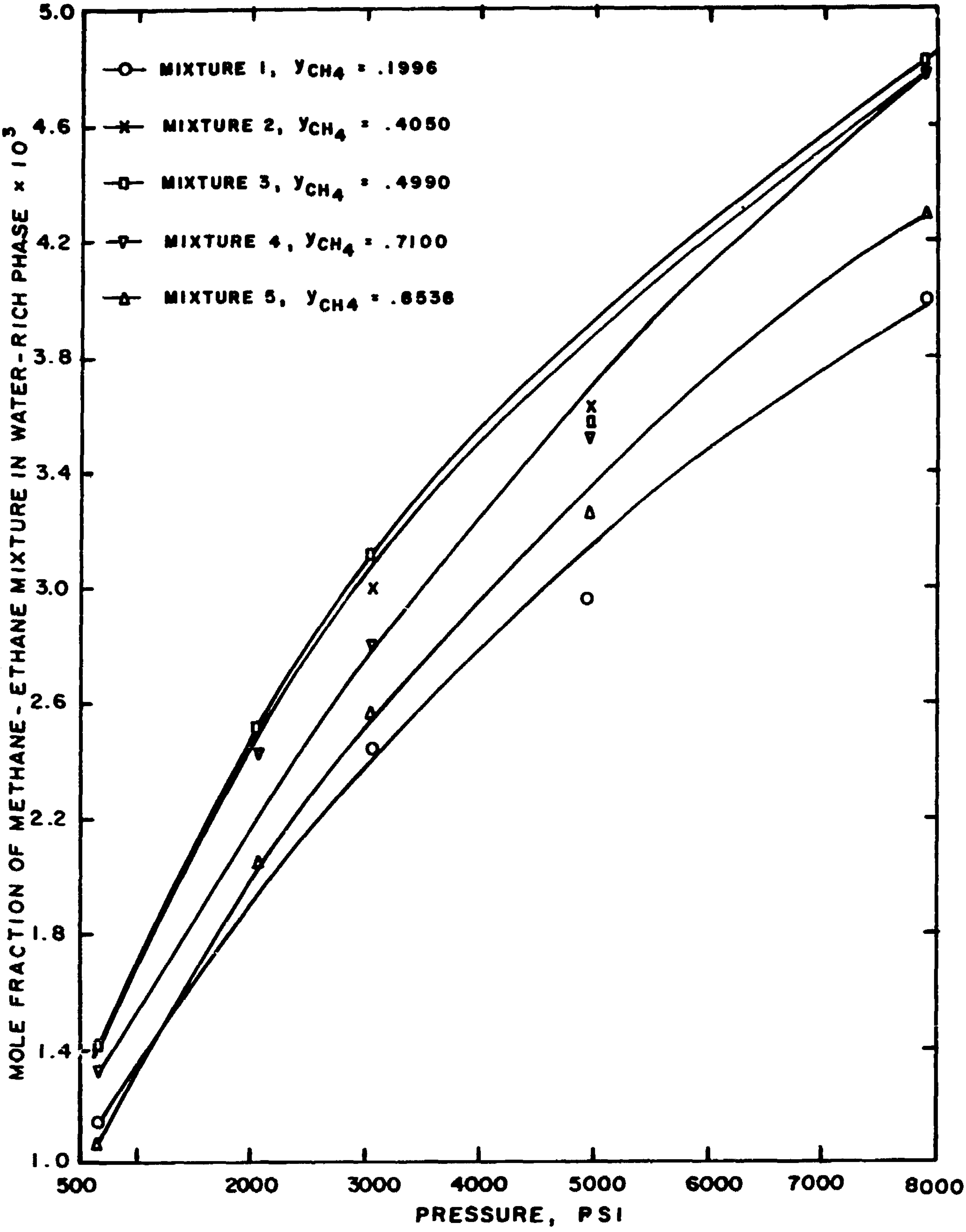

FIGURE VI-5 TOTAL SOLUBILITY OF METHANE-ETHANE MIXTURES AT 160° F.

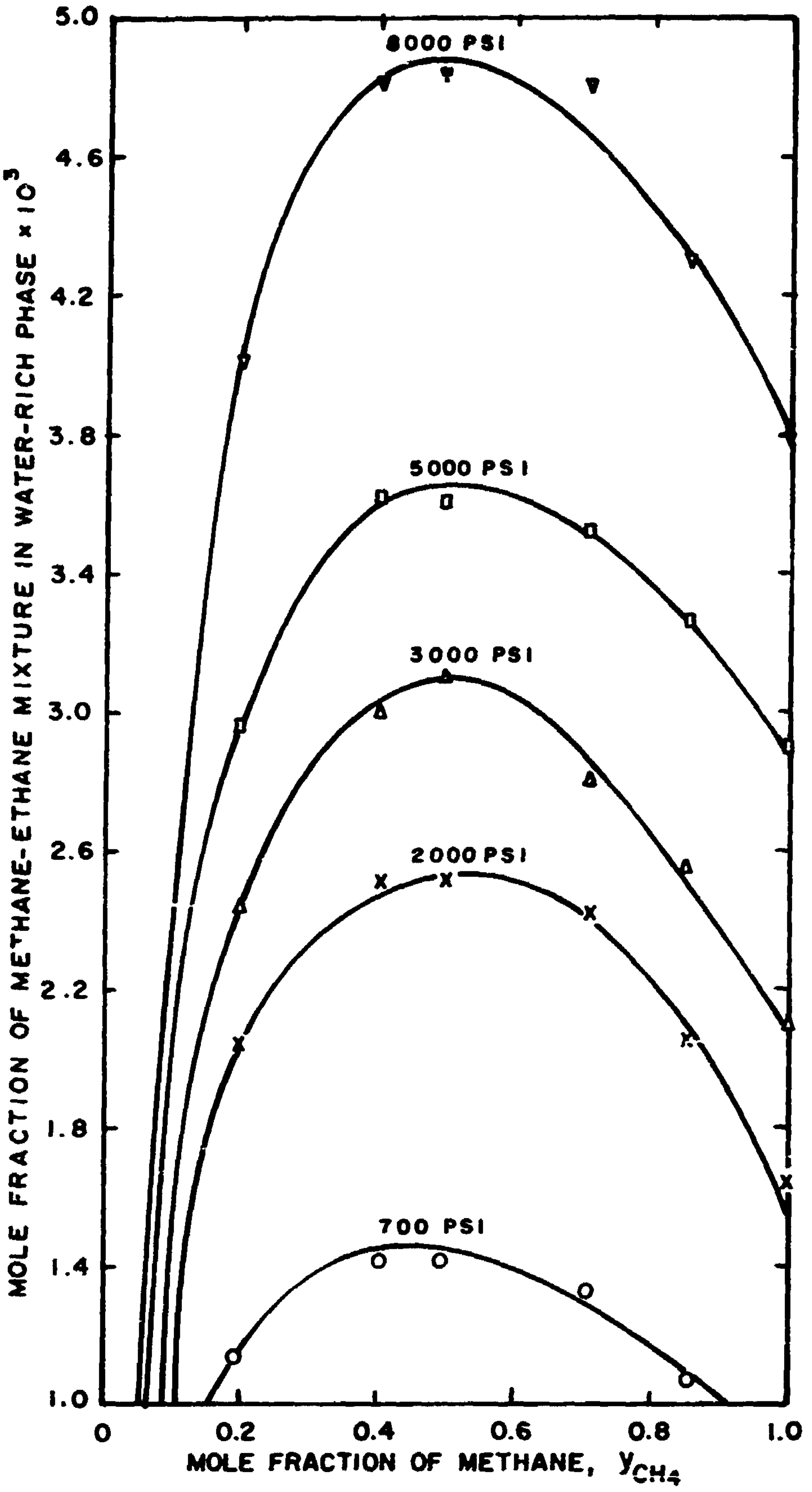

FIGURE VI-6 TOTAL SOLUBILITY OF METHANE-ETHANE MIXTURES AT 160° F.

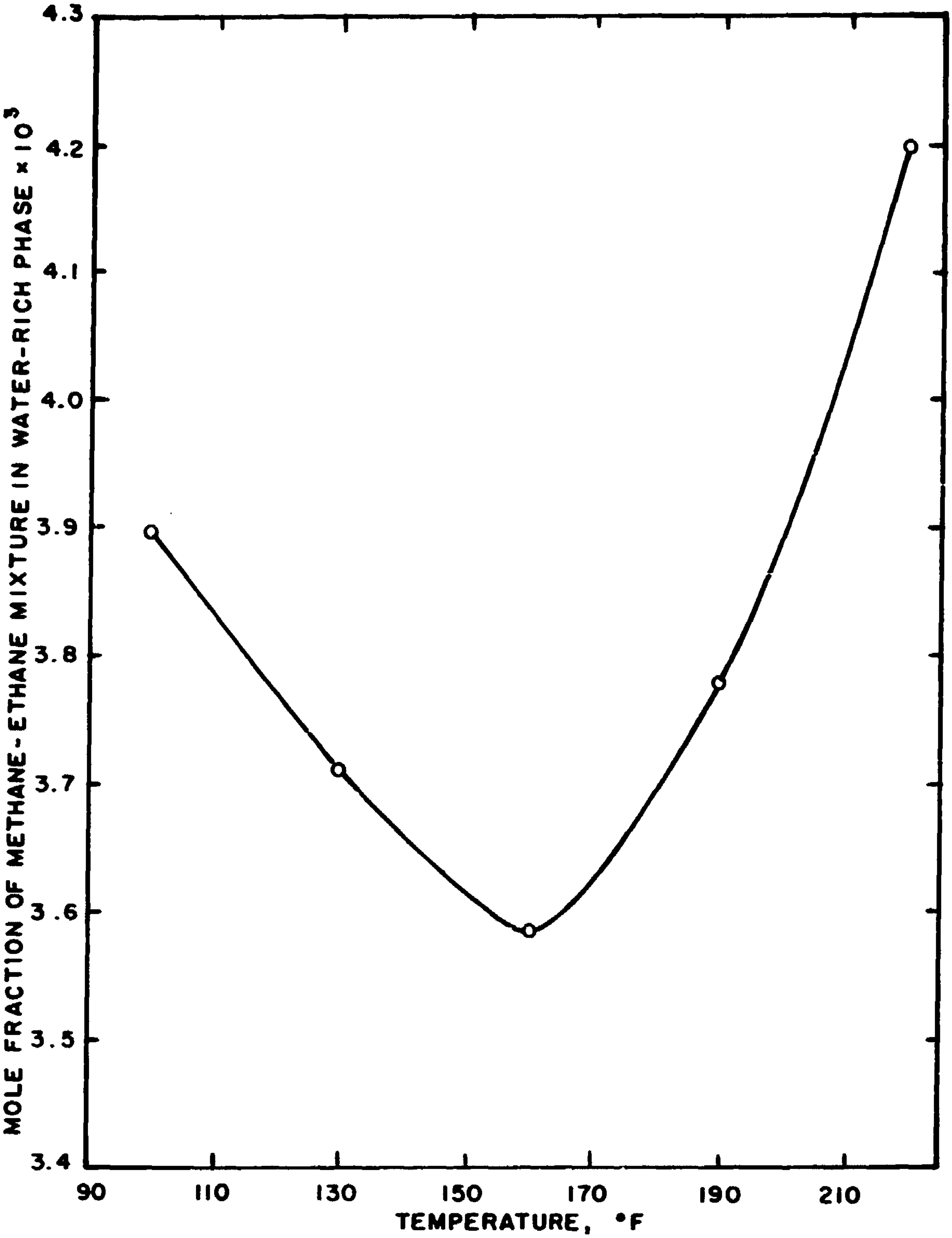

FIGURE VI-7 TOTAL SOLUBILITY OF METHANE-ETHANE MIXTURE ($y_{CH_4}$ = 0.499) AT 5000 PSI.

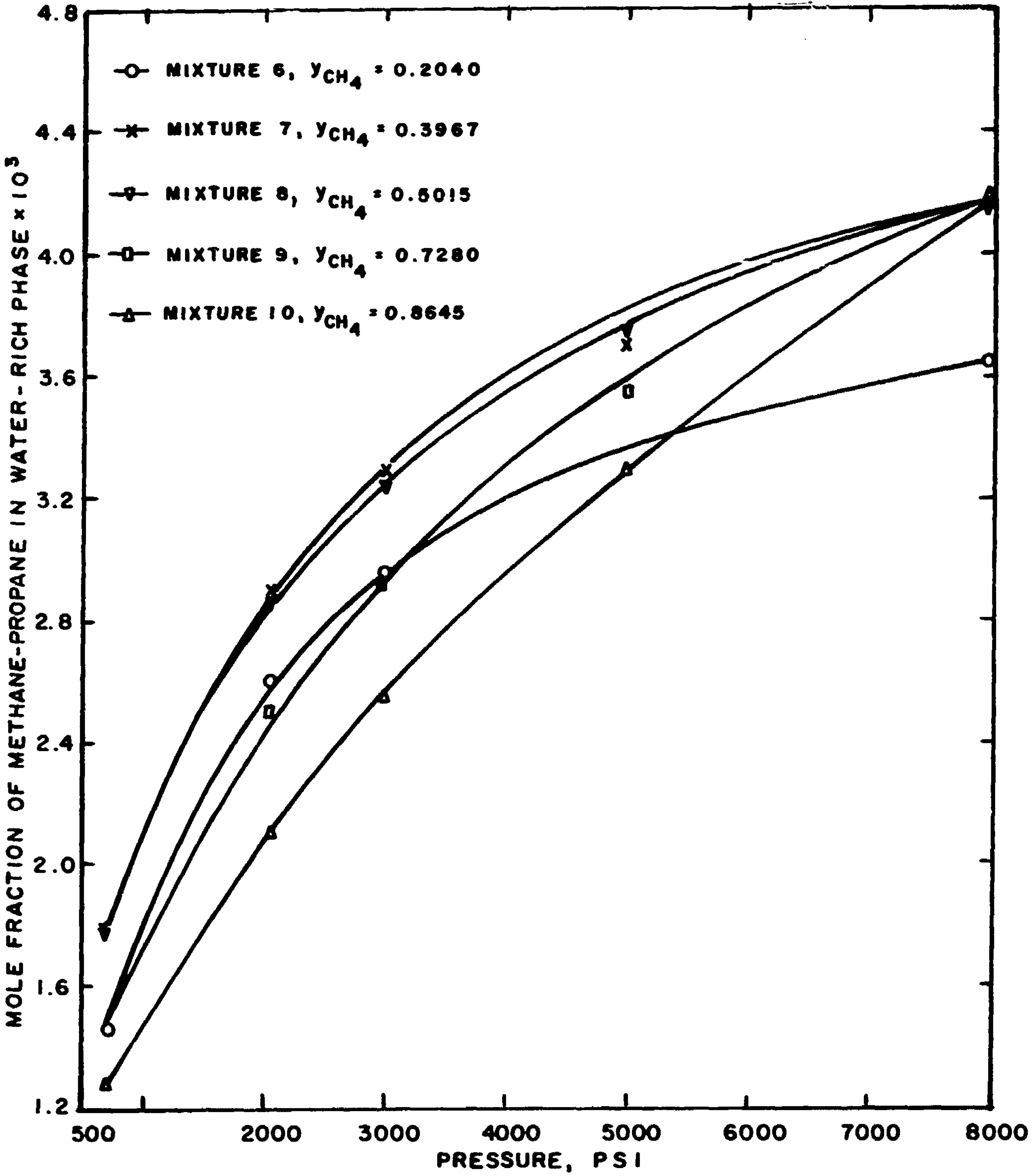

FIGURE VI - 8 TOTAL SOLUBILITY OF METANE - PROPANE MIXTURES AT 220° F.

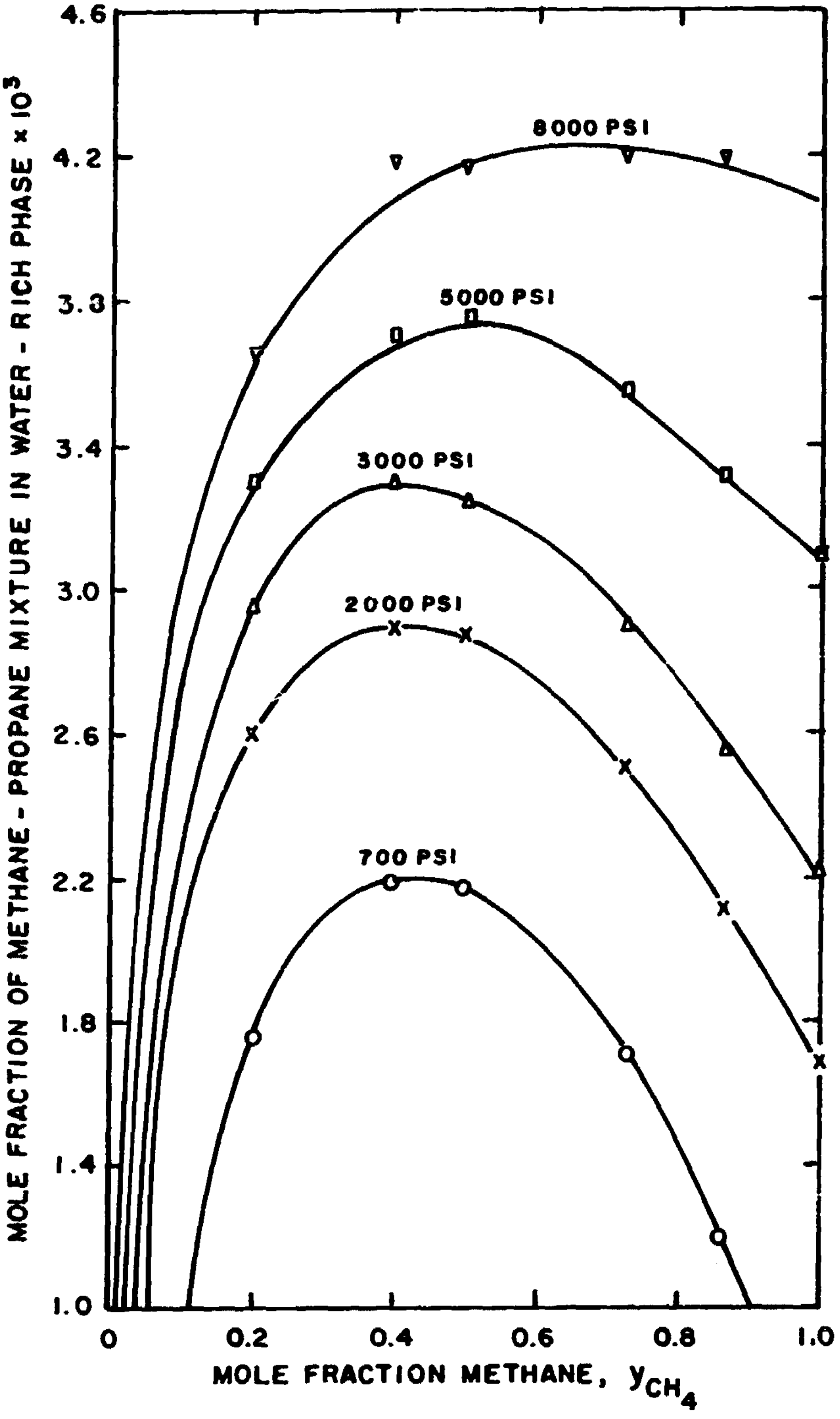

FIGURE VI-9 TOTAL SOLUBILITY OF METHANE - PROPANE MIXTURES AT 220° F

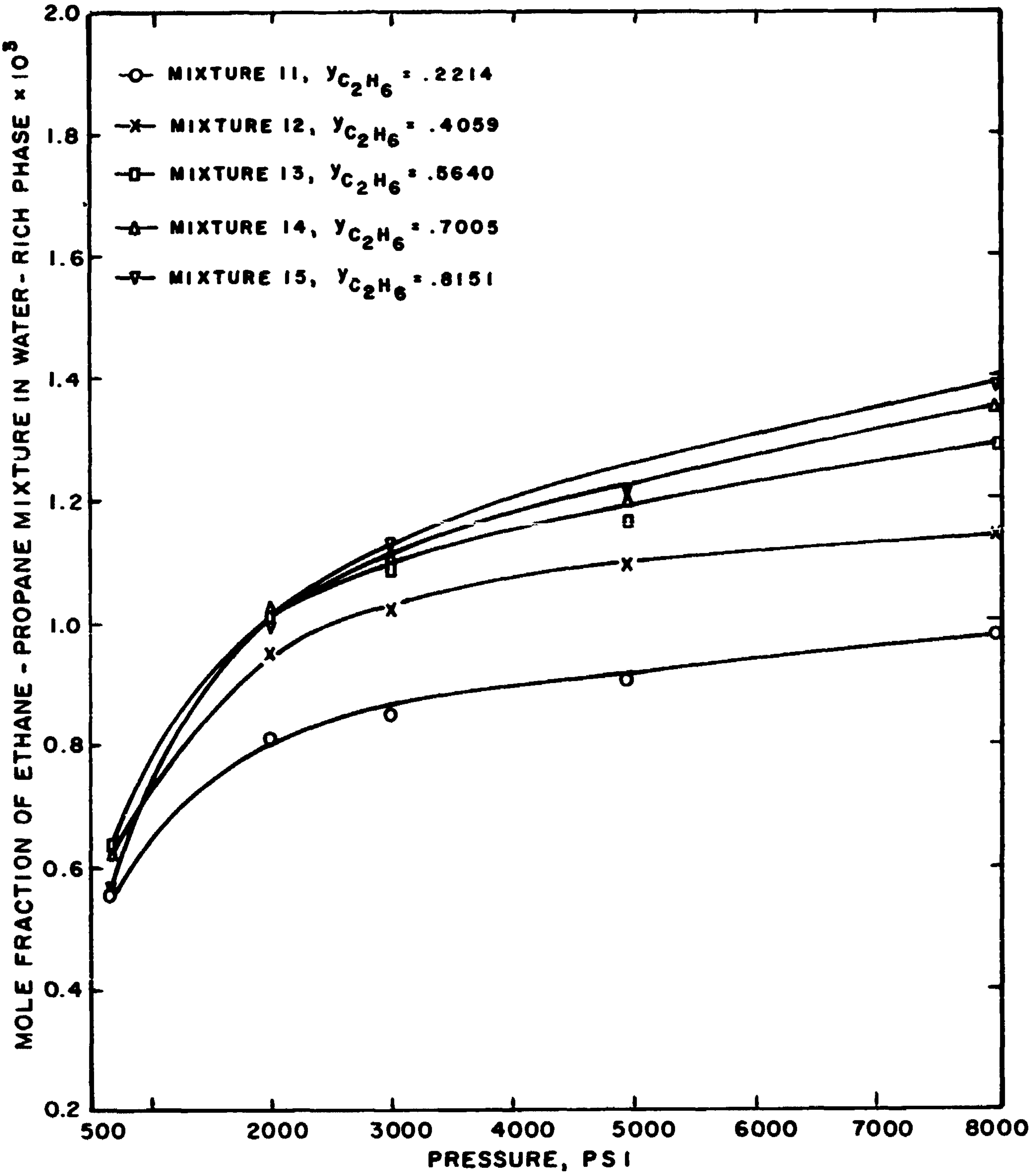

FIGURE VI-10 TOTAL SOLUBILITY OF ETHANE - PROPANE MIXTURES AT 220°F

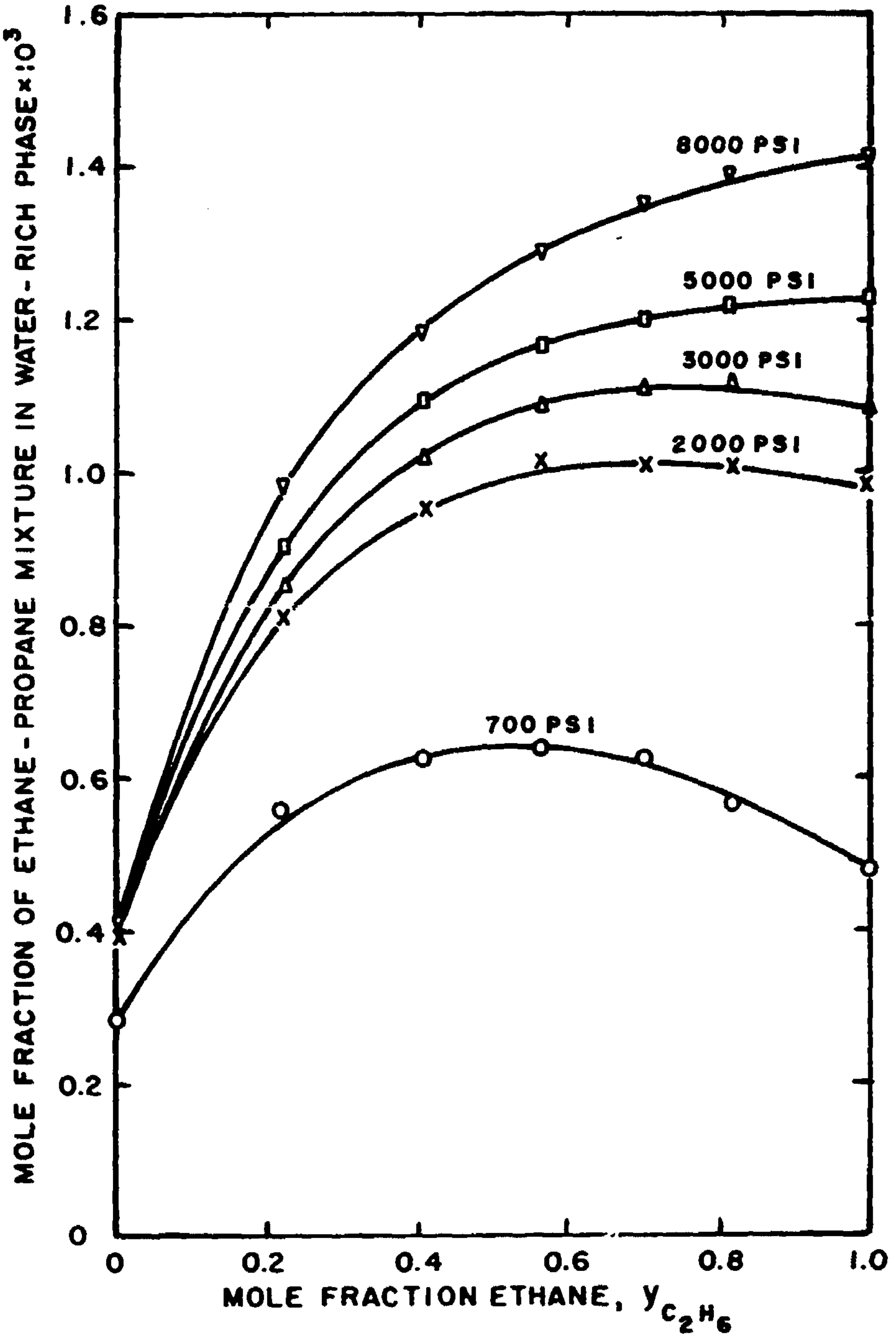

FIGURE VI-11 TOTAL SOLUBILITY OF ETHANE-PROPANE MIXTURES AT 220° F.

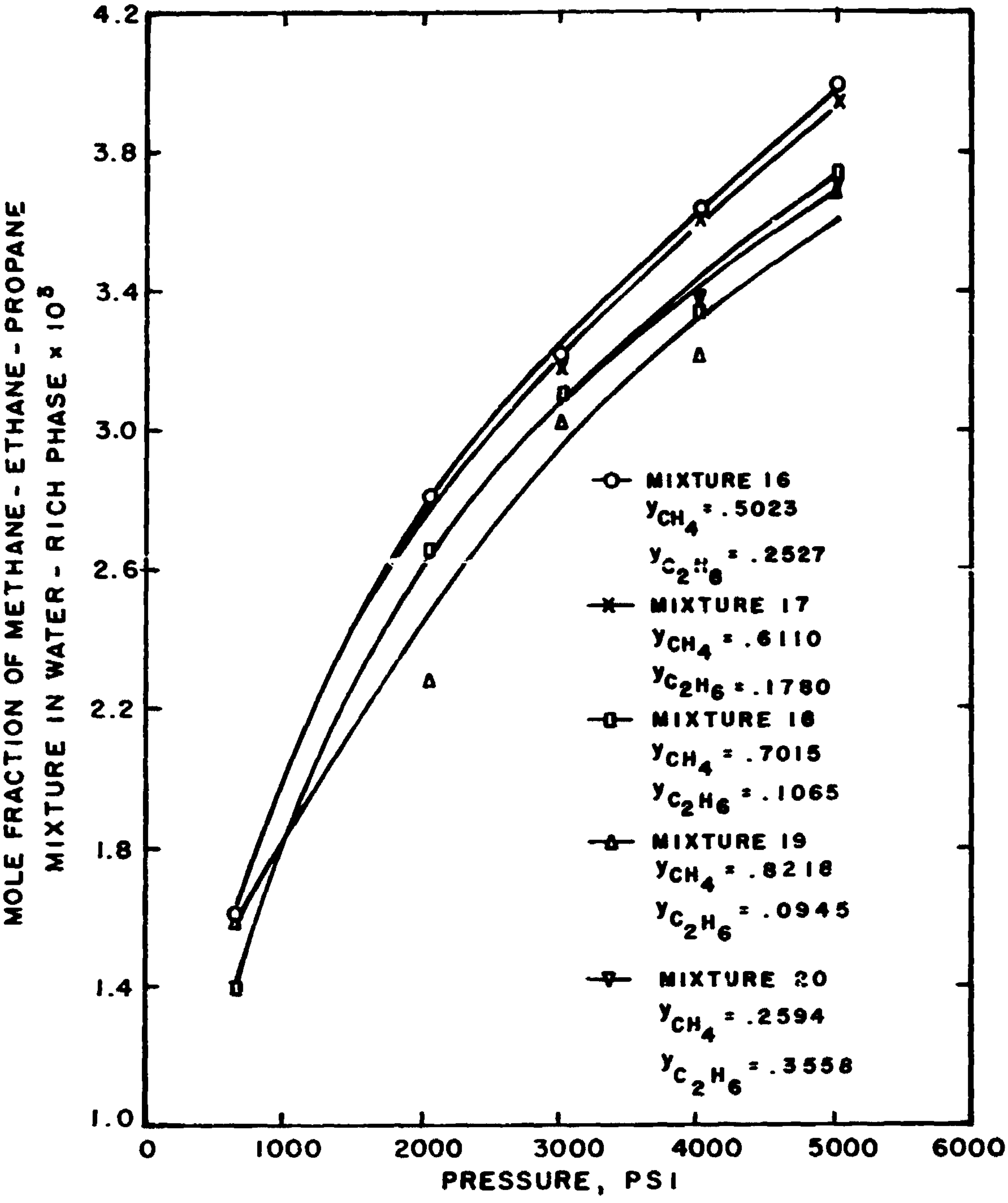

FIGURE VI-12 TOTAL SOLUBILITY OF METHANE-ETHANE-PROPANE MIXTURES AT 220° F.

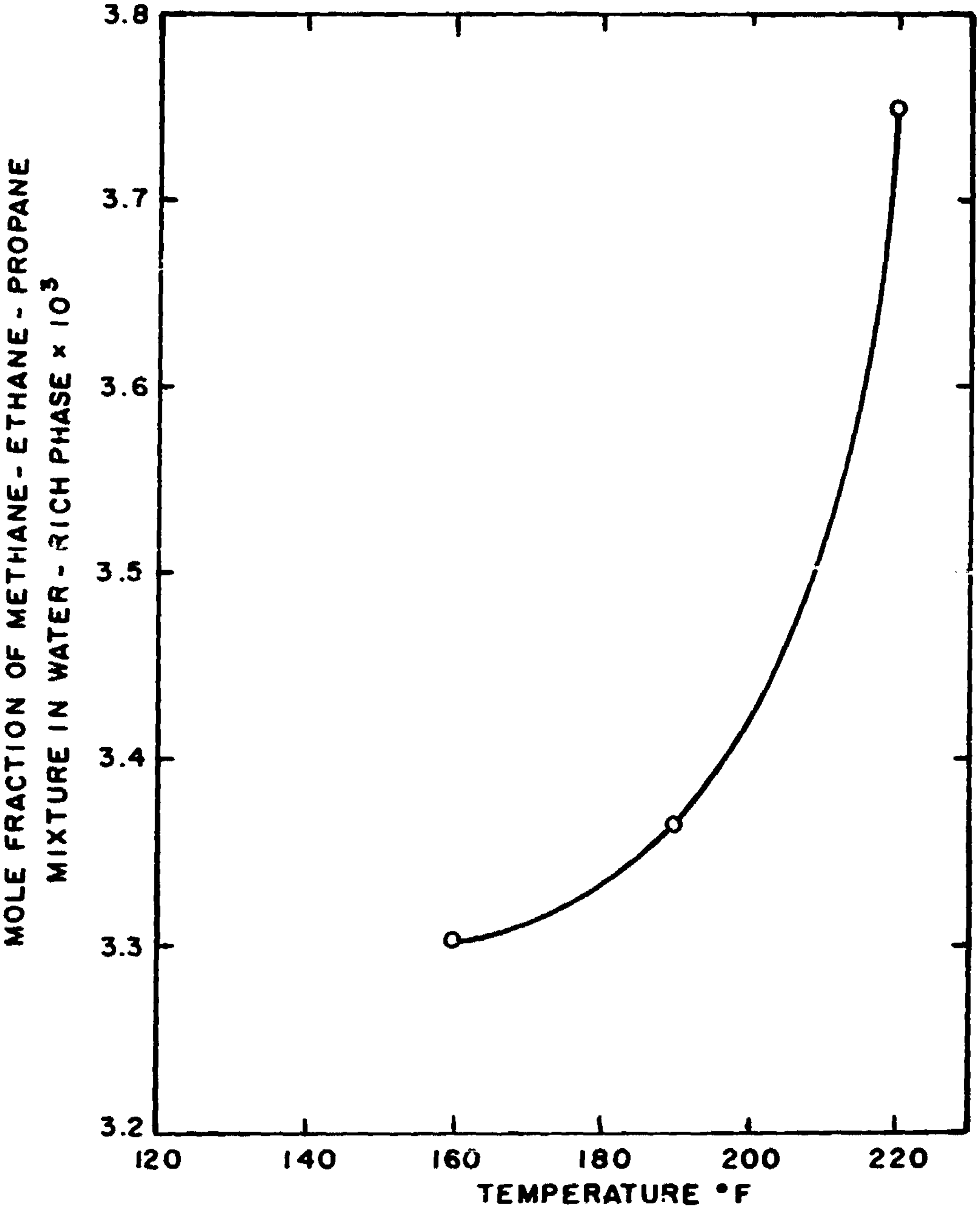

FIGURE VI-13 TOTAL SOLUBILITY OF METHANE-ETHANE-PROPANE MIXTURE ($y_{CH_4}$ = .7015, $y_{C_2H_6}$ = .1065) AT 5000 PSI

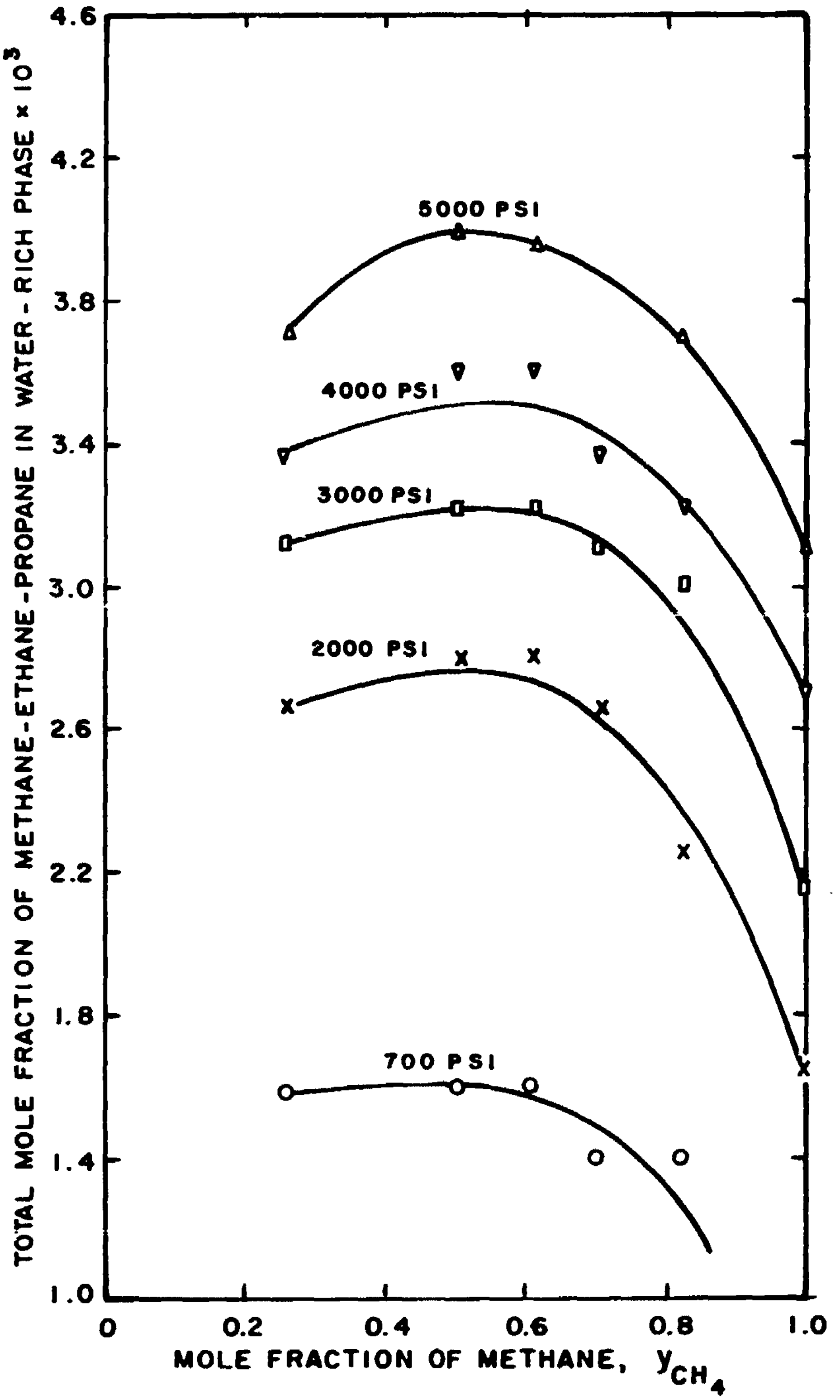

FIGURE VI-14 TOTAL SOLUBILITY OF METHANE-ETHANE-PROPANE MIXTURES AT 220° F.

## CHAPTER VII

## CONCLUSIONS

Solubility of methane-ethane, methane-propane, ethane-propane, and methane-ethane-propane mixtures in water, at temperatures above the critical temperature of the hydrocarbon mixture and pressures from 700 to 8000 psi, have been determined.

An empirical equation, capable of predicting total solubilities of binary hydrocarbon mixtures from the solubilities of their pure components, has been developed. The maximum deviation between the calculated and experimental values for binary hydrocarbon mixtures is less than 4 per cent. The equation was also tested by calculating total solubilities for methane-n-butane and comparing them with the experimental results obtained by McKetta (15). The results compared reasonably well, with a difference of less than 10 per cent.

Examination of experimental data resulted in the following observations:

1. The total solubility of all binary and ternary mixtures increased with an increase in pressure.
2. The solubility of methane-ethane mixture in water at 5000 psi has a minimum value at 160 F.
3. Solubilities of methane-ethane and methane-propane mixtures, having more than 40 mole per cent methane, are greater than the solubility

of pure methane at the same temperature and pressure.

4. All hydrocarbon-water solutions tested in this work showed a positive deviation from Raoult's law.

5. The total solubility of methane-ethane-propane mixtures in water is greater than the solubility of pure methane at the same temperature and pressures up to 5000 psi. However, the difference between the solubility of the mixture and pure methane decreases as the pressure increases.

6. The new method described for sampling liquid and gas phases and direct chromatographic analyses of the samples proved to be very simple and accurate.

The proposed correlation has been extended to ternary hydrocarbon mixtures. The calculated and experimental values for $C_1$-$C_2$-$C_3$ mixtures compare within 7 per cent. A general correlation for multicomponent hydrocarbon mixtures is also suggested.

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# APPENDIX A

# NOMENCLATURE

## TABLE (A-1)

## NOMENCLATURE

| | |
|---|---|
| a | Constant in Equations (IV-2) to (IV-9) |
| a | Activity |
| A | Helmholtz free energy |
| $A_o$ | Constant in Equations (IV-8) and (IV-9) |
| b | Constant in Equations (IV-2) to (IV-9) |
| b' | Constant in Equation (IV-10B) |
| B | Constant in Equation (III-28) |
| $B_o$ | Constant in Equations (IV-8) and (IV-9) |
| c | Constant in Equations (IV-3), (IV-6), (IV-8) to (IV-10A) |
| C | Constant in Equation (III-28) |
| C' | Constant in Equation (IV-10B) |
| $C_o$ | Constant in Equation (IV-9) |
| d | Derivative of |
| D | Constant in Equation (III-28) |
| exp | Exponential |
| f | Fugacity |
| F | Degrees Fahrenheit |
| G | Gibbs free energy |
| h | Enthalpy per mole |
| hp | Planck's constant |
| H | Enthalpy |
| k | Henry's constant |
| K | Constants in Equations (IV-14) to (IV-16) |
| KMR | Kay's mixing rule |

| | |
|---|---|
| ln | Natural logarithm |
| MW | Molecular weight |
| MWCR | Molecular weight correction |
| $n$ | Number of moles |
| $p$ | Partial pressure |
| $P$ | Pressure |
| PCR | Pressure correction |
| $R$ | Universal gas constant |
| $^oR$ | Degrees Rankine |
| $S$ | Entropy |
| $T$ | Temperature |
| $U$ | Internal energy |
| $v$ | Specific volume, volume per mole |
| $V$ | Volume |
| $x$ | Mole fraction in the liquid phase |
| $y$ | Mole fraction in the gas phase |
| $Y^*$ | Corrected mole fraction in the gas phase |
| $Z$ | Gas compressibility factor |

## GREEK LETTERS

| | |
|---|---|
| $\gamma$ | Activity coefficient |
| $\delta$ | Defined in Equation (IV-13) |
| $\partial$ | Partial derivative of |
| $\Delta$ | A small change in |
| $\epsilon$ | Defined in Equation (IV-13) |
| $\phi$ | Defined in Equation (III-18) |
| $\psi$ | Potential function |

| | |
|---|---|
| $k$ | Boltzmann's constant |
| $\lambda$ | Defined in Equation (IV-13) |
| $\mu$ | Chemical potential |
| $\rho$ | Density |
| $\omega$ | Accentric factor |

## SUPERSCRIPTS

| | |
|---|---|
| E | Excess thermodynamic properties |
| f | Free |
| g | Gas phase |
| i, j, k | Phase i, j, k |
| 1, 2, 3 | Phase 1, 2, 3 |
| l | Liquid phase |
| - | Partial molal quantity |
| * | Pure state |
| 0 | On pressure 0 designates vapor pressure |
| o | Designates infinite dilution |
| ' | Pseudocritical properties |

## SUBSCRIPTS

| | |
|---|---|
| A, B | Components A, B |
| c | Critical property |
| i, j, k | Component i, j, k |
| 1, 2, 3 | Component 1, 2, 3 |
| m | Mixture |
| mix | Mixing |
| o | Designates the solvent |
| r | Reduced property |
| s | Saturation condition |

# APPENDIX B

# PHYSICAL CONSTANTS

## TABLE (B-1)

## PHYSICAL CONSTANTS

| Compound | Molecular Weight | Critical Temperature °R | Critical Pressure Psi |
|---|---|---|---|
| Methane | 16.042 | 343.9 | 673 |
| Ethane | 30.068 | 549.8 | 708 |
| Propane | 44.094 | 665.9 | 617 |
| n-Butane | 58.120 | 765.2 | 551 |
| Water | 18.016 | 1165.3 | 3208 |

Universal gas constant, R = 10.73 psi-ft$^3$/lb mole°R

= 82.06 atm-cc/g mole°K

# APPENDIX C

# AVASTHI AND KENNEDY'S EQUATION FOR GASEOUS HYDROCARBON MIXTURES

# AVASTHI AND KENNEDY'S EQUATION FOR GASEOUS HYDROCARBON MIXTURES

Avasthi and Kennedy (19) have used experimental data on 264 natural gas and condensate systems, including 2043 PVT points to develop the following correlation for the molal volumes of gaseous hydrocarbon mixtures:

$$
\begin{aligned}
V_M - V_b = {} & -\ln(B_o + B_1(y_{C_1}/(1.01 - y_{C_1}))^2 + B_2(y_{C_1}/(1.01 - y_{C_1}))^3 + B_3 \\
& (y_{C_1}/(1.01 - y_{C_1}))^4 + B_4(6y_{C_2} + 5y_{C_3} - y_{iC_4} - y_{nC_4})^{\frac{1}{2}} + B_5 y_{C_5} + \\
& B_6(y_{C_5} + y_{C_6} + y_{C_{7+}}) + B_7(y_{C_1}/(.01 + y_{C_{7+}})) + B_8(y_{C_1}/(.01 + y_{C_{7+}}))^2 + \\
& B_9(y_{N_2}/(1.01 - y_{N_2}))^3 + B_{10}((y_{C_2} + y_{CO_2} + y_{H_2S})/(1.01 - y_{C_2} - \\
& y_{CO_2} - y_{H_2S})) + B_{11}((y_{C_2} + y_{CO_2} + y_{H_2S})/(1.01 - y_{C_2} - y_{CO_2} - \\
& y_{H_2S}))^{\frac{1}{2}} + B_{12}(1.1y_{C_1} + 1.2y_{C_2} + 0.9y_{C_3} + 3.8y_{C_5} + 4.9y_{C_6} + y_{N_2} + \\
& 0.8y_{CO_2} + 1.2y_{H_2S}) + B_{13}\rho_{C_{7+}} + B_{14}(y_{C_{7+}}MW_{C_{7+}}/50.0)(1 + 2/(0.01 + \\
& \rho_{C_{7+}})) + B_{15}((y_{C_{7+}}MW_{C_{7+}}/50.0)(1 + 2/(0.01 + \rho_{C_{7+}}))^2 + B_{16} \\
& ((y_{C_{7+}}MW_{C_{7+}}/50.0)(1 + 2/(0.01 + \rho_{C_{7+}}))^{\frac{1}{2}} + B_{17}(\ln(y_{C_{7+}}T \times 1\bar{0}^{2} + \\
& .01)/(MW_{C_{7+}}\rho_{C_{7+}} + .01)) + B_{18}T^{\frac{1}{2}} + B_{19}(T/P) + B_{20}(T\ln(P \times 1\bar{0}^{3})) + \\
& B_{21}(P\ln(T \times 1\bar{0}^{2}))) \qquad \text{(C-1)}
\end{aligned}
$$

where $V_M$ = molal volume, cu ft/lb mole

$V_b$ = reference mole volume, cu ft/lb mole

y = mole fraction of component in a mixture

B = constant coefficients

Values of coefficients $B_o$ through $B_{21}$ are given in Table (C-1).

## TABLE (C-1)

## COEFFICIENTS FOR AVASTHI-KENNEDY EQUATION

$B_o = .13530821 \times 10$
$B_1 = .19848504 \times 10^{-2}$
$B_2 = -.19844088 \times 10^{-3}$
$B_3 = .51379175 \times 10^{-5}$
$B_4 = .24836420 \times 10^{-1}$
$B_5 = -.62588112 \times 10$
$B_6 = .44694647 \times 10$
$B_7 = -.14129608 \times 10^{-2}$
$B_8 = .34589052 \times 10^{-4}$
$B_9 = -.10669628 \times 10$
$B_{10} = -.12601651$
$B_{11} = .12378339$
$B_{12} = -.28777369$
$B_{13} = -.30461668$
$B_{14} = -.81160977$
$B_{15} = .94223921 \times 10^{-1}$
$B_{16} = .32539924$
$B_{17} = .30306454 \times 10$
$B_{18} = .10854281 \times 10^{-1}$
$B_{19} = -.33153892$
$B_{20} = -.15405355 \times 10^{-3}$
$B_{21} = .52470355 \times 10^{-5}$

The authors claim that the average absolute deviation in terms of molal volumes obtained from Equation (C-1) is 1.01 per cent when applied to all data points.

# APPENDIX D

# EXPERIMENTAL DATA

## TABLE (D-1)

## MOLE FRACTION OF METHANE IN WATER-RICH PHASE

| Pressure Psia | 100 F | | 160 F | |
|---|---|---|---|---|
| | Peak Height Tenth of Inch | Mole Fraction | Peak Height Tenth of Inch | Mole Fraction |
| 590 | 10.2 | 0.000760 | 14.8 | 0.000600 |
| 2050 | 35.8 | 0.001960 | 26.6 | 0.001610 |
| 3050 | 47.6 | 0.002520 | 39.2 | 0.002150 |
| 4900 | 60.4 | 0.003350 | 52.2 | 0.002800 |

## TABLE (D-2)

## COMPOSITION OF THE BINARY AND TERNARY MIXTURES

| Mixture | Mole Fraction of Hydrocarbon in the Water-Free Gas Phase | | |
|---|---|---|---|
| | $Y_{C_1}$ | $Y_{C_2}$ | $Y_{C_3}$ |
| 1 | 0.1996 | 0.8004 | - |
| 2 | 0.4050 | 0.5950 | - |
| 3 | 0.4990 | 0.5010 | - |
| 4 | 0.7100 | 0.2900 | - |
| 5 | 0.8536 | 0.1464 | - |
| 6 | 0.2040 | - | 0.7960 |
| 7 | 0.3967 | - | 0.6033 |
| 8 | 0.5015 | - | 0.4985 |
| 9 | 0.7280 | - | 0.2720 |
| 10 | 0.8645 | - | 0.1355 |
| 11 | - | 0.2214 | 0.7786 |
| 12 | - | 0.4059 | 0.5941 |
| 13 | - | 0.5640 | 0.4360 |
| 14 | - | 0.7005 | 0.2995 |
| 15 | - | 0.8157 | 0.1849 |
| 16 | 0.5023 | 0.2527 | 0.2450 |
| 17 | 0.6110 | 0.1780 | 0.2110 |
| 18 | 0.7015 | 0.1065 | 0.1920 |
| 19 | 0.8218 | 0.0945 | 0.0837 |
| 20 | 0.2594 | 0.3558 | 0.3848 |

## TABLE (D-3)

## EXPERIMENTAL DATA FOR METHANE-ETHANE, METHANE-PROPANE, ETHANE-PROPANE, AND METHANE-ETHANE-PROPANE MIXTURES

| | | | Gas Phase Analysis Peak Heights (1/10") | | | Liquid Phase Analysis Peak Heights (1/10") | | |
|---|---|---|---|---|---|---|---|---|
| Mixture | T(F) | P(Psi) | $C_1$ | $C_2$ | $C_3$ | $C_1$ | $C_2$ | $C_3$ |
| #1 | 160 | 665 | 9.0 | 73.0 | - | 5.1 | 15.2 | - |
| | " | 2065 | " | " | - | 10.6 | 28.4 | - |
| | " | 3065 | " | " | - | 13.2 | 35.2 | - |
| | " | 4965 | " | " | - | 17.0 | 42.8 | - |
| | " | 7915 | " | " | - | 25.0 | 61.8 | - |
| #2 | 160 | 665 | 23.0 | 43.5 | - | 10.2 | 14.0 | - |
| | " | 2065 | " | " | - | 21.6 | 25.6 | - |
| | " | 3065 | " | " | - | 27.6 | 31.0 | - |
| | " | 4965 | " | " | - | 35.4 | 38.0 | - |
| | " | 7915 | " | " | - | 49.5 | 53.2 | - |
| #3 | 100 | 5000 | 35.5 | 48.7 | - | 42.2 | 39.0 | - |
| | 130 | " | 33.5 | 46.0 | - | 39.2 | 36.4 | - |
| | 160 | " | 31.0 | 43.0 | - | 37.4 | 35.0 | - |
| | 190 | " | 28.5 | 40.5 | - | 38.8 | 36.0 | - |
| | 220 | " | 27.0 | 38.5 | - | 44.0 | 40.8 | - |
| | 160 | 665 | 31.0 | 43.0 | - | 11.0 | 13.2 | - |
| | " | 2065 | " | " | - | 23.0 | 24.0 | - |
| | " | 3065 | " | " | - | 31.0 | 30.0 | - |
| | " | 4965 | " | " | - | 37.4 | 35.0 | - |
| | " | 7915 | " | " | - | 52.0 | 49.8 | - |
| #4 | 160 | 665 | 47.0 | 23.5 | - | 11.8 | 10.0 | - |

TABLE (D-3)--Continued

| Mixture | T(F) | P(Psi) | Gas Phase Analysis Peak Heights (1/10") | | | Liquid Phase Analysis Peak Heights (1/10") | | |
|---|---|---|---|---|---|---|---|---|
| | | | $C_1$ | $C_2$ | $C_3$ | $C_1$ | $C_2$ | $C_3$ |
| #4 | 160 | 2065 | 47.0 | 23.5 | - | 26.2 | 18.2 | - |
| | " | 3065 | " | " | - | 32.2 | 21.2 | - |
| | " | 4965 | " | " | - | 43.0 | 27.2 | - |
| | " | 7915 | " | " | - | 57.4 | 38.2 | - |
| #5 | 160 | 665 | 56.0 | 11.5 | - | 11.2 | 5.0 | - |
| | " | 2065 | " | " | - | 26.5 | 9.6 | - |
| | " | 3065 | " | " | - | 36.0 | 12.2 | - |
| | " | 4965 | " | " | - | 47.8 | 15.6 | - |
| | " | 7915 | " | " | - | 60.0 | 20.8 | - |
| #6 | 220 | 715 | 8.0 | - | 38.5 | 11.4 | - | 16.0 |
| | " | 2065 | " | - | " | 18.8 | - | 22.0 |
| | " | 3015 | " | - | " | 22.2 | - | 24.6 |
| | " | 5015 | " | - | " | 26.8 | - | 26.8 |
| | " | 8015 | " | - | " | 29.6 | - | 28.5 |
| #7 | 220 | 715 | 20.0 | - | 35.4 | 22.5 | - | 13.5 |
| | " | 2065 | " | - | " | 33.0 | - | 17.0 |
| | " | 3015 | " | - | " | 39.2 | - | 19.0 |
| | " | 5015 | " | - | " | 45.0 | - | 20.6 |
| | " | 8015 | " | - | " | 51.0 | - | 23.0 |
| #8 | 220 | 715 | 27.0 | - | 26.2 | 24.0 | - | 12.0 |
| | " | 2065 | " | - | " | 35.0 | - | 15.2 |
| | " | 3015 | " | - | " | 41.0 | - | 17.0 |
| | " | 5015 | " | - | " | 48.2 | - | 19.0 |

TABLE (D-3)--Continued

| | | | Gas Phase Analysis Peak Heights (1/10") | | | Liquid Phase Analysis Peak Heights (1/10") | | |
|---|---|---|---|---|---|---|---|---|
| Mixture | T(F) | P(Psi) | $C_1$ | $C_2$ | $C_3$ | $C_1$ | $C_2$ | $C_3$ |
| #8 | 220 | 8015 | 27.0 | - | 26.2 | 53.0 | - | 20.5 |
| #9 | 220 | 715 | 44.0 | - | 16.0 | 19.8 | - | 8.3 |
| | " | 2065 | " | - | " | 32.5 | - | 11.4 |
| | " | 3015 | " | - | " | 39.0 | - | 13.0 |
| | " | 5015 | " | - | " | 49.0 | - | 15.2 |
| | " | 8015 | " | - | " | 56.8 | - | 17.6 |
| #10 | 220 | 715 | 52.0 | - | 8.6 | 16.0 | - | 3.0 |
| | " | 2065 | " | - | " | 31.5 | - | 5.0 |
| | " | 3015 | " | - | " | 40.2 | - | 6.4 |
| | " | 5015 | " | - | " | 53.0 | - | 7.4 |
| | " | 8015 | " | - | " | 63.0 | - | 9.6 |
| #11 | 220 | 665 | - | 16.5 | 38.3 | - | 4.0 | 7.0 |
| | " | 2015 | - | " | " | - | 6.4 | 9.8 |
| | " | 3015 | - | " | " | - | 6.6 | 10.2 |
| | " | 4965 | - | " | " | - | 7.0 | 10.8 |
| | " | 8015 | - | " | " | - | 7.6 | 11.4 |
| #12 | 220 | 665 | - | 31.0 | 30.4 | - | 6.0 | 6.5 |
| | " | 2015 | - | " | " | - | 9.4 | 9.6 |
| | " | 3015 | - | " | " | - | 10.4 | 10.2 |
| | " | 4965 | - | " | " | - | 11.0 | 11.0 |
| | " | 8015 | - | " | " | - | 11.8 | 11.6 |
| #13 | 220 | 665 | - | 44.5 | 24.0 | - | 6.8 | 6.4 |
| | " | 2015 | - | " | " | - | 11.0 | 9.6 |

TABLE (D-3)--Continued

| Mixture | T(F) | P(Psi) | Gas Phase Analysis Peak Heights (1/10") | | | Liquid Phase Analysis Peak Heights (1/10") | | |
|---|---|---|---|---|---|---|---|---|
| | | | $C_1$ | $C_2$ | $C_3$ | $C_1$ | $C_2$ | $C_3$ |
| #13 | 220 | 3015 | - | 44.5 | 24.0 | - | 11.6 | 10.2 |
| | " | 4965 | - | " | " | - | 12.5 | 11.0 |
| | " | 8015 | - | " | " | - | 14.0 | 11.8 |
| #14 | 220 | 665 | - | 58.1 | 17.5 | - | 7.8 | 5.0 |
| | " | 2015 | - | " | " | - | 13.0 | 8.0 |
| | " | 3015 | - | " | " | - | 14.0 | 9.0 |
| | " | 4965 | - | " | " | - | 15.2 | 9.5 |
| | " | 8015 | - | " | " | - | 17.2 | 10.5 |
| #15 | 220 | 665 | - | 68.6 | 11.5 | - | 8.0 | 4.0 |
| | " | 2015 | - | " | " | - | 14.2 | 6.5 |
| | " | 3015 | - | " | " | - | 16.2 | 7.0 |
| | " | 4965 | - | " | " | - | 17.4 | 8.0 |
| | " | 8015 | - | " | " | - | 20.0 | 9.0 |
| #16 | 220 | 665 | 27.5 | 18.0 | 14.8 | 16.9 | 8.4 | 0.4 |
| | " | 2065 | " | " | " | 36.4 | 15.2 | 0.7 |
| | " | 3015 | " | " | " | 43.0 | 17.4 | 0.9 |
| | " | 4015 | " | " | " | 49.0 | 19.8 | 0.9 |
| | " | 5015 | " | " | " | 53.2 | 22.0 | 0.8 |
| #17 | 220 | 665 | 35.0 | 12.6 | 18.0 | 19.0 | 5.6 | 1.0 |
| | " | 2065 | " | " | " | 30.5 | 10.0 | 1.8 |
| | " | 3015 | " | " | " | 47.0 | 11.5 | 2.0 |
| | " | 4015 | " | " | " | 52.5 | 13.2 | 2.2 |
| | " | 5015 | " | " | " | 56.6 | 14.3 | 2.5 |

TABLE (D-3)--Continued

| | | | Gas Phase Analysis Peak Heights (1/10") | | | Liquid Phase Analysis Peak Heights (1/10") | | |
|---|---|---|---|---|---|---|---|---|
| Mixture | T(F) | P(Psi) | $C_1$ | $C_2$ | $C_3$ | $C_1$ | $C_2$ | $C_3$ |
| #18 | 160 | 5000 | 47.0 | 8.2 | 13.0 | 51.5 | 6.9 | 3.9 |
| | 190 | 5000 | 44.5 | 7.8 | 12.3 | 52.0 | 7.0 | 4.1 |
| | 220 | 5000 | 42.0 | 7.5 | 12.0 | 56.6 | 7.8 | 4.5 |
| | " | 665 | " | " | " | 17.8 | 3.0 | 1.5 |
| | " | 2065 | " | " | " | 40.0 | 5.4 | 3.2 |
| | " | 3015 | " | " | " | 48.0 | 6.4 | 3.8 |
| | " | 4015 | " | " | " | 51.8 | 6.9 | 4.0 |
| #19 | 220 | 665 | 50.0 | 6.4 | 5.5 | 18.0 | 2.2 | 0.9 |
| | " | 2065 | " | " | " | 35.0 | 3.9 | 1.2 |
| | " | 3015 | " | " | " | 49.0 | 5.4 | 1.5 |
| | " | 4015 | " | " | " | 52.0 | 5.9 | 1.8 |
| | " | 5015 | " | " | " | 58.2 | 6.8 | 2.0 |
| #20 | 220 | 665 | 11.4 | 26.0 | 21.8 | 10.0 | 13.0 | 4.4 |
| | " | 2065 | " | " | " | 19.0 | 22.0 | 7.0 |
| | " | 3015 | " | " | " | 23.5 | 26.0 | 8.3 |
| | " | 4015 | " | " | " | 26.5 | 28.5 | 9.0 |
| | " | 5015 | " | " | " | 30.3 | 31.4 | 11.4 |

# APPENDIX E

# COMPUTER PROGRAMS

## COMPUTER PROGRAM NO. 1

```
C      CALCULATION OF THE CRITICAL TEMPERATURE FOR BINARY MIXTURES OF
C      METHANE-ETHANE, METHANE-PROPANE, AND ETHANE-PROPANE ACCORDING TO
C      GRIEVES-THODOS'S EQUATION.
       N=1
1      GOTO(100,101,102),N
100    A12=1.450
       A21=0.650
       TC1=343.9
       TC2=549.8
       GOTO103
101    A12=2.040
       A21=0.420
       TC1=343.9
       TC2=665.9
       GOTO103
102    A12=0.966
       A21=0.986
       TC1=549.8
       TC2=665.9
       GOTO103
C      A12 AND A21 REPRESENT COEFFICIENTS IN GRIEVES-THODOS'S EQUATION.
C      TC1 AND TC2 REPRESENT CRITICAL TEMPERATURE OF COMPONENT 1 OR 2.
C      X1 AND X2 REPRESENT MOLE FRACTIONS.
103    X1=0.005
4      X2=1.-X1
       TCM=(TC1/(1.0+(X2/X1)*A12))+(TC2/(1.0+(X1/X2)*A21))
```

COMPUTER PROGRAM NO. 1--<u>Continued</u>

```
C       TC1, TC2, AND TCM ARE IN DEGREES RANKINE.
        WRITE(6,10) X1,X2,TCM
10      FORMAT(1P3E20.10)
        IF(X1-.995)3,5,5
3       X1=X1+.005
        GOTO4
5       N=N+1
        IF(N-3)1,1,11
11      CONTINUE
        END
```

## COMPUTER PROGRAM NO. 2

```
C     CALCULATION OF THE CRITICAL TEMPERATURE FOR METHANE-ETHANE-
C     PROPANE MIXTURES OF DIFFERENT COMPOSITIONS ACCORDING TO
C     GRIEVES-THODOS'S EQUATION.
      A12=1.450
      A21=0.650
      A13=2.040
      A31=0.420
      A23=0.966
      A32=0.986
      TC1=343.9
      TC2=549.8
      TC3=665.9
C     AIJ REPRESENT COEFFICIENTS IN GRIEVES-THODOS'S EQUATION.
C     TCI REPRESENT CRITICAL TEMPERATURE OF PURE COMPONENT I.
C     XI REPRESENT COMPOSITION.
      X1=0.01
1     I=1
5     X2=0.05*I
      X3=1.-X2-X1
C     TCM REPRESENTS CRITICAL TEMPERATURE OF THE MIXTURE.
C     TCI AND TCM ARE IN DEGREES RANKINE.
      TCM=(TC1/(1.+(X2/X1)*A12+(X3/X1)*A13))+(TC2/(1.+(X1/X2)*
     1A21+(X3/X2)*A23))+(TC3/(1.+(X1/X3)*A31+(X2/X3)*A32))
      WRITE(6,10) X1,X2,X3,TCM
10    FORMAT(1P4E20.10)
```

## COMPUTER PROGRAM NO. 2--Continued

```
      Z=X1*X2
      IF(Z-.95)6,4,4
6     I=I+1
      GOTO5
4     IF(X1-0.90)3,2,2
3     X1=X1+0.01
      GOTO1
2     CONTINUE
      END
```

## COMPUTER PROGRAM NO. 3

```
C     COMPUTER PROGRAM FOR CALCULATING THE TOTAL SOLUBILITY OF METHANE-
C     ETHANE , METHANE-PROPANE, OR ETHANE-PROPANE MIXTURES IN WATER AT
C     FIVE DIFFERENT PRESSURES FOR FIVE DIFFERENT COMPOSITIONS.
C     THIS PROGRAM IS FOR C1-C3 MIXTURES AT220F.
C     THE SOLUBILITY OF C1-C2 AND C2-C3 WAS DETERMINED AT 160 F AND 220 F,
C     RESPECTIVELY.
C     XPI AND PCI REPRESENT THE SOLUBILITY OF PURE COMPONENT I AND CRITI-
C     CAL PRESSURE OF PURE COMPONENT I, RESPECTIVELY.
      DIMENSION P(10),XP1(10),XP2(10)
      READ(5,50) PC1,PC2,WM1,WM2
50    FORMAT(4F7.0)
      DO200 I=1,5
      READ(5,55) P(I),XP1(I),XP2(I)
200   CONTINUE
55    FORMAT(3F10.0)
      N=1
1     GOTO(100,101,102,103,104),N
100   Y1=0.2040
      Y2=1.0000-Y1
      GOTO10
C     WMI AND YI REPRESENT MOLECULAR WEIGHT AND MOLE FRACTION OF
C     COMPONENT I, RESPECTIVELY.
C     THE COMPOSITIONS FOR C1-C2 AND C2-C3 MIXTURES WERE DIFFERENT
C     FROM C1-C3 MIXTURES
```

## COMPUTER PROGRAM NO. 3--Continued

```
101    Y1=0.3967
       Y2=1.0000-Y1
       GOTO10
102    Y1=0.5015
       Y2=1.0000-Y1
       GOTO10
103    Y1=0.7280
       Y2=1.0000-Y1
       GOTO10
104    Y1=0.8645
       Y2=1.0000-Y1
       GOTO10
10     DO11 I=1,5
       TERM=Y1*XP1(I)+Y2*XP2(I)
C      CORR1, CORR2, CORR3, TOTCR, AND XTOT REPRESENT COMPOSITION
C      CORRECTION, PRESSURE CORRECTION, MOLECULAR WEIGHT CORRECTION,
C      TOTAL CORRECTION, AND TOTAL SOLUBILITY, RESPECTIVELY.
       CORR1=Y1*Y2*(XP1(I)*XP2(I))/TERM
       CORR2=((PC1+PC2)/(0.5*P(I)))**0.125
       CORR3=(WM2/WM1)**2.52
       TOTCR=CORR1*CORR2*CORR3
       XTOT=TERM+TOTCR
       WRITE(6,22) TERM,TOTCR,XP1(I),XP2(I)
       WRITE(6,22) P(I),Y1,Y2,XTOT
22     FORMAT(1P4E20.10)
```

## COMPUTER PROGRAM NO. 3--*Continued*

```
11     CONTINUE
       N=N+1
       IF(N-5)1,1,2
2      CONTINUE
       STOP
       END
/DATA
```

## COMPUTER PROGRAM NO. 4

```
C      COMPUTER PROGRAM FOR CALCULATING THE TOTAL SOLUBILITY OF
C      METHANE-ETHANE-PROPANE MIXTURE IN WATER AT 220 F.
C      XPI AND PCI REPRESENT THE SOLUBILITY OF PURE COMPONENT I
C      AND CRITICAL PRESSURE OF PURE COMPONENT I, RESPECTIVELY.
C      WMI AND YI REPRESENT MOLECULAR WEIGHT AND MOLE FRACTION
C      OF COMPONENT I, RESPECTIVELY.
       DIMENSION P(10),XP1(10),XP2(10),XP3(10)
       READ (5,50) PC1,PC2,PC3,WM1,WM2,WM3
50     FORMAT(6F7.0)
       DO 200 I=1.5
       READ(5,55) P(I),XP1(I),XP2(I),XP3(I)
200    CONTINUE
55     FORMAT(4F10.0)
       N=1
1      GOTO(100,101,102,103,104),N
100    Y1=.5023
       Y2=.2527
       Y3=1.0000-Y1-Y2
       GOTO10
101    Y1=.6110
       Y2=.1780
       Y3=1.0000-Y1-Y2
       GOTO10
102    Y1=.7015
       Y2=.1065
       Y3=1.0000-Y1-Y2
```

## COMPUTER PROGRAM NO. 4--Continued

```
      GOTO10
103   Y1=.8218
      Y2=.0945
      Y3=1.0000-Y1-Y2
      GOTO10
104   Y1=.2594
      Y2=.3558
      Y3=1.0000-Y1-Y2
      GOTO10
10    DO 11 I=1,5
      TERM=Y1*XP1(I)+Y2*XP2(I)+Y3*XP3(I)
C     SYMBOLS CRXIJ, CRPIJ, CRMIJ, AND XTOT STAND FOR CORRECTIONS
C     DUE TO COMPOSITION, PRESSURE, MOLECULAR WEIGHT, TOTAL
C     CORRECTION, AND TOTAL SOLUBILITY, RESPECTIVELY.
      CRX12=(XP1(I)*XP2(I))/TERM
      PP=0.5*P(I)
      CRP12=((PC1+PC2)/PP)**0.125
      CRM12=(WM2/WM1)**2.52
      CR12=Y1*Y2*CRX12*CRP12*CRM12
      WRITE(6,300) CRX12,CRP12,CRM12,CR12
300   FORMAT(1P4E20.10)
      CRX13=(XP1(I)*XP3(I))/TERM
      CRP13=((PC1+PC3)/PP)**0.125
      CRM13=(WM3/WM1)**2.52
      CR13=Y1*Y3*CRX13*CRP13*CRM13
```

COMPUTER PROGRAM NO. 4--<u>Continued</u>

```
      WRITE(6,301) CRX13,CRM13,CR13
301   FORMAT(1P3E20.10)
      CRX23=(XP2(I)*XP3(I))/TERM
      CRP23=((PC2+PC3)/PP)**0.125
      CRM23=(WM3/WM2)**2.52
      CR23=Y2*Y3*CRX23*CRP23*CRM23
      WRITE(6,302) CRX23,CRP23,CRM23,CR23
302   FORMAT(1P4E20.10)
      TOTCR=CR12+CR13+CR23
      XTOT=TERM+TOTCR
      WRITE(6,22) TERM, TOTCR,XP1(I),XP2(I),XP3(I)
      WRITE(6,23) P(I),Y1,Y2,Y3,XTOT
22    FORMAT(1P5E20.10)
23    FORMAT(1P5E20.10)
11    CONTINUE
      N=N+1
      IF(N-5)1,1,2
2     CONTINUE
      STOP
      END
/DATA
```