THE UNIVERSITY OF MICHIGAN

INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

VAPOR LIQUID EQUILIBRIA OF LIGHT HYDROCARBON SYSTEMS CONTAINING HYDROGEN AT LOW TEMPERATURE

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ABSTRACT

The purpose of this work was to complete the experimental vapor-liquid equilibria study of hydrogen-light hydrocarbon binary systems; to add to our knowledge of the behavior of hydrogen-light hydrocarbon ternary systems; to obtain some vapor-liquid equilibria data for a six-component hydrogen-light hydrocarbon system; and to correlate the data with the view of obtaining a generalized correlation from the study of binary and ternary systems.

Vapor-liquid equilibria data were obtained using vapor-recirculation type of equipment built to withstand pressure up to 10,000 lb/in.^{2} Data were obtained for the hydrogen-methane binary system at temperatures of -150, -200, and -250°F and at pressures from 500 to 4000 lb/in.^{2}; for the hydrogen-methane-propane ternary system at temperatures of 0, -100, and -200°F and at pressures of 500 and 1000 lb/in.^{2}; for the hydrogen-methane-propylene system at -100°F and 500 lb/in.^{2}; for the complex system containing hydrogen, methane, ethylene, ethane, propylene and propane for five sets of conditions including temperatures of 0 and -100°F and pressures of 500 and 1000 lb/in.^{2}

A study was made of methods of correlating the equilibrium constants of hydrogen and light hydrocarbons as obtained from the experimental data reported in this thesis and from that reported in the literature.

The equilibrium constants for hydrogen in the hydrogen-methane system were correlated by a fugacity relationship previously used by R. B. Williams for correlation of other hydrogen binary systems.

The equilibrium constants for hydrogen in the hydrogen-methane-propane system were correlated as a function of the temperature, pressure, and the molal average boiling point of the liquid phase. By adding the vapor phase concentration of hydrogen to the correlation as a variable, it was found possible to obtain a correlation to describe the equilibrium constants in both the hydrogen-methane-propane system and in the hydrogen-methane-ethylene system described in the literature.

The equilibrium constants for methane in the hydrogen-methane-propane system were correlated as functions of the temperature, pressure and molal average boiling point of the liquid phase. By adding the molal average boiling point of the vapor phase variable, it was found possible to obtain a correlation to describe the equilibrium constants of methane in both the hydrogen-methane-propane system and in the hydrogen-methane-ethylene system reported in the literature.

Nomographic correlations of the equilibrium constants of ethylene, ethane, propylene and propane are given as functions of the temperature, pressure and the molal average boiling point of the liquid phase.

The six-component system of hydrogen, methane, ethylene, ethane, propylene and propane was not adequately described by the variables of temperature, pressure and the molal average boiling points of the vapor and liquid phases.

Since a further examination of methods of correlation using the temperature, pressure and two concentration variables did not uncover any satisfactory correlation of the six-component data with that of the binary and ternary systems, it has been asserted that at least one, and possibly two more, phase rule variables will be required.

NOMENCLATURE

Latin Letters

A	Temperature function, $A = T/\sqrt{T_B}\,[1 + 450/(T_c - T)^2]$,
a_{12}	Constant in vanLaar equation, $a_{12} = \sqrt{b_1 b_2}$,
b_i	Constant for ith constituent in vanLaar equation,
C	Correction factor, $C = K/K'$,
ΔE^M	Energy-of-mixing,
$\Delta \overline{E}_i^V$	Energy-of-vaporization/mole,
F	Degrees of freedom (phase rule),
$\overline{F}_i$	Partial-molal free energy for ith component.
$\overline{F}_i^o$	Partial molal free energy for ith component in the pure state,
$\Delta \overline{F}_i^M$	Partial molal free-energy-of-mixing, $\overline{F}_i - \overline{F}_i^o$,
f_i	Fugacity of the ith component,
f_i^o	Fugacity of the ith component in the pure state,
H(T)	Henry's law constant,
$\overline{H}_i$	Partial molal enthalpy of the ith component,
$\overline{H}_i^o$	Partial molal enthalpy of the ith component in the pure state,
$\Delta \overline{H}_i^M$	Partial molal enthalpy-of-mixing, $\overline{H}_i - H_i^o$,
K_i	Equilibrium constant for the ith component,
M_i	Molecular weight of the ith component,
MABP	Molal average boiling point, $\Sigma z_i(nBP_i)$,
MW	Molal average molecular weight, $\Sigma z_i M_i$,
m/e	Mass to charge ratio for an ion,
N	Number of components (phase rule),
N_i	Number of moles of ith component,
nBP_i	Normal boiling point for ith component,
P	Pressure,
P	Phases (phase rule),

P_{c_i}	Critical pressure of i,
P'_c	Pseudo critical pressure, $\sum z_i P_{c_i}$,
P'_R	Pseudo reduced pressure, P/P'_c,
P_K	Correlating pressure,
p_i	Partial pressure of i,
p_i^o	Vapor pressure of i,
log Q	Modified Henry's law constant,
R	Gas constant,
$\overline{S}_i$	Partial molal entropy of i,
$\overline{S}_i^o$	Partial molal entropy of i in the pure state,
$\overline{S}_i^M$	Partial molal entropy-of-mixing, $\overline{S}_i - \overline{S}_i^o$,
T	Temperature,
T_B	Normal boiling point, nBP
T_{c_i}	Critical temperature of i,
T_c^i	Pseudo critical temperature, $\sum z_i T_{c_i}$,
T'_R	Pseudo reduced temperature, T/T'_c,
$\overline{V}_i$	Partial molal volume of i,
$\overline{V}_i^f$	Partial molal free volume of i,
W_L	Weight equivalent molecular weight,
x_i	Mole per cent of i in liquid phase,
y_i	Mole per cent of i in vapor phase,
z_i	Mole per cent of i in a mixture.

Greek Letters

γ_i	Activity coefficient of i,
$_{12}$	Parameter in heat-of-mixing term,
δ_i	$(\Delta \overline{E}_i^V/\overline{V}_i)^{1/2}$,

ϕ_i	Volume fraction of i,
ϕ_L	Liquid phase activity coefficient,
ϕ_V	Vapor phase activity coefficient.

Subscripts

A,B,i or 1,2,3	component,
L	Liquid phase,
V	Vapor phase.

I. INTRODUCTION

A. The Problem

Low temperature processes are becoming increasingly important and there is presently a great need for data of all kinds in the low temperature region. This dissertation was undertaken to obtain further insight into the vapor-liquid equilibria at low temperatures and high pressures of light hydrocarbon systems which contain hydrogen.

Hydrogen is radically different from the hydrocarbons both in structure and behavior. The first vapor-liquid study of a hydrogen-hydrocarbon system was made by Kay (28) in 1941. He found that hydrogen displays a reverse order solubility over a considerable range of temperatures and pressures.

Several workers have made studies of the vapor-liquid behavior of hydrogen in light hydrocarbon systems as shown in Table I.

As shown in Table I, hydrogen binary system data is available for systems from hydrogen-methane up to hydrogen-n-butane. Ternary system data is available for the hydrogen-methane-ethylene, and hydrogen-methane-ethane systems.

The ultimate aim of the present work was to complete the study of binary systems; to add to our knowledge of ternary systems with data which would lend itself to the formulation of a generalized theory or correlation; and to obtain some multi-component data which could be used to check the adequacy of a theory or correlation that might be derived from a study of binary and ternary systems.

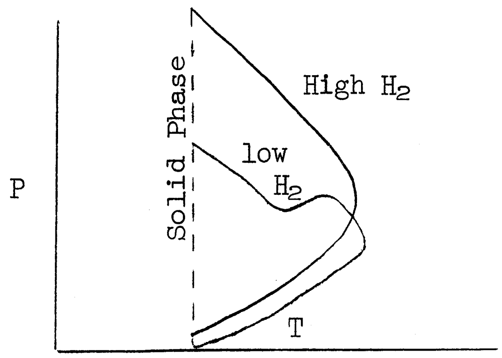
TABLE I

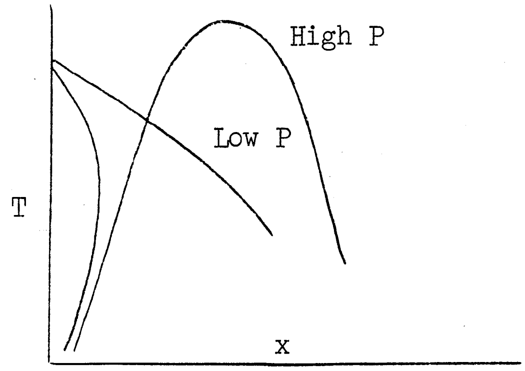
SOURCES OF VAPOR-LIQUID EQUILIBRIUM DATA FOR LIGHT HYDROCARBON SYSTEMS CONTAINING HYDROGEN

System	Author	Temp. Range °F
Hydrogen-Methane	Levitskaya (35)	-140 to -175
Hydrogen-Methane	Fastowsky and Gonikberg (13)	-230 to -298
Hydrogen-Methane	Freeth and Verschoyle (15)	-295 to -310
Hydrogen-Ethylene	Likhter and Tikhonovich (37)	-120 to -175
Hydrogen-Ethylene	Williams and Katz (45)	0 to -250
Hydrogen-Ethane	Levitskaya (35)	-120 to -175
Hydrogen-Ethane	Williams and Katz (45)	+50 to -275
Hydrogen-Propylene	Williams and Katz (45)	+75 to -275
Hydrogen-Propane	Williams and Katz (45)	+75 to -300
Hydrogen-Propane	Burris et al. (8)	+40 to +190
Hydrogen-Isobutane	Dean and Tooke (9)	+100 to +250
Hydrogen-n-Butane	Aroyan and Katz (4)	+75 to -200
Hydrogen-n-Butane	Nelson and Bonnell (38)	+75 to +240
Hydrogen-Methane-Ethylene	Likhter and Tikhonovich (37)	-120 to -175
Hydrogen-Methane-Ethane	Levitskaya (35)	-120 to -175

B. General Principles and Theory

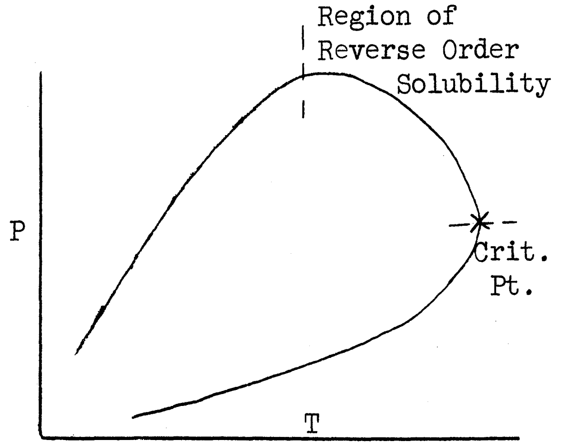
Since the work of Kay (28) in 1941 it has been known that hydrogen dissolved in hydrocarbon systems exhibits what is known as reverse-order solubility over a considerable range of temperatures and pressures. Reverse-order solubility means that the solubility of a substance increases with an increase in temperature. Ordinarily we are used to the opposite behavior, i.e., where the solubility decreases with an increase in temperature. From Kay's results with the solubility of hydrogen in a petroleum naphtha, he obtained phase diagrams such as the following for a hydrogen-hydrocarbon system which contains low concentrations of hydrogen. He found that at higher concentrations, hydrogen did not exhibit a minimum in the bubble-point curve but that it did exhibit reverse order solubility.

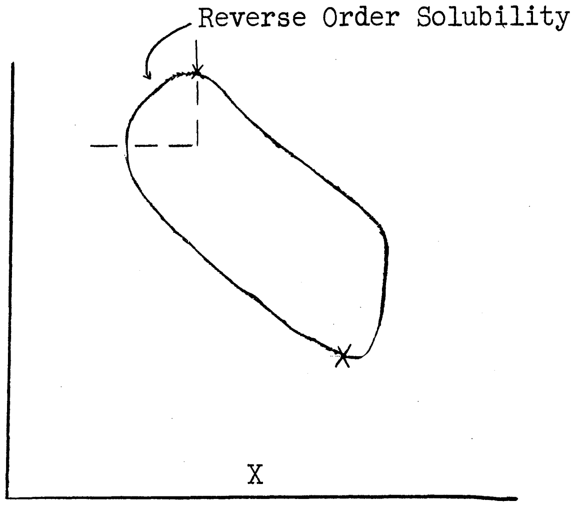




Aroyan (3) has given a very good description of minimum solubility and reverse order solubility in his doctorate thesis. He showed that these are not basically unusual phenomenon and that ordinary substances exhibit minimum solubility and reverse order solubility in the region of isobaric retrograde vaporization as described by Katz and Kurata (31).

The following drawings show the zone of reverse-order solubility as exists in a typical hydrocarbon system.





1. Some Concepts of Vapor-Liquid Equilibrium

For many years, attempts have been made to describe vapor-liquid equilibrium theoretically, but there has not yet been a description to satisfy all cases.

One of the first expressions used to describe vapor-liquid equilibrium was Raoult's Law. This law now has been used as a definition of an ideal solution. Combined with Dalton's Law of additive partial pressures we obtain the following:

$$p_A = p_A^o x_A , \tag{1.1}$$

or

$$Py_A = p_A^o x_A , \tag{1.2}$$

or

$$K_A = \frac{y_A}{x_A} = \frac{p_A^o}{P} , \tag{1.3}$$

where

p_A = partial pressure of A in vapor,

p_A^o = vapor pressure of A at the temperature, T,

x_A = mol fraction of A in the liquid,

y_A = mol fraction of A in the vapor,

P = total pressure on the system, and

K_A = equilibrium constant of A.

This law was first used by Dolezak (11) to predict solubility. It is generally said to hold for the solvent in solution.

An expression which is sometimes used for the prediction of the solubility of a solute is Henry's law which states the solubility is proportional to the pressure at constant temperature.

$$HP = x \qquad (2.1)$$

where

H = Henry's law constant, usually derived from experimental data.

Part of the failure of Raoult's law to predict solubility is due to the non-ideality of the vapor phase, but ideal equilibrium constants can be derived and used to eliminate this error. These constants may be obtained from the fugacity concept of G. N. Lewis (36).

$$(f_A)_L = (f_A^o)_L \, x_A \, . \qquad (3.1)$$

Also assuming an ideal solution in the vapor phase we get

$$(f_A)_V = (f_A^o)_V \, y_A \qquad (3.2)$$

where

$(f_A)_L$ = fugacity of A in the liquid phase,

$(f_A)_V$ = fugacity of A in the vapor phase,

$(f_A^o)_L$ = fugacity of pure A at the temperature T and the vapor pressure of A at T,

$(f_A^o)_V$ = fugacity of pure A at the temperature T and the pressure, P.

Since at equilibrium the fugacity of A is the same in both phases,

$$f_L = f_V \, , \qquad (3.3)$$

then

$$(f_A^o)_L\, x_A = (f_A^o)_V\, y_A\,, \qquad (3.4)$$

and

$$K_A = \frac{y_A}{x_A} = \frac{(f_A^o)_L}{(f_A^o)_V}\,. \qquad (3.5)$$

These approaches have helped us in understanding something about vapor-liquid equilibrium, but they have not supplied a good reliable calculation of results. This is due principally to the existence of non-ideal solutions in both the liquid and vapor phases.

A different approach to the use of fugacity relationships for the prediction of vapor-liquid equilibrium was put forward by Krichevsky and Kasarnovsky (34) who described systems containing a slightly soluble substance. Their relationship was derived by Kobayashi (33). Starting with the free energy relationship at constant temperature and composition,

$$d\overline{F}_T = \overline{V}dP = RTd\ln f \qquad (4.1)$$

We may apply the free energy relationship to the liquid phase and integrate between the vapor pressure of the solvent and the pressure in question, keeping the temperature constant. Consideration of any actual system will disclose that lowering the pressure on a saturated liquid maintained at constant temperature to the vapor pressure of the solvent will result in vaporization of some of the liquid. The Kobayashi approach to evaluating the fugacity of this system, now consisting of both liquid and vapor was to relate it to a pseudo Henry's Law constant which says that the fugacity of the system of liquid and vapor is proportional to the overall composition. The integration is then carried out:

$$\int_{p_B^o}^{P} \overline{V}dP = \int_{f \text{ at } p_B^o}^{f \text{ at } P} RTd\ln f\,. \qquad (4.2)$$

Considering the slightly soluble substance, A, and assuming the molal volume, $\overline{V}_A$, to be constant, we derive:

$$\overline{V}_A\ (P - p_B^o) = RT\ln \frac{f_A\ (P,T)}{f_A(p_B^o, T)} \tag{4.3}$$

as explained above, we now assume:

$$f_A\ (p_B^o, T) = H(T)\ x_A. \tag{4.4}$$

The fugacity of A in the liquid at P and T is equal to that in the vapor phase if we have equilibrium and we may assume ideal solutions in the vapor phase so that:

$$(f_A)_L = (f_A)_V = f_A^o\ (P,T)\ y_A\ . \tag{4.5}$$

Now

$$\overline{V}_A\ (P - p_B^o) = RT\ln \frac{f_A^o\ (P,T)\ y_A}{H(T)\ x_A}\ . \tag{4.6}$$

By manipulation:

$$\ln f_A^o\ (P,T)\ \frac{y_A}{x_A} = \frac{\overline{V}_A}{RT}\ P + \ln H\ (T) - \frac{\overline{V}_A}{RT}\ p_B^o\ . \tag{4.7}$$

We may combine $\ln H\ (T) - (\overline{V}_A/RT)\ p_B^o$ to form lnQ. Q represents a modified Henry's Law constant. Now we have

$$\ln f^o\ (P,T)\ \frac{y_A}{x_A} = \frac{\overline{V}_A}{RT}\ P + \ln Q\ . \tag{4.8}$$

This relationship has been used by Fastowsky and Gonikberg (13) in a slightly different form for the description of their hydrogen-methane data. It was used by Kobayashi (33) for the description of water-hydrocarbon systems and it was used by Williams (44) for the description of his hydrogen-light hydrocarbon binary data.

It can be shown that at least one of the assumptions contain errors, e.g., at high pressures the molal volume does change. Williams has used the constant molal volume region for description of his systems. He has correlated the molal volumes and modified Henry's law constants as functions of temperature for each constituent.

One approach to an evaluation of the nonideality of systems has been to calculate activity coefficients which represent the deviation from Raoult's law.

$$y_A P = \gamma_A p_A^o x_A \tag{5.1}$$

or

$$\gamma_A = \frac{y_A P}{x_A p_A^o} = \frac{K \text{ actual}}{K \text{ ideal}} . \tag{5.2}$$

Various semi-empirical expressions have been used to relate the activity coefficients to the concentration. One example of such an expression is the White's (43) modified van Laar's expression written for a binary system:

$$T \log \gamma_1 = \frac{1}{b_1} \left[\frac{a_{21} x_2}{b_1 x_1 + b_2 x_2} \right]^2 \tag{6.1}$$

$$T \log \gamma_2 = \frac{1}{b_2} \left[\frac{a_{12} x_2}{b_1 x_1 + b_2 x_2} \right]^2 . \tag{6.2}$$

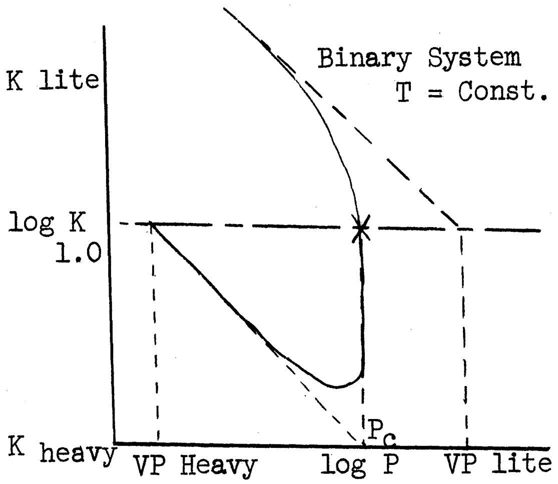
This approach has proved useful in the region below the critical temperature of both substances. If conditions are above the critical temperatures of one of the substances, it may be possible to extend the vapor pressure curve and to use the extrapolated value for calculation of the activity coefficient.

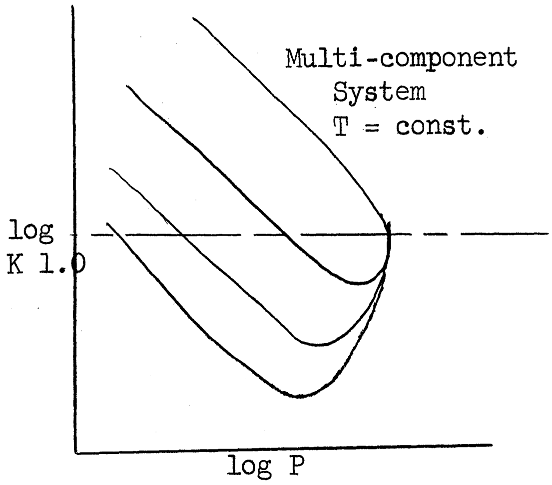
White (43) has shown how the van Laar constants may be combined to describe a ternary system:

$$T \log \gamma_1 = \frac{1}{b_1} \left[\frac{a_{21} x_2 + a_{31} x_3}{b_1 x_1 + b_2 x_2 + b_3 x_3} \right] \tag{7.1}$$

Other similar expressions for describing the activity coefficients are in common use.

Another approach has been to examine plots of the logarithmic equilibrium constant as a function of the logarithm of the total pressure. Typical examples of such plots are shown below.





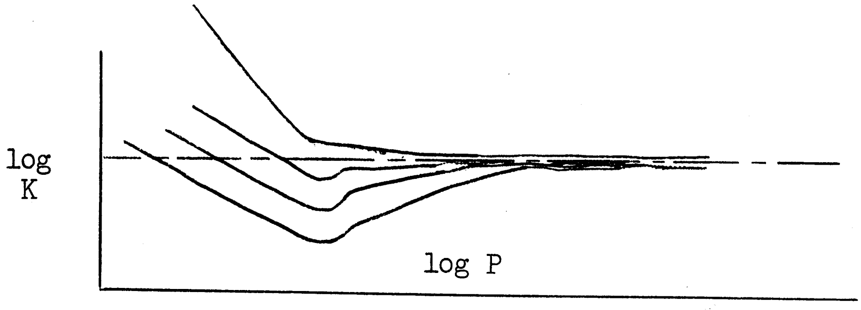
The dotted lines in the plot for a binary system indicate Raoult's law dependence, the solid lines indicate a typical behavior for hydrocarbons. The pressure at which the equilibrium constants for both constituents become one and equal for a binary system is the critical pressure at the temperature in question. It was noted by Katz (29) in a paper on the application of equilibrium constants that complex systems also showed a similar behavior, i.e., where the K's converge to unity at a pressure later called the convergence pressure. This was also shown in data presented by Katz and Hackmuth (30) in 1937. If the mixture under consideration is at its critical temperature then the equilibrium constants for all the constituents will converge to unity at the critical pressure. If the system is not at its critical temperature, the K's still converge to unity at some pressure but the critical pressure significance has been lost.

In 1945, Hanson, Rzasa and Brown (21) published methane equilibrium constants as functions of the temperature, pressure and convergence pressure.

Hadden (20) presented a correlation of hydrocarbon equilibrium constants as functions of pressure, temperature, and convergence pressure. He suggested the following method for finding the convergence pressure.

He suggested that first the complex mixture be made into a pseudo binary system consisting of methane and an ethane plus others fraction. Some molal average properties could be calculated for the ethane plus fraction to establish a critical pressure and temperature. Next, by using the methane binary critical loci as a guide, a critical-locus could be sketched in on a pressure versus temperature plot. Now the convergence pressure could be read from the plot as that pressure corresponding to the critical pressure at the temperature in question for the pseudo binary system.

Data published by Roland (40) shows that convergence pressure correlations for complex mixtures may be considerably in error. As shown below, Roland's data contains a point of inflection in the log K versus log P plots as the equilibrium constants approached unity. His data would tend to show that, at least for the system he studied, a convergence pressure does not exist for systems not at their critical temperature.



Organick (39) studied the vapor-liquid equilibrium data of binary and complex hydrocarbon systems with a view toward correlating the data as a function of convergence pressure. He presented a correlation of the data in the following manner:

1. Equilibrium constants were given for the individual constituents as functions of pressure, temperature and correlating pressure.
2. The correlating pressure corresponds to the convergence pressure for a methane binary system which has the same equilibrium constants as the complex system at the pressure and temperature in question.
3. He correlated the correlating pressure as a function of the molal average boiling point of the vapor and of the weight equivalent molecular weight of the liquid.

The Organick correlation was not based upon the prediction of equilibrium constants for a multicomponent mixture by specification of the temperature, pressure and convergence pressure of that mixture. It was based on the prediction of equilibrium constants for a multicomponent mixture by specification of the temperature, pressure and convergence pressure of a methane binary system having the same equilibrium constant. The convergence pressure of that binary was related to the molal average boiling point of the vapor and the weight equivalent molecular weight of the liquid for the multicomponent system in question.

2. Application of the Phase Rule in Correlating Data

The phase rule of J. Willard Gibbs (17) may be used to predict certain things about the type of data required to define a vapor-liquid system.

The phase rule is written mathematically:

$$F = N - P + 2 \qquad (8.1)$$

where

F = degrees of freedom,

N = number of constituents, and

P = number of phases.

If we restrict ourselves to the consideration of two-phase systems, then the rule becomes $F = N$ or the degrees of freedom allowed for a non-reacting two-phase system are equal to the number of constituents. The phase rule variables are the pressure, temperature and the compositions of each phase.

Consideration of a one-component system with two phases would show that one degree of freedom is allowed. This implies that description of the system may be made by the following functional relationship

$$\phi(P,T) = 0 . \qquad (9.1)$$

This function is commonly called the vapor pressure curve. Specification of either the pressure or the temperature will serve to completely describe the state of the system.

Consideration of a binary system shows that two degrees of freedom are allowed. This infers the existence of relationships like the following:

$$\phi(P,x_A,x_B) = 0, \ \phi(P,T,x_A) = 0, \ \phi(P,T,y_A) = 0, \qquad (10.1)$$

$$\phi(P,x_A,y_A) = 0, \ \phi(P,T,x_B) = 0, \ \phi(P,T,y_B) = 0, \qquad (10.6)$$

Two dimensional graphical representation requires that one variable be held constant. The most common plots used are:

$$P \text{ vs. } x_A \qquad T = \text{constant} , \tag{10.7}$$

$$P \text{ vs. } y_A \qquad T = \text{constant} , \tag{10.8}$$

$$T \text{ vs. } x_A \qquad P = \text{constant} , \tag{10.9}$$

$$T \text{ vs. } y_A \qquad P = \text{constant} , \tag{10.10}$$

$$P \text{ vs. } T \qquad x_A = \text{constant} , \tag{10.11}$$

$$P \text{ vs. } T \qquad y_A = \text{constant} . \tag{10.12}$$

A derived concentration variable, the equilibrium constant, has come into use and is defined as $K_i = (y/x)_i$. The same type of functions for a binary system would be predicted as:

$$\phi(K_A,P,T) = 0, \ \phi(K_B,P,T), \qquad (10.13),(10.14)$$

Other derived concentration variables may be used, such as:

$$(MABP)_L = \sum_{i=1}^{i=n} x_i \,(nBP_i), \ (MABP)_V = \sum y_i \,(nBP_i) , \qquad (10.15)\text{-}(10.18)$$

$$(MW)_L = \sum_{i=1}^{n} M_i x_i , \ (MW)_V = \sum M_i y_i ,$$

where

nBP_i = the normal boiling point of the ith component,

M_i = the molecular weight of the ith component.

For a three-component system, three degrees of freedom would be allowed and the following types of functions would be expected:

$$\phi(x_A,x_B,P,T) = 0, \ \phi(y_A,y_B,P,T) = 0, \qquad (11.1),(11.2)$$

$$\phi(x_A,y_A,P,T) = 0, \ \phi(x_A,x_C,P,T) = 0, \qquad (11.3),(11.4)$$

$$\phi(K_A,x_A,P,T) = 0, \ \phi(K_B,x_B,P,T) = 0, \qquad (11.5),(11.6)$$

Also, $\phi(K_A, MABP_L, P, T) = 0, \ \phi(K_B, MABP_L, P, T) = 0,$ (11.7),(11.8)

$$\phi(K_C, MABP_L, P, T) = 0, \tag{11.9}$$

For a ternary system then, a system could be specified by the molal average boiling point of the liquid, the pressure and temperature, or by any other such set of three variables.

Now it may be seen that the specification of a system of N components requires a knowledge of N phase rule variables. If we choose to speak of a system at a certain pressure and temperature, then N - 2 concentration variables such as mol fractions or derived variables such as the following would be required to specify the system: the molal average boiling point of the liquid, the molal average boiling point of the vapor, the molal average molecular weight of each phase, the pseudo-critical temperature of each phase, or the pseudo-critical pressure of each phase.

The correlation of vapor-liquid equilibrium data usually revolves around some scheme for accounting for the effect of various concentration variables upon the equilibrium constants of the individual constituents.

The simplest possible correlation would take no account of the concentration but would depend only on temperature and pressure. Such a correlation would be adequate for a binary system but would not be expected to hold for a more complex system except in the ideal case. If a system may be described by Raoult's law then the pressure and temperature do specify the system in a practical sense.

All of the correlations now available and in use for the prediction of the vapor-liquid equilibria of complex systems are semi-empirical. They may include from one to five concentration variables, but are often used for as much as a ten-component mixture.

Smith and Watson (42) compiled vapor-liquid equilibrium data from 184 different paraffin mixtures and made a correlation of them.

In essence their correlation involves the use of a liquid phase and a vapor phase activity coefficient to be used as follows:

$$K \text{ ideal} = f_L^o / f_V^o \tag{12.1}$$

$$K \text{ actual} = f_L^o \phi_L / f_V^o \phi_V = K \text{ ideal } (\phi_L/\phi_V) \tag{12.2}$$

The correlation is made to take into account the effect of concentration by using the following variables:

1. The correlation of the vapor phase activity coefficient:

$$\phi_V = f\ [(T_R'),(P_R'),(T_{C_i}/T_C')]_V \tag{12.3}$$

T_R' = pseudo reduced temperature = T/T_C',

T_C' = pseudo critical temperature = $\Sigma\ y_i T_{C_i}$,

T_{C_i} = critical temperature for the ith component,

P_R' = pseudo critical pressure = P/P_C',

P_C' = pseudo critical pressure for the vapor = $\Sigma\ y_i P_{C_i}$,

P_{C_i} = critical pressure of ith component.

2. The correlation of the liquid phase activity coefficient:

$$\phi_L = f\ [T_R', P_R', x_i, T_B]_L \tag{12.4}$$

where

x_i = liquid composition used in connection with T_B,

T_B = normal boiling point.

Some of the functions are graphical, some, algebraic, but the method of obtaining them is clearly empirical. We have three relationships for the liquid composition and two for the vapor composition. The phase rule tells us that in order to define an N component system, we must specify N factors. The five relationships represent derived concentrations so that we have five concentration variables plus the temperature and pressure. This should define a given seven component system if there is no implicit relationship between the concentration relations used. The phase rule, however, tells us nothing concerning the application of the correlation to different seven component systems, but it does tell us that this correlation need not explain a ten-component system.

As previously described, Organick (39) has arrived at an empirical correlation of hydrocarbon equilibrium constants at high pressures. His functional relationship may be expressed as

$$K_i = f(P,T,P_k) \qquad (13.1)$$

$$P = g\,[(MABP)_V, W_L, P] \qquad (13.2)$$

where

P_k = correlating pressure,

W_L = weight average molecular weight of the liquid.

Since this correlation includes a specification of four variables it would be expected to correlate the data for a four-component system if there is no implicit relationship between the concentration variables. However, as explained above, the extension of the correlation to other four-component systems or to systems composing more than four components depends upon the sensitiveness of the variables chosen.

The equation of state of Benedict, Webb, and Rubin (5) was used to extend the fugacity concept of Lewis for obtaining equilibrium constants. In generalizing their results (6), they have used the following functional relationship:

$$K_i = f\ [(MABP)_V, (MABP)_L, T, P]\ . \qquad (14.1)$$

This correlation involves the use of four variables so it would be expected to correlate the results of a system of four components. As described above for other correlations, extension of the correlation to different systems or to more complex systems depends upon the variables chosen. The phase rule can only predict that the system might work for different four-component systems and that it might not work for a five or more component system.

3. Solubility Theory

The problem of predicting the solubility of non-electrolytes has received considerable attention since the first papers of Hildebrand in the 1920's. Some of the people who have been most active in this work have been J. H. Hildebrand, R. L. Scott, George Scatchard, P. J. Flory, E. A. Guggenheim, M. L. Huggins, and J. G. Kirkwood.

The thermodynamic requirements for a heterogeneous system to be in equilibrium are that the chemical potentials, pressure and temperature be the same in each phase. A more natural and common choice of variables has been the temperature, pressure and mole fractions of the constituents in each phase.

The starting point for most thermodynamic considerations of phase equilibria is the free energy relation:

$$\overline{F} = \overline{H} - T\overline{S}. \qquad (15.1)$$

The free energy involved in taking pure A at temperature T and adding it to a solution is described as:

$$\overline{F}_A - \overline{F}_A^o = \overline{H}_A - \overline{H}_A^o - T\,(\overline{S}_A - \overline{S}_A^o)\ . \qquad (15.2)$$

The problem may now be broken down into a consideration of the heat-of-mixing $(\overline{H}_A - \overline{H}_A^o)$ and the entropy-of-mixing $(\overline{S}_A - \overline{S}_A^o)$.

Early considerations of liquid structure were made by Frenkel (16) who considered the liquid as an imperfect solid having a more or less definite lattice structure. This theory has now been discarded and liquids are considered to be fluids in which the molecules are free to move. Considerations of a liquid existing with a lattice structure have been mathematically useful in making contributions to the theory of solubility.

Kirkwood and Buff (32) have considered the heat of mixing term and have described it as:

$$\overline{H}_1 - \overline{H}_1^o = \overline{V}_1\,\Delta_{12}\,\phi_2^2 \qquad (16.1)$$

where

$\overline{V}_1$ = molal volume of pure liquid 1,

Δ_{12} = parameter,

ϕ_2 = volume fraction of 2 .

They derived a general expression for Δ_{12} from the theory of the grand ensemble.

Hildebrand (22) has derived an expression for the energy-of-mixing for a system which contains no interaction of the molecules,

$$\Delta E^M = \frac{N_1 N_2 \overline{V}_1 \overline{V}_2}{N_1\overline{V}_1 + N_2\overline{V}_2}\left\{\left[\frac{\Delta\overline{E}_1^V}{\overline{V}_1}\right]^{1/2} - \left[\frac{\Delta\overline{E}_2^V}{\overline{V}_2}\right]^{1/2}\right\}^2 . \qquad (17.1)$$

Differentiation of this expression gives us the heat of mixing per mole:

$$\Delta\overline{H}_2^M = \overline{V}_2\, \phi_1^2\, (\delta_1 - \delta_2)^2 \qquad (17.2)$$

where

ϕ_1 = volume fraction of constituent 1,

δ_1 = $(\Delta\overline{E}_1^V/\overline{V}_1)^{1/2}$, δ_2 = etc.

Extensive consideration has been given to the entropy of mixing. The simplest case to consider is that of an ideal solution which is composed of two liquids with equal molecular volumes and zero heat-of-mixing. In this case it has been shown that the increase in entropy is given by the decreased probability, x_2, that a molecule in the solution is one of this species, that is,

$$\overline{S}_2 - \overline{S}_2^o = -R\ln x_2 . \qquad (18.1)$$

Flory (14) and Huggins (27) each considered a liquid solution as having a quasi-lattice structure and derived the following expression for the entropy of mixing:

$$\overline{S}_2 - \overline{S}_2^o = -R\, [\ln\phi_2 - \phi_1\, (1 - \overline{V}_2/\overline{V}_1)] . \qquad (19.1)$$

A different relationship for the entropy of mixing has been given by Hildebrand (23) and improved on by Scatchard (41).

$$\Delta\overline{S}^M = -R\, \{x_1 \ln\, [x_1\overline{V}_1^f/(x_1\overline{V}_1^f + x_2\overline{V}_2^f)]\} + x_2 \ln\, [x_2\overline{V}_2^f\, (x_1\overline{V}_1^f + x_2\overline{V}_2^f)] \qquad (20.1)$$

in which $\overline{V}_1^f$ = the free volume for 1. Hildebrand assumed that $\overline{V}^f$ was proportional to $\overline{V}$. Scatchard suggested that it be made proportional to the surface area of the molecule. This relation leads to the Guggenheim (18,19) formula and to the Flory-Huggins equation in the limit.

An ideal solution is one in which the individual molecules are subject to the same forces of attraction and repulsion as in the pure liquids. This solution gives rise to Raoult's law as follows:

$$\bar{F}_1 - \bar{F}_1^o = \bar{H}_1 - \bar{H}_1^o - T\,(\bar{S}_1 - \bar{S}_1^o) = 0 - T\,(-R\ln x_1) \qquad (21.1)$$

also

$$\bar{F}_1 - \bar{F}_1^o = \bar{V}dP = RT\ln\,(f_1/f_1^o) \qquad (21.2)$$

so

$$f_1/f_1^o = x_1 \qquad (21.3)$$

or

$$f_1 = x_1 f_1^o \,. \qquad (21.4)$$

A discussion of the conditions for the application of Raoult's law has been given by Hildebrand (24).

Hildebrand (26) invented the term "regular solution" to describe those solutions which, display nearly ideal entropy of mixing although the enthalpy may be non-ideal. This gives an expression for the free energy of mixing:

$$\Delta\bar{F}_2^M = RT\ln\,(f_2/f_2^o) = \bar{V}_2\phi_1^2\,(\delta_1 - \delta_2)^2 + RT\ln x_2 \,. \qquad (22.1)$$

Non-ideal solutions may be approximated by use of the van Laar-Scatchard-Hildebrand heat term and the Flory-Huggins entropy term,

$$\Delta\bar{F}_2^M = RT\ln\,(f_2/f_2^o) = \bar{V}_2\phi_1^2\,(\delta_1 - \delta_2)^2 + RT\,[\ln\phi_2 + \phi_1\,(1 - \bar{V}_2/\bar{V}_1]\,. \qquad (23.1)$$

Other expressions may be used for the heat term such as the expression given above by Kirkwood and Buff (32) and other entropy expressions may be used but the above discussion shows the general procedure for the handling of solubility by the statistical mechanical method.

In the 1950 Annual Review of Physical Chemistry (25) Hildebrand has said that only in special cases can solutions of molecules of different size show an ideal entropy-of-mixing.

Another approach has been through the equation of state. The prime requirement of this method is an equation of state which will describe both the vapor and the liquid states and one which can also be expressed in terms of the concentrations of the constituents. If this is possible, then equilibrium conditions may be determined by evaluation of the temperatures, pressures and fugacities of the two phases. Equilibrium conditions are those at which the temperature, pressure and fugacity in each phase are equal.

This is roughly the procedure that has been used by Benedict, Webb, Rubin, and Friend (6).

II. EXPERIMENTAL PROGRAM

A. Conditions for Study

The existing binary data listed in Table I was examined for completeness and consistency. It was found that the binary data for the hydrogen-methane system contained large deviations from the smoothed values.

It was decided that in order to complete and to get more accurate data for the binary systems, the hydrogen-methane system should be given further experimental study with the intention of getting more accurate data than has been reported in the literature. The experimental conditions chosen for study are given in Table II.

Published data is available for the ternary systems of hydrogen-methane-ethylene (37) and hydrogen-methane-ethane (35). This data was studied and it was decided that the most desirable new data for a ternary system would be data for the system hydrogen-methane-propane and hydrogen-methane-propylene.

As a guide to the behavior of hydrogen in a complex system and as a check upon the use of any correlation which might be obtained from consideration of the binary and ternary systems with a view to predicting the behavior in complex systems, it was decided that data for a six-component system containing hydrogen, methane, ethylene, ethane, propylene and propane should be obtained.

TABLE II

EXPERIMENTAL CONDITIONS FOR STUDY

System	Temperatures °F	Pressures lb/in.^{2}
Hydrogen-Methane	-150, -200, -250	500, 1000, up to 4000
Hydrogen-Methane-Propane	0, - 100, - 200	500, 1000
Hydrogen-Methane-Propylene	-100	500
Hydrogen-Methane-Ethylene-Ethane-Propylene-Propane	0, -100	500, 1000

B. Materials Used in Study

The materials used for this study are listed with their approximate analysis as obtained from the Mass Spectrometer in Table III.

TABLE III

PURITY OF MATERIALS

Substance	Minimum Purity mol %	Impurities
Hydrogen	99.5	H_2O,N_2
Methane	99.0	C_2H_4,C_2H_6
Ethylene	99.0	CH_4,C_3H_8
Ethane	99.1	CH_4,C_3H_6,C_3H_8
Propane	99.0	
Propylene	99.0	

The hydrogen used in this work had been produced electrolytically and pumped over water.

The pure grade hydrocarbons were obtained from the Phillips Petroleum Company. They were specified as 99 mol per cent minimum.

C. Description of Equipment

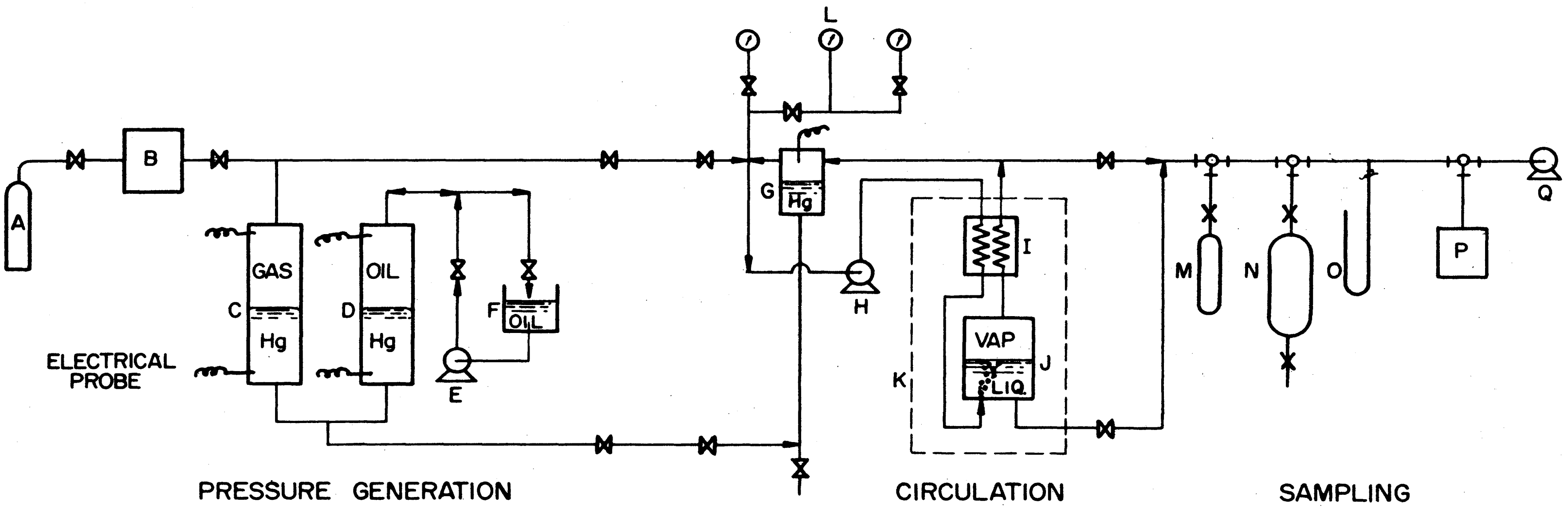
The apparatus used to obtain the data for this thesis was of the vapor-recirculation type. It was designed for investigation at temperatures from room temperature down to -300°F and at pressures up to 8,000 lb/in.

The equipment may best be described with reference to the schematic diagram, Figure 1. Functionally the equipment consists of the following three parts:

1. The pressure generation section.
2. The equilibrium cell and circulation system.
3. The sampling section.

The purpose of the pressure generation section is to provide high pressure gas and high pressure mercury for use in the equilibrium cell and circulation system.

In Figure 1, A represents a cylinder of pure gas. Gas is charged to the high pressure cylinder, C, after water, carbon dioxide, and the heavier hydrocarbons have been removed by passage of the gas through a dessicator train, B. This train contains silica gel, ascarite and activated charcoal in that order. Compression of the gas is carried out in the cylinder, C. A gear pump, E, pumps oil from reservoir F into a high pressure cylinder, D. Cylinders C and D are connected at the bottom. When oil is forced into the top of cylinder D, mercury is caused to flow into cylinder C, thereby compressing the gas it contains. Pressure gages are located in the oil lines. Both high pressure gas and mercury may be obtained from C as shown. Electrical probes were located in the top and bottom of the cylinders C and D to help indicate the location of the mercury interface.



LEGEND:

A	CYLINDER OF GAS	J	EQUILIBRIUM CELL
B	DRYING TUBE	K	CONSTANT TEMPERATURE BATH
C	HIGH PRESSURE GAS COMPRESSION CYLINDER	L	PRESSURE GAGES
D	HIGH PRESSURE COMPRESSION CYLINDER	M	SAMPLE BULB
E	HIGH PRESSURE PUMP	N	SAMPLE BULB FOR MASS SPECTROMETER
F	OIL RESERVOIR	O	MANOMETER
G	HIGH PRESSURE RESERVOIR	P	THERMAL CONDUCTIVITY CELL
H	MAGNETICALY OPERATED CIRCULATION PUMP	Q	VACUUM PUMP
I	HEAT EXCHANGER		

Figure 1. Schematic Diagram of Apparatus Used in Obtaining Vapor-Liquid Equilibrium Data.

The second section is the heart of the apparatus. It consists essentially of a high pressure cell contained in an insulated air bath and of a system for circulating the vapor phase in the cell up through the liquid phase.

As described by Aroyan (3) and by Williams (44), the cell was built of two machined halves of 304 stainless steel welded together. The external dimensions of the cell are 9-3/4 inches high and four inches in diameter.

The cell contains a thermo-well which is fitted with a three-couple thermopile for indicating the temperature in the cell. There are two baffles in the cell to facilitate good contacting of the liquid and vapor. It has been estimated that the internal volume of the cell is about 300 ml.

The vapor phase circulating system was operated in the following manner. The vapor was first warmed by counter-current exchange (I) with vapor which passes to the bottom of the cell. It was then brought to a high pressure cell (G) which was used to maintain the pressure in the system whenever a sample of liquid or vapor was taken. This was done by injecting high pressure mercury into the cell, thereby varying the volume of the system. From this cell, the gas was passed to a plunger-type pump (H). The pump was magnetically operated and has been described by Aroyan (3) and Williams (44). A similar pump has also been described by Exline and Endine (12). The pump consisted essentially of a magnetic plunger inside a nonmagnetic cylinder; the plunger is raised by a solenoid around the cylinder and is returned by gravity and a spring. An electronic timer was used to apply the electric current to the pump at intervals, thereby producing the pumping action.

From the pump, the gas was forced to the heat exchanger (I) and then to the bottom of the equilibrium cell (J).

Three pressure gauges (L) were attached to the system as shown in Figure 1. The first had a range of 0-600 lb/in.^{2} with graduations of 10 lb/in.^{2}. The second had a range of 0-3000 lb/in.^{2} with 25 lb/in.^{2} graduations. The third had a range of 0-10,000 lb/in.^{2} with 50 lb/in.^{2} graduations.

All of the tubing in the apparatus was 1/4-in. O.D. high-pressure, stainless steel, and the valves were of high pressure construction.

The internal dimensions of the insulated air bath (K) containing the cell were 6 x 12 x 18 inches. It was insulated with two inches of rock cork insulation over the sides and bottom and six inches across the top. The sides and bottom were further insulated with six inches of loose Santocell insulation. The bath contained an electric heater and a circulation fan.

Seven thermocouples were located at various points in the bath to aid in controlling the temperature. The thermocouples were copper-constantan and were located as follows:

Thermocouple No.	Location
1	Gas return line to bottom of cell
2	At side of cell three inches from bottom
3	Inside heat exchanger two inches from cold end
4	In air bath two inches above top of cell
5	In air bath two inches below bottom of cell
6	In the thermowell of equilibrium cell
7	Control couple fastened to side of cell three inches from bottom.

Couple number six had three junctions in series and was used to indicate the temperature within the cell. A Leeds-Northrup portable precision potentiometer was used to read the emf's developed by the thermocouples.

The temperature was controlled by a Brown potentiometric controller recorder of the self-balancing galvanometer type. It was designed for use with a single iron-constantan couple for temperatures up to 2,000°F. It was connected to couple No. 7 which had seven copper-constantan thermocouples in series which gave a nearly full scale reading at -250°F.

Crushed dry ice was introduced into the bath when temperatures between room temperature and the dry ice point (about -110°F) were being investigated. The controller regulated the temperature in the bath by turning on a small heater.

For temperatures below -100°F, liquid nitrogen was used as the coolant. An air pressure system was used to force liquid nitrogen from its container into the bath. A cooling effect was derived from evaporation of the nitrogen in the bath. In this case, the temperature was regulated by putting air pressure into the container, thereby forcing nitrogen into the bath.

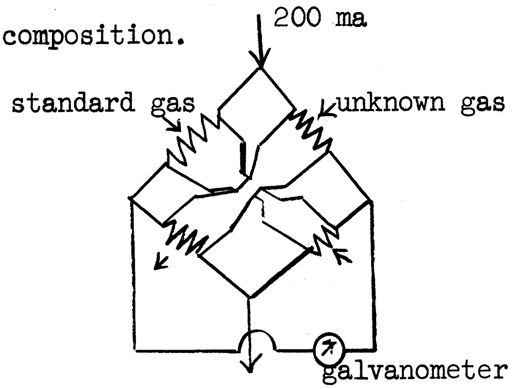
The third section of the equipment was composed of the sampling apparatus. Liquid samples passed from the bottom of the cell to a needle valve. The vapor sample was taken from a line immediately above the cell. The sample lines were 1/4 in. O.D. by 3/32 I.D. stainless steel tubing with 14 gage chromel A wire inside to reduce the holdup. This procedure is recommended by Dodge and Dunbar (10). Since both the liquids and the vapors for all of the systems studied in this work existed as a gas at room temperature and atmospheric pressure, their treatment after passing through the sample valve was identical.

As shown in Figure 1, the sampling system consisted essentially of a sample bulb for mass spectrometer analysis (M), a bulb for density determination (N), a thermal-conductivity cell (p), a manometer (o) and a vacuum pump (Q).

The sample bulbs used for obtaining samples for mass spectrometer analysis had a volume of approximately 25 cc. They were closed by an evacuated hollow core stopcock and carried a 10/30 mole ground glass tapered joint.

When the analysis was made by determining the density of the sample, the sample was obtained in the bulb (N). This bulb had a volume of about 300 ml and was closed at each end by a stopcock.

A Gow-Mac Gas Master containing a stainless steel two-pass thermal conductivity cell was used to obtain rapid semi-quantitative results for the analysis of binary gas mixtures. As shown below, the instrument consisted essentially of a bridge with a standard or reference gas passing by two elements of the bridge and an unknown gas passing by the remaining two elements of the bridge. The unbalance in the bridge was a measure of the composition.



The cell which was used had four M/K-K filaments. A six-volt storage battery was used to supply current to the bridge. A Weston milliameter was used to indicate the current which could be regulated by a rheostat. The divisions on the milliameter were 2-1/2 milliamps and the current could easily be estimated to ± 1 milliamp. A current of 200 milliamps was passed through the bridge. A Leeds-Northrup precision potentiometer was used to read the unbalance in the bridge.

The apparatus for obtaining the density of the sample is essentially the same as that described by Aroyan (3).

The Consolidated Engineering Corporation 21-103B Mass Spectrometer was used in analyzing some of the binary samples, and all of the ternary and multi-component samples. This instrument is described further in Appendix B.

D. Procedure

In general terms, the experimental procedure consisted of charging the components to the cell; maintaining the temperature and pressure constant over the period of time required to obtain equilibrium between the liquid and vapor in the cell; and then obtaining and analyzing samples of the liquid and vapor.

The criteria adopted for the establishment of equilibrium was a constancy of temperature, pressure and phase composition over a period of time. Figure 2 shows a plot of the mole per cent hydrogen in the liquid phase as a function of time for a typical experimental run. Equilibrium was usually attained after four to six hours.

A detailed description of the experimental procedure has been included in Appendix A.

E. Results

A total of 50 data points were obtained in this study. The experimental conditions and the distribution for these runs are given in Table IV.

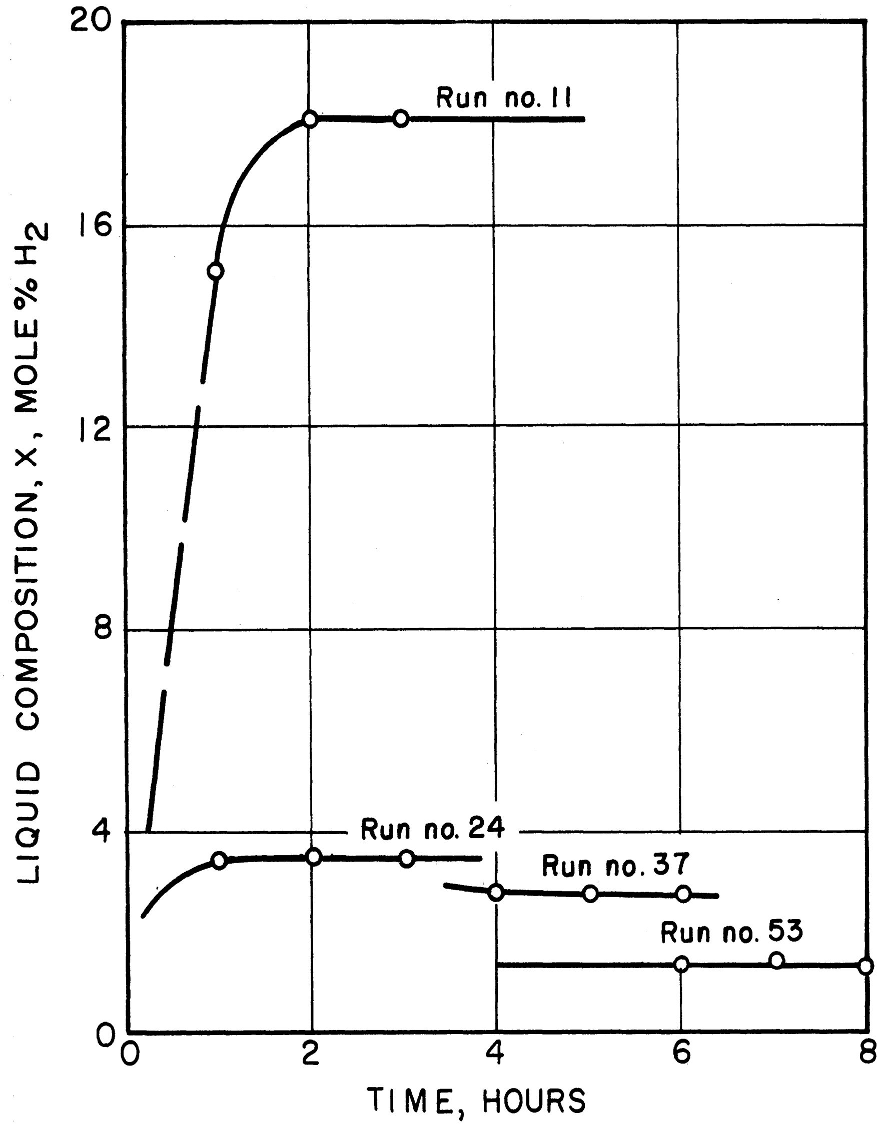


Figure 2. Liquid Phase Approach to Equilibrium Composition.

TABLE IV

EXPERIMENTAL CONDITIONS

System	Temp. °F	Pressure lb/in.^{2}	Number of Runs
H_2-CH_4	-150	500 to 1500	4
	-200	500 to 3000	5
	-250	500 to 4000	4
H_2-CH_4-C_3H_8	0	500	7
	-100	500	6
	-200	500	3
	0	1000	5
	-100	1000	4
	-200	1000	5
H_2-CH_4-C_3H_6	-100	500	2
H_2-CH_4-C_2H_4-C_2H_6-C_3H_6-C_3H_8	0	500	1
	-100	500	2
	0	1000	1
	-100	1000	1

Table V gives the actual experimental data for the system hydrogen-methane, Table IX (Appendix C) gives the smoothed data. Plots of the data are given in Figures 3, 4, 5, 6, and 7.

Figure 3 shows a plot of the pressure as a function of the phase compositions at constant temperature. The critical region has been dotted to indicate an extrapolation.

Figure 4 is a plot of the temperature as a function of the phase compositions at constant pressure. The isobar for 500 lb/in.^{2} clearly shows both a region of normal solubility and a region of reverse order solubility. The critical regions of the envelopes have been dashed. The envelopes terminate at about -298°F at which temperature of a solid phase is formed.

TABLE V

ORIGINAL DATA FOR HYDROGEN-METHANE SYSTEM

Run No.	Temp. ^{o}F	Press. lb/in.^{2}	Phase Compositions		Equilibrium Constants	
			Vapor mol % H_2	Liquid mol % H_2	$K = y/x$ H_2	$K = y/x$ CH_4
3	-150	500	15.83	1.70	9.32	0.859
4	-150	1000	40.60	8.77	4.64	0.650
8	-150	1280	46.31	12.55	3.69	0.614
9	-150	1500	46.78	16.22	2.88	0.636
2A	-200	500	63.92	3.43	18.60	0.374
5	-200	1000	76.18	7.81	9.75	0.258
11	-200	1490	79.31	13.10	6.05	0.238
2B	-200	1990	78.23	18.05	4.34	0.266
15	-200	3000	74.57	34.99	2.14	0.392
12	-250	490	92.79	3.18	29.18	0.074
13	-250	1490	94.66	9.50	9.96	0.059
14	-250	2300	93.83	13.94	6.73	0.0717
16	-250	4000	92.89	31.70	2.93	0.104

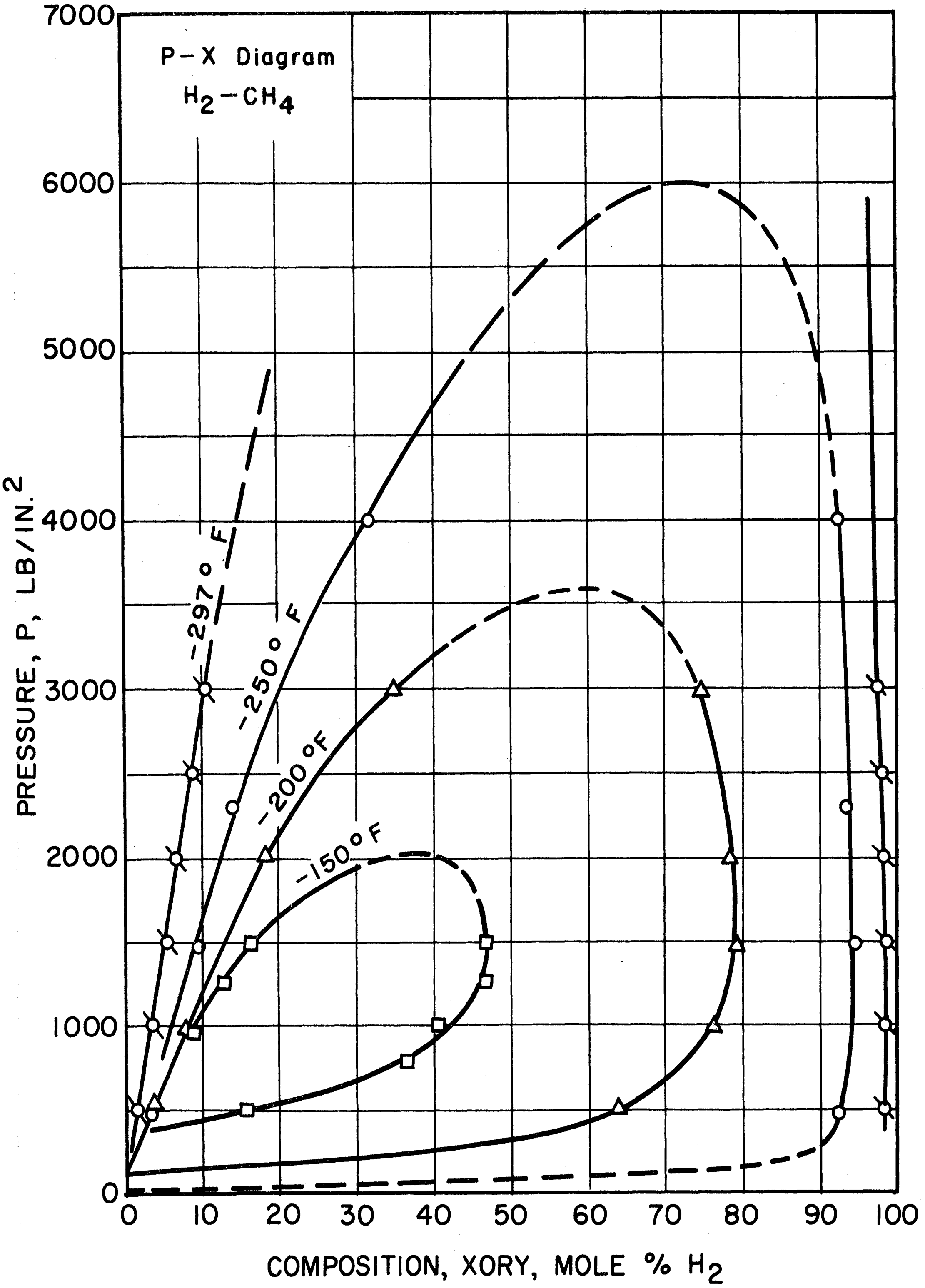


Figure 3. Pressure-Composition Diagram for Hydrogen-Methane Binary System.

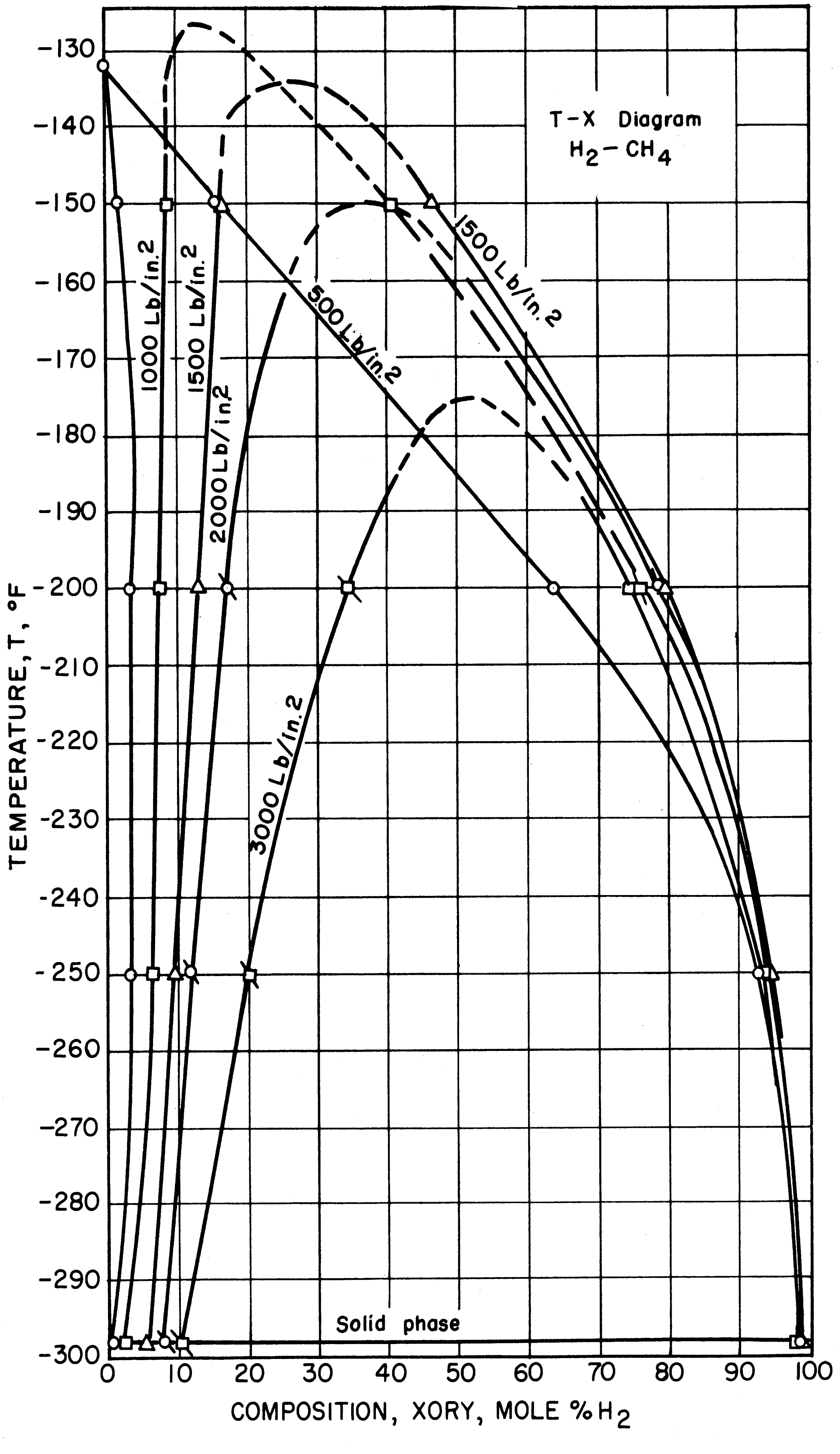


Figure 4. Temperature-Composition Diagram for Hydrogen-Methane Binary System.

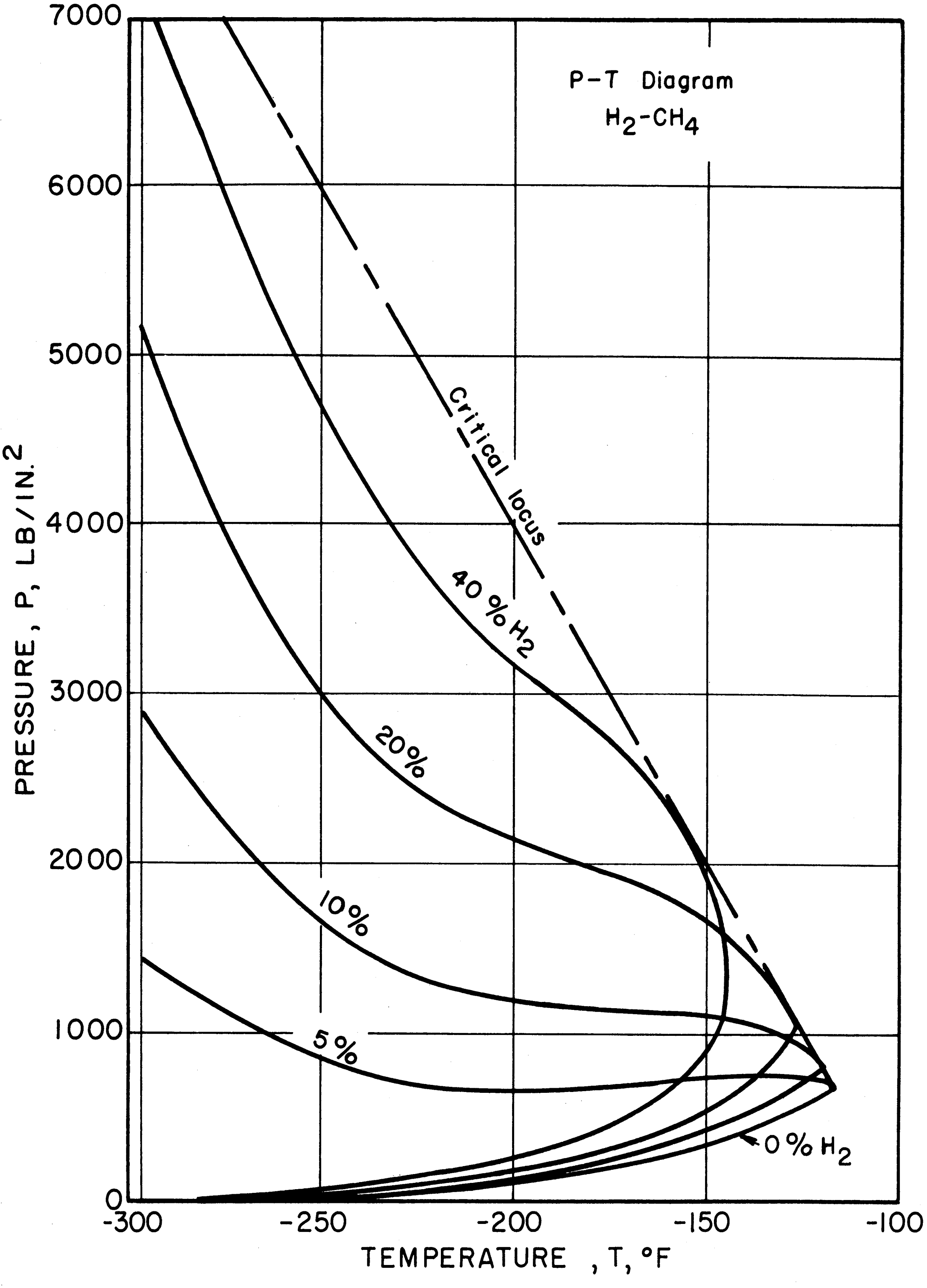


Figure 5. Pressure-Temperature Diagram for Hydrogen-Methane Binary System.

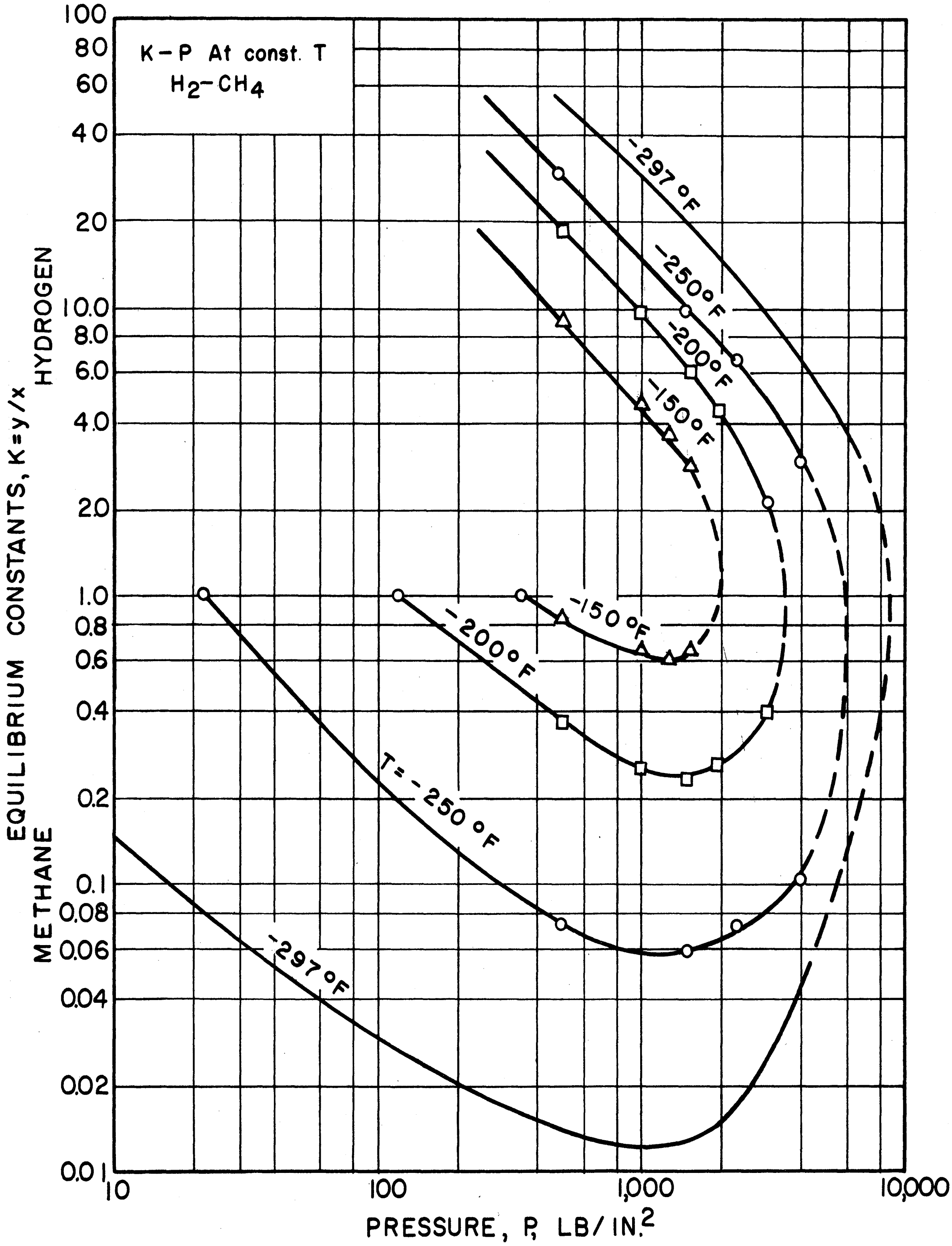


Figure 6. Equilibrium Constants versus Pressure for the Hydrogen-Methane System.

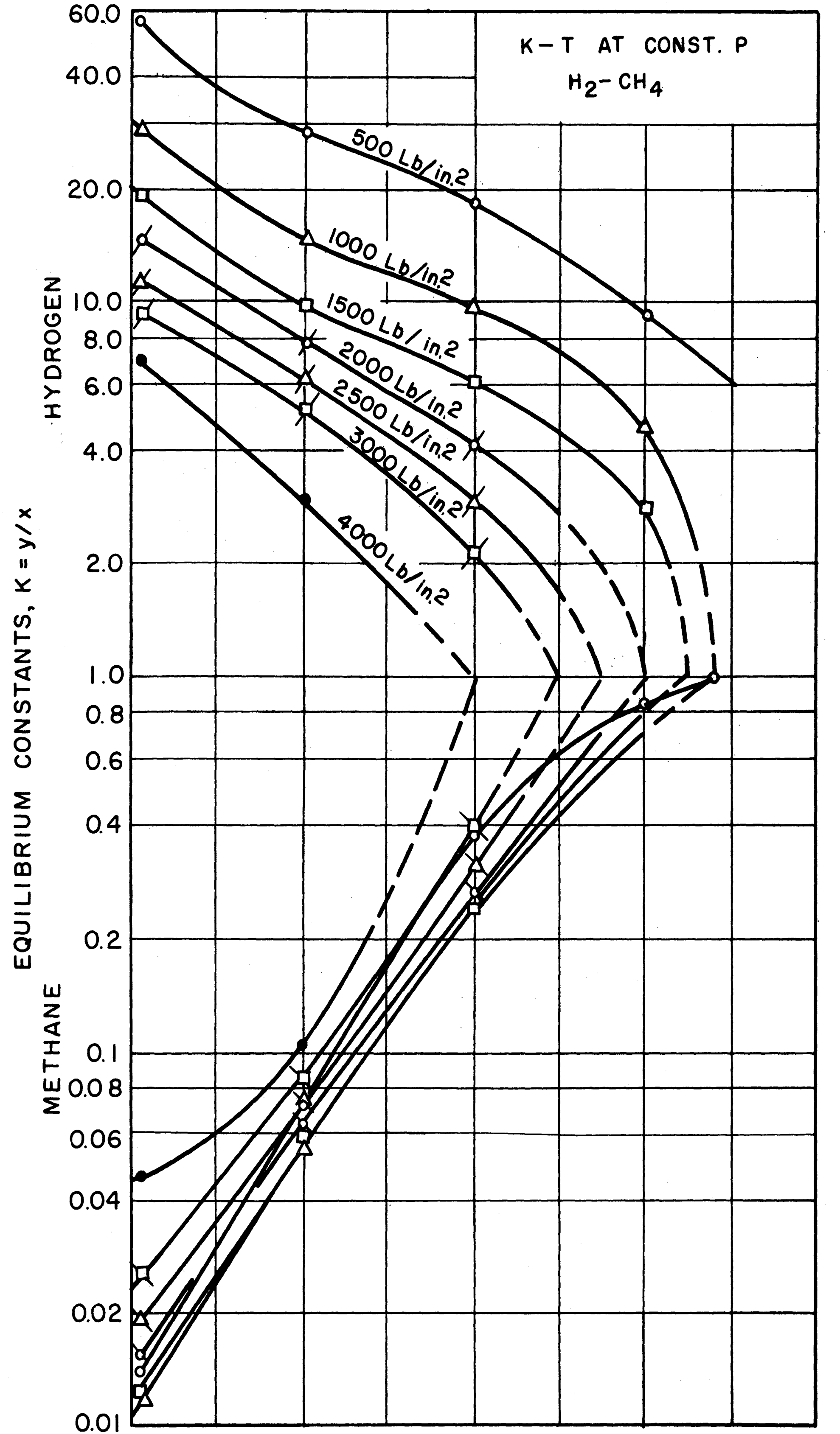


Figure 7. Equilibrium Constants versus Temperature for the Hydrogen-Methane System.

Figure 5 shows the pressure-temperature plot for mixtures of certain compositions. The envelope for five per cent hydrogen exhibits a minimum in the bubble point curve. The envelopes for higher concentrations of hydrogen show reverse order solubility. The estimated solid phase line has been drawn.

Figure 6 is a plot of the logarithm of the equilibrium constants for hydrogen and methane as functions of the logarithm of the pressure at constant temperature. The data of Freeth and Verschoyle (15) at -297°F has been included on the plot.

Figure 7 is a plot of the logarithm of the equilibrium constant as a function of the temperature at constant pressure.

Table VI gives the experimental data obtained for the system of hydrogen, methane and propane, and Table X (Appendix C) gives the smoothed data. Plots of the data are given in Figures 8 through 16.

Figure 8 is a conventional triangular composition diagram for the ternary system at 0°F and 500 lb/in.^{2}. As shown, both the binary of hydrogen with propane and the binary of methane with propane may exist at 0°F and 500 lb/in.^{2}.

Figure 9 shows the data for -100°F and 500 lb/in.^{2}. The binaries of hydrogen with propane and methane with propane may exist at these conditions.

Figure 10 is a triangular plot of the ternary data at -200°F and 500 lb/in.^{2}. At these conditions the hydrogen-propane and the hydrogen-methane binaries are shown.

Figure 11 shows the triangular plot of data at 0°F and 1000 lb/in.^{2}. The hydrogen-propane and the methane-propane binaries are shown.

TABLE VI

ORIGINAL DATA FOR HYDROGEN-METHANE-PROPANE SYSTEM

Run No.	Liquid Composition			Vapor Composition		
	mol % H_2	mol % CH_4	mol % C_3H_8	mol % H_2	mol % CH_4	mol % C_3H_8
				Temperature = 0°F Pressure = 500 lb/in.^{2}		
25	0.15	25.83	74.02	3.98	84.08	11.94
26	0.329	23.57	76.10	8.31	80.26	11.43
27	0.717	20.98	78.30	13.96	73.29	12.75
28	0.907	16.13	82.96	27.90	60.70	11.40
29	1.13	13.67	85.20	37.26	52.08	10.66
30	1.31	11.72	86.98	45.76	43.37	10.87
31	1.00	7.97	91.03	58.75	31.66	9.59
(45)	2.30	0.00	97.70	90.70	0.00	9.30
				Temperature = -100°F Pressure = 500 lb/in.^{2}		
(1)	0.00	62.0	38.0	0.0	98.70	1.30
20	0.452	49.58	49.97	14.36	84.43	1.21
21	0.645	44.99	54.36	22.13	76.73	1.14
22	0.683	42.38	56.94	24.57	74.21	1.22
19	1.09	24.93	73.98	59.80	39.25	0.95
18	1.22	21.40	77.38	68.72	30.46	0.82
24	1.16	16.07	82.77	67.83	31.04	1.13
(45)	1.55	0.00	98.45	99.02	0.00	0.976
				Temperature = -200°F Pressure = 500 lb/in.^{2}		
(45)	0.86	0.0	99.14	99.9+	0.00	--
46	0.789	8.59	90.62	95.73	3.79	0.48
44	1.79	43.67	54.54	83.40	15.92	0.68
48	2.85	87.07	10.08	--	--	--
2A	3.43	96.57	0.00	63.92	36.08	0.00
				Temperature = 0°F Pressure = 1000 lb/in.^{2}		
(1)	0.00	53.00	47.0	0.00	90.30	9.70
32	2.02	32.77	65.21	25.54	66.09	8.37
33	2.67	25.70	71.63	45.49	47.77	6.74
34	2.75	24.30	72.95	46.89	45.78	7.33
35	3.09	17.90	79.01	58.95	34.57	6.48
36	3.79	13.03	83.18	66.57	26.57	6.86
(45)	4.75	0.00	95.25	94.08	0.00	5.92

TABLE VI (cont.)

Run No.	Liquid Composition			Vapor Composition		
	xH_2	xCH_4	xC_3H_8	yH_2	yCH_4	yC_3H_8
				Temperature = -100°F Pressure = 1000 lb/in.^{2}		
(45)	3.02	0.00	96.98	99.31	0.00	0.69
37	2.76	14.70	82.54	85.62	13.39	0.99
38	3.27	34.28	62.45	61.82	36.81	1.37
39	3.27	46.37	50.36	--	--	--
40	3.66	58.44	37.90	43.23	53.01	3.76
				Temperature = -200°F Pressure = 1000 lb/in.^{2}		
(45)	1.63	0.00	98.37	99.9+	0.00	--
45	1.79	10.14	88.07	99.00	0.37	0.63
43	3.00	55.93	41.07	87.70	12.04	0.26
42	2.96	57.84	39.20	87.70	12.04	0.26
41	3.12	59.14	37.74	86.66	13.07	0.27
47	5.97	81.22	12.81	80.08	19.61	0.31
5	7.81	92.19	0.00	76.18	23.82	0.00

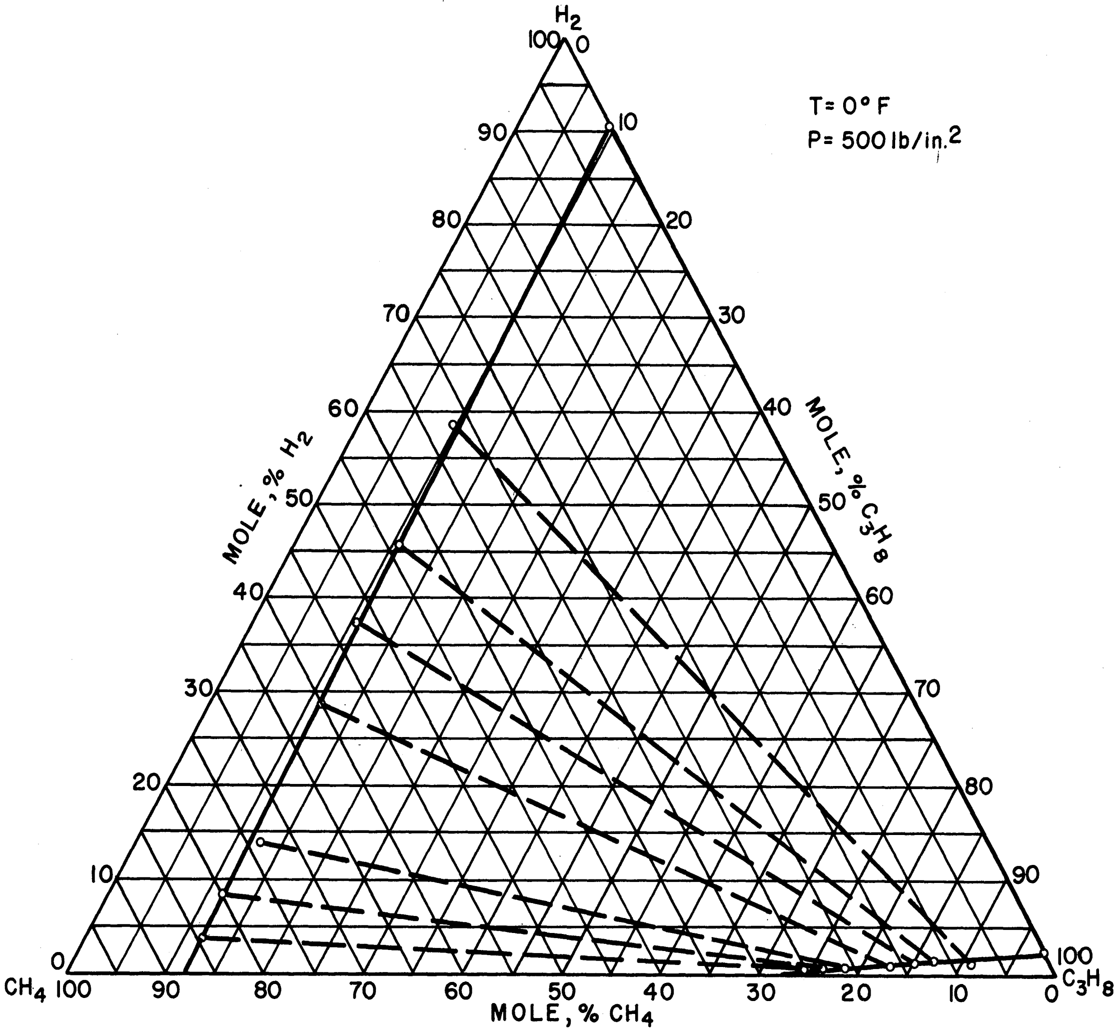


Figure 8. Triangular Composition Diagram for Hydrogen-Methane-Propane System at 0° F and 500 lb/in^2.

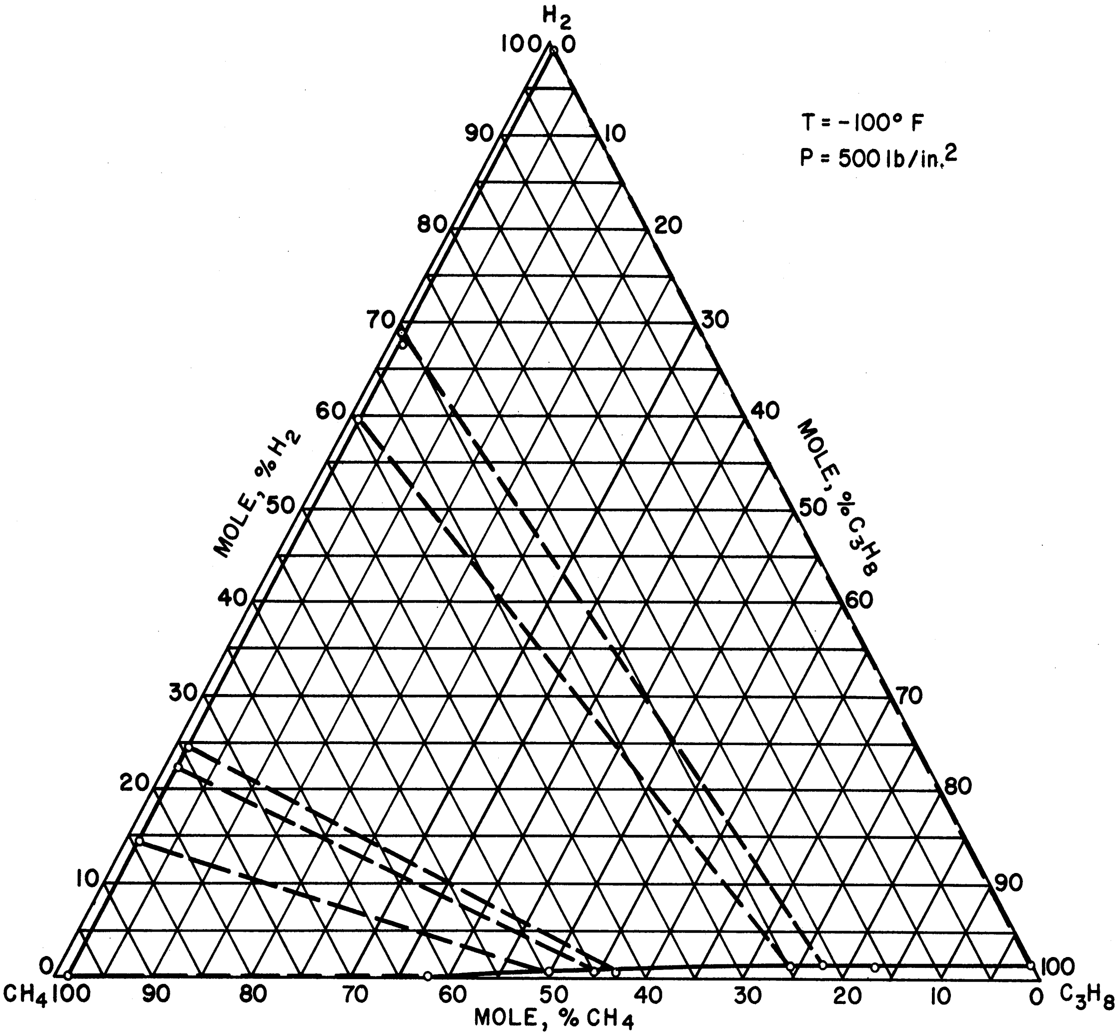


Figure 9. Triangular Composition Diagram for Hydrogen-Methane-Propane System at -100° F and 500 lb/in².

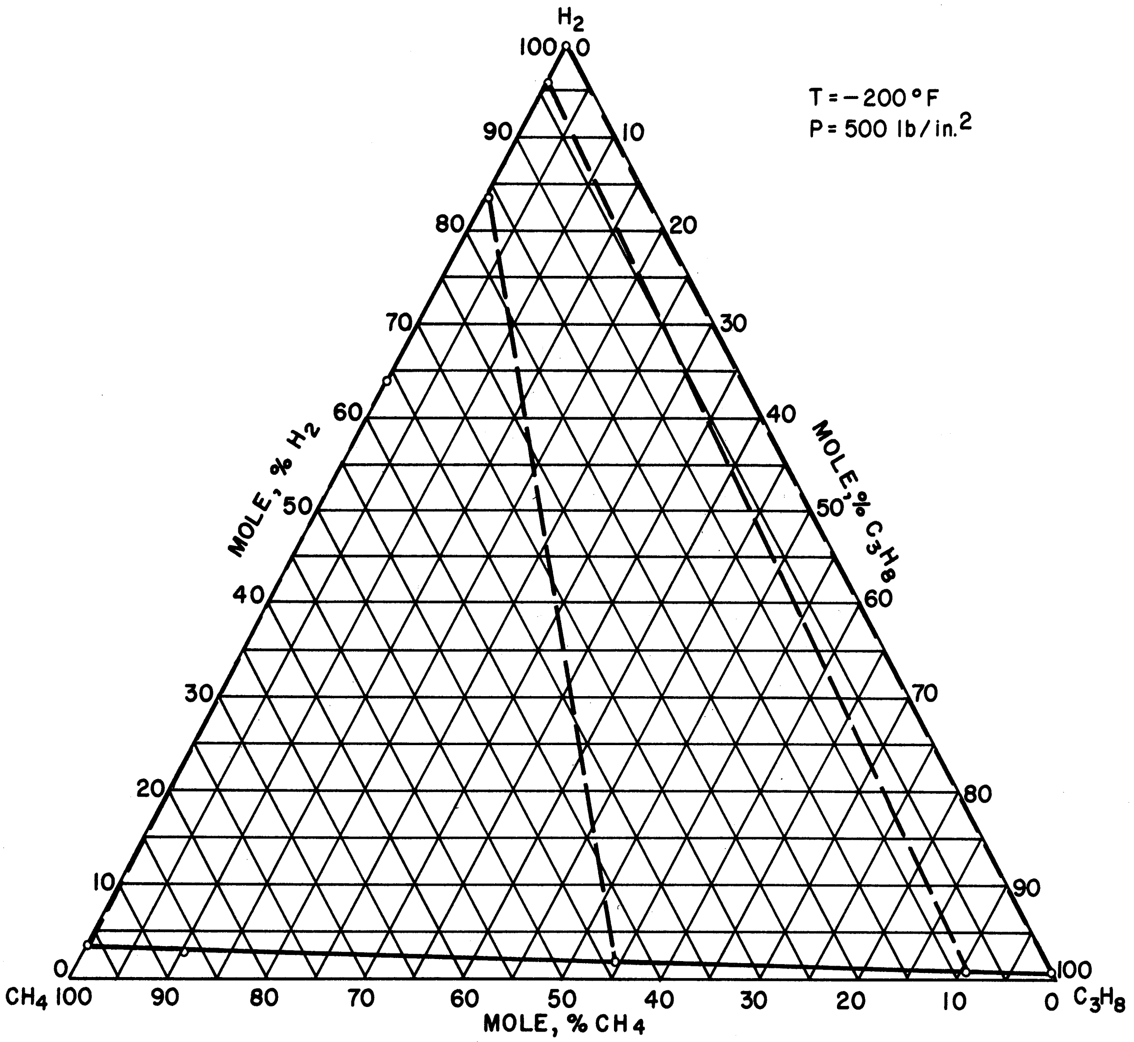


Figure 10. Triangular Composition Diagram for Hydrogen-Methane-Propane System at -200° F and 500 lb/in^2.

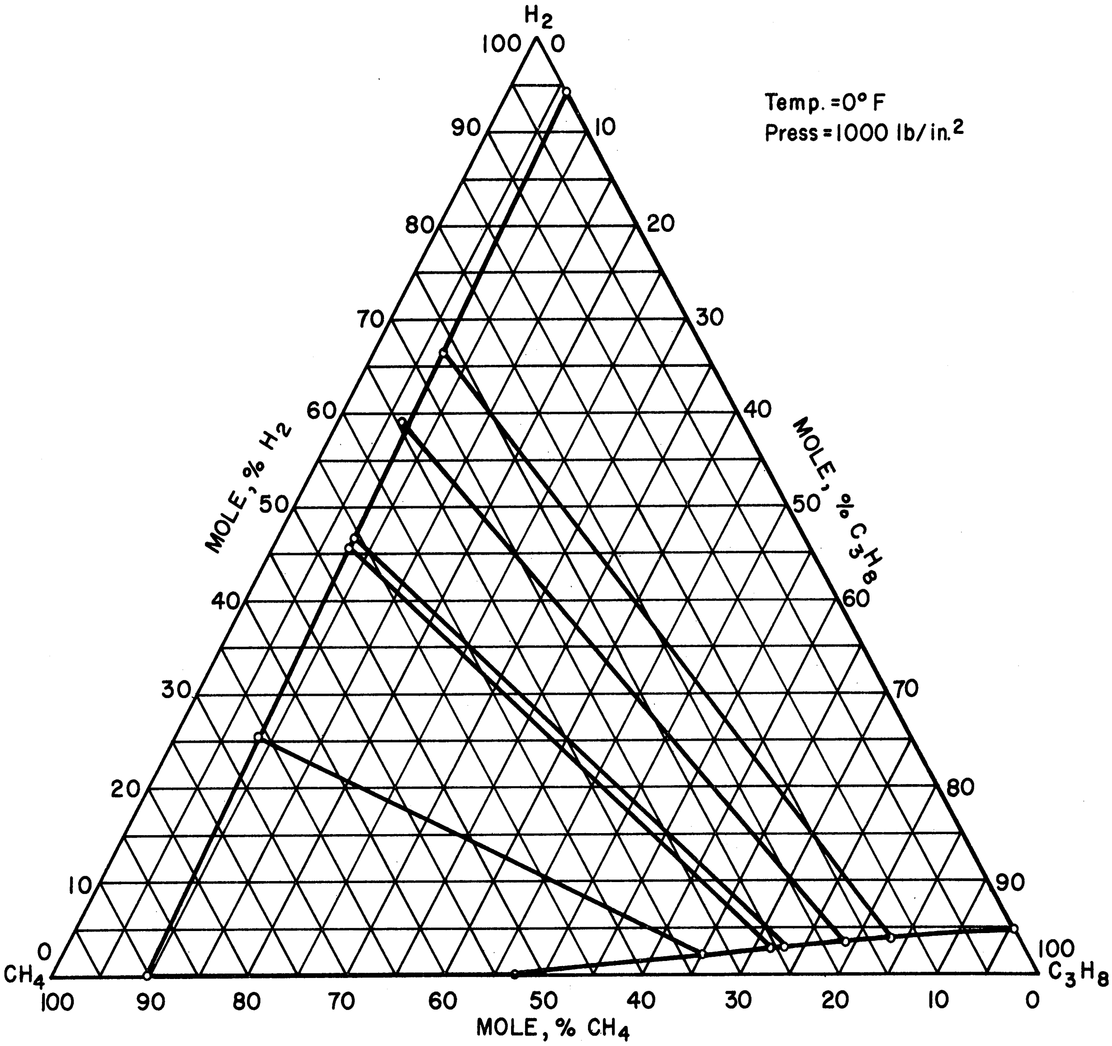


Figure 11. Triangular Composition Diagram for Hydrogen-Methane-Propane System at 0° F and 1000 lb/in^2.

Figure 12 shows the triangular diagram for the ternary system at -100°F and 1000 lb/in.^{2}. The diagram should include a three-component critical, but the critical point data were not obtained. The hydrogen-propane binary is shown.

Figure 13 shows the data at -200°F and 1000 lb/in.^{2}. The hydrogen-propane and the hydrogen-methane binaries are shown.

The binary points for the system hydrogen-propane shown Figures 8 to 13 were obtained from the work of Williams (45). The methane-propane data points were obtained from the work of Akers, et al. (1).

Equilibrium constants were calculated for hydrogen, methane and propane in the ternary system from the data in Table X. These equilibrium constants are definitely a function of the composition of the system, as well as being functions of the temperature and pressure. This effect is clearly shown in Figures 14, 15, and 16. Figure 14 shows a plot of the logarithm of the equilibrium constant for hydrogen at constant temperature and pressure as a function of the mol fraction of propane in the liquid phase for the ternary system of hydrogen, methane and propane.

It may be seen from Figure 14 that as methane is added to the hydrogen-propane system, the equilibrium constant for hydrogen decreases for all the conditions studied.

Figure 15 shows a plot of the equilibrium constants for methane at constant temperature and pressure as a function of the mole fraction of propane in the liquid phase. It may be seen from Figure 15 that at low temperatures the equilibrium constant for methane is nearly constant. However, as the composition changes at higher temperatures, the equilibrium constant does change. From the data, it is seen that the effect upon the

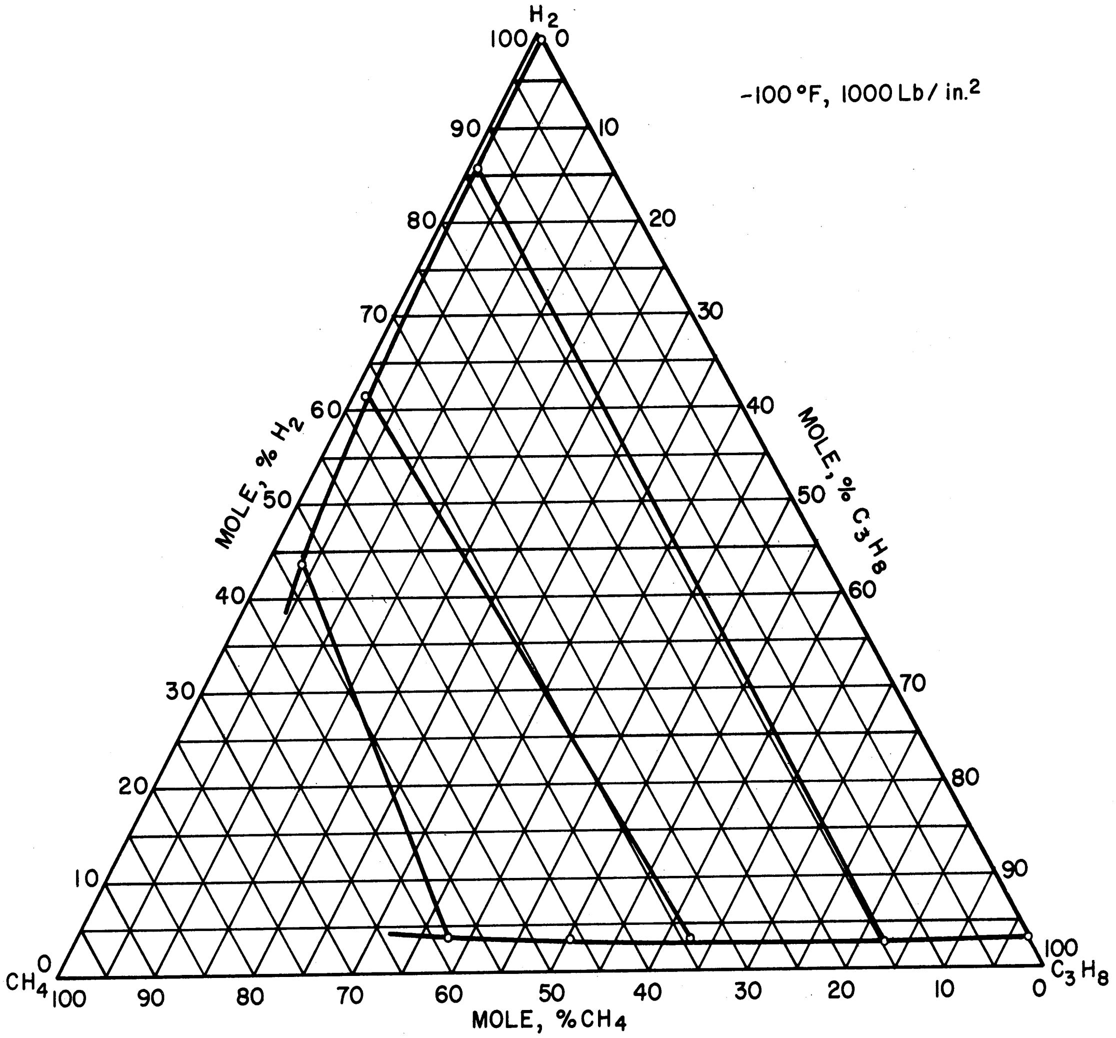


Figure 12. Triangular Composition Diagram for Hydrogen-Methane-Propane System at -100° F and 1000 lb/in^2.

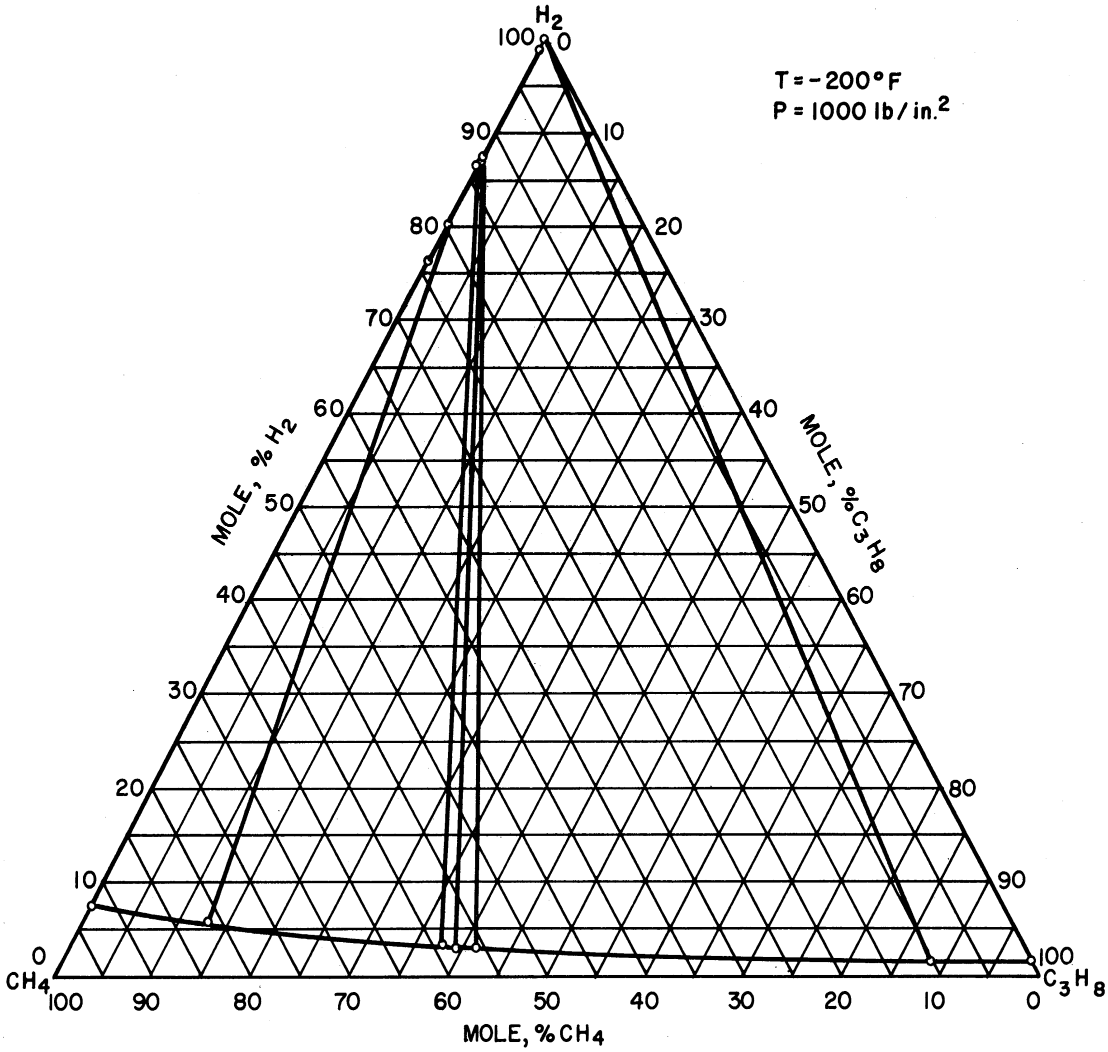


Figure 13. Triangular Composition Diagram for Hydrogen-Methane-Propane System at -200° F and 1000 lb/in^2.

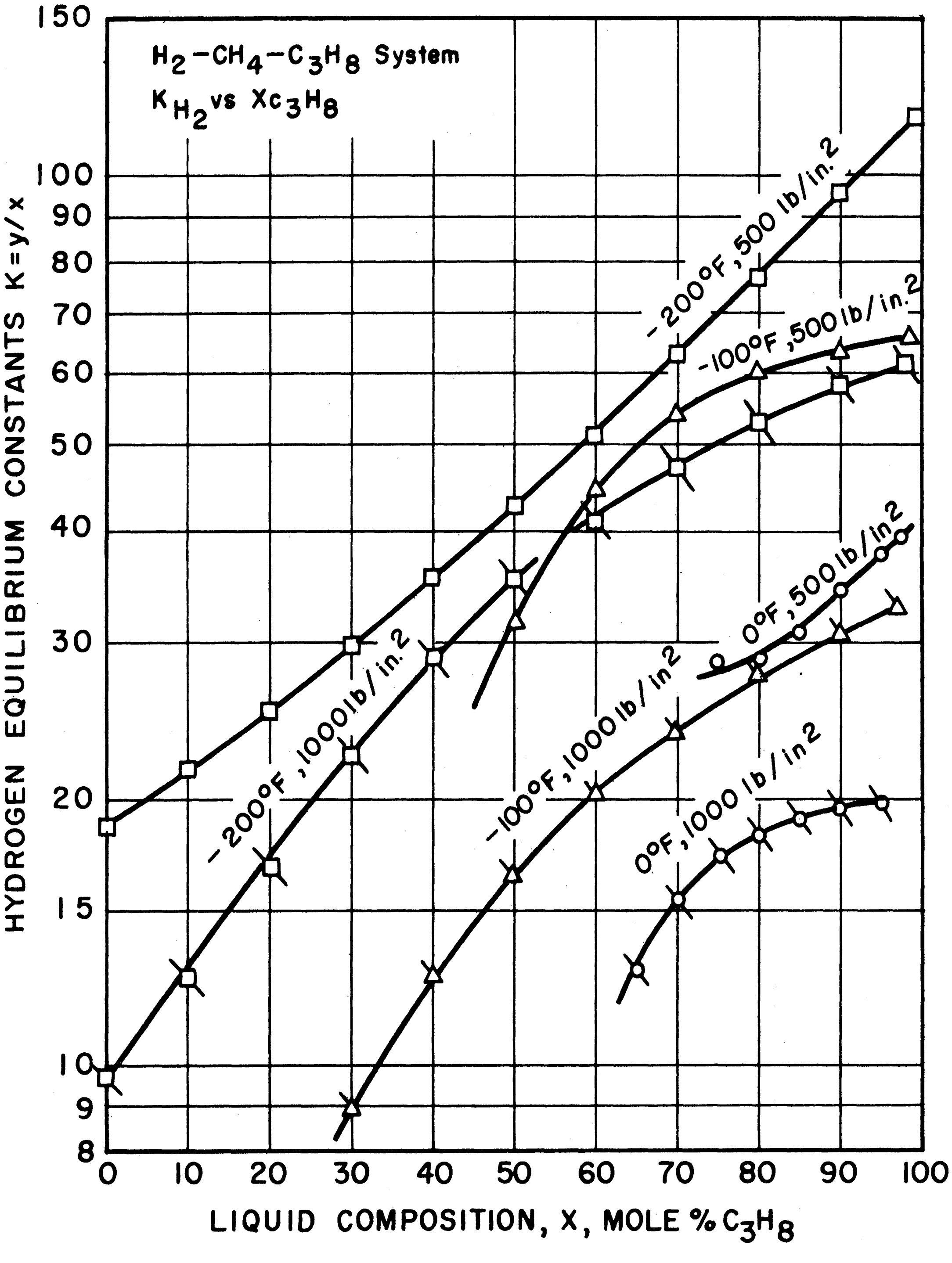


Figure 14. Equilibrium Constants for Hydrogen in the Hydrogen-Methane-Propane System as a Function of Mole % Propane in the Liquid Phase.

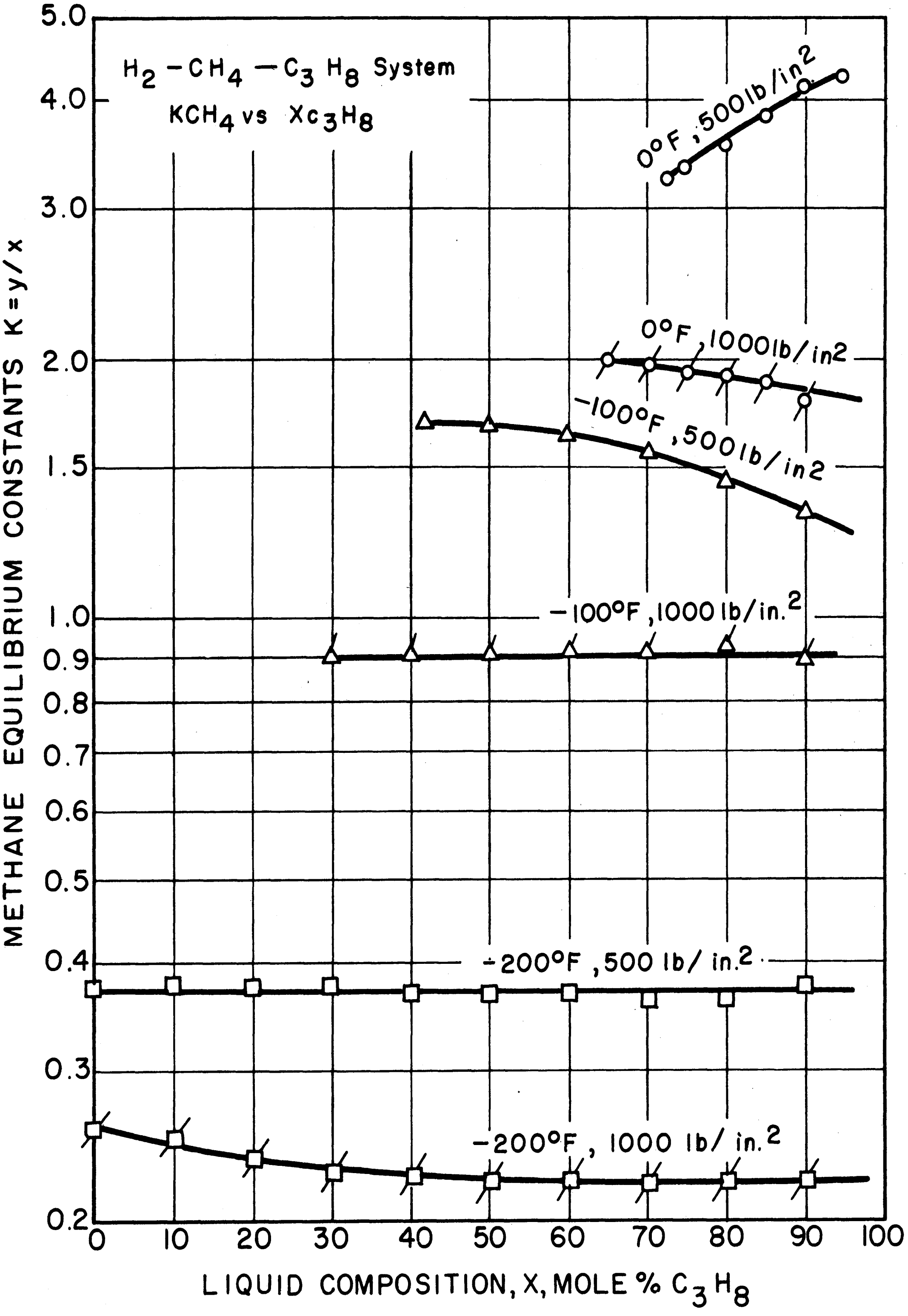


Figure 15. Equilibrium Constants for Methane in the Hydrogen-Methane-Propane System as a Function of Mole % Propane in the Liquid Phase.

equilibrium constant for methane of adding propane to a hydrogen-methane-propane system depends upon the temperature and pressure; under certain conditions the methane equilibrium constant increases with an increase in the amount of propane while under other conditions it decreases.

Figure 16 shows a plot of the equilibrium constants for propane at constant temperature and pressure as a function of the mole fraction of propane in the liquid. From this plot, it can be seen that the addition of methane to the hydrogen-propane system results in an increase in the equilibrium constant for propane.

Table VII gives the original data obtained for the hydrogen-methane-propylene system. Data were taken for a temperature of -100°F and 500 lb/in.^{2}. Table XI*contains the smoothed data for this system, and Figure 17 contains a triangular plot of the data.

Figure 18 shows the effect of composition upon the equilibrium constants of hydrogen, methane and propylene. The equilibrium constants have been plotted as functions of the mole fraction of propylene in the liquid phase.

Table VIII contains the data for the five runs obtained for the six component system of hydrogen, methane, ethylene, ethane, propylene and propane. The equilibrium constants for the constituents were calculated and are shown in Figure 19 where they have been plotted versus the normal boiling points of the individual constituents. Most of the data lie on a straight line.

F. Analysis of Results

An examination of the experimental technique discloses that the accuracy of the experimental results depends upon the accuracy of the determination of the temperature, pressure and phase compositions.

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*Presented in Appendix C.

TABLE VII

ORIGINAL DATA FOR HYDROGEN-METHANE-PROPYLENE SYSTEM

Run No.	Liquid Composition			Vapor Composition		
	xH_2	xCH_4	xC_3H_6	yH_2	yCH_4	yC_3H_6
49	0.728	51.26	48.01	14.93	83.37	1.70
50	0.986	41.15	57.86	29.33	69.09	1.58
(45)	1.36	0.00	98.64	98.72	0.00	1.28

TABLE VIII

ORIGINAL DATA FOR COMPLEX SYSTEM
CONTAINING HYDROGEN, METHANE, ETHYLENE, ETHANE, PROPYLENE AND PROPANE

Run No.		52	53	54	55	56
Temp, ^{o}F		0	-100	-100	0	-100
Press., lb/in.^{2}		500	500	500	1000	1000
	H_{2_1}	1.04	1.34	1.48	2.36	1.97
Liquid	H_4	7.67	14.84	12.77	16.45	17.82
Phase	C_2H_4	9.42	9.06	18.23	17.32	17.97
Compositions	C_2H_6	5.07	4.66	4.21	4.02	3.74
mol %	C_3H_6	8.39	7.77	7.07	6.67	6.00
	C_3H_8	68.41	62.33	56.24	53.18	52.50
	H_2	38.28	65.79	68.60	46.93	77.26
Vapor	CH_4	31.37	30.45	25.45	35.18	19.66
Phase	C_2H_4	8.56	2.00	4.06	9.64	2.09
Compositions	C_2H_6	3.44	0.65	0.60	1.73	0.38
mol %	C_3H_6	2.63	0.26	0.24	0.86	0.10
	C_3H_8	15.72	0.85	1.05	5.66	0.51
Equilibrium	H_2	36.8	49.1	46.4	19.9	39.2
Constants	CH_4	4.09	2.05	1.99	2.14	1.10
K = y/x	C_2H_4	0.91	0.22	0.223	0.56	0.12
	C_2H_6	0.68	0.14	0.143	0.43	0.10
	C_3H_6	0.31	0.0335	0.0339	0.13	0.0167
	C_3H_8	0.23	0.0136	0.0187	0.106	0.00971

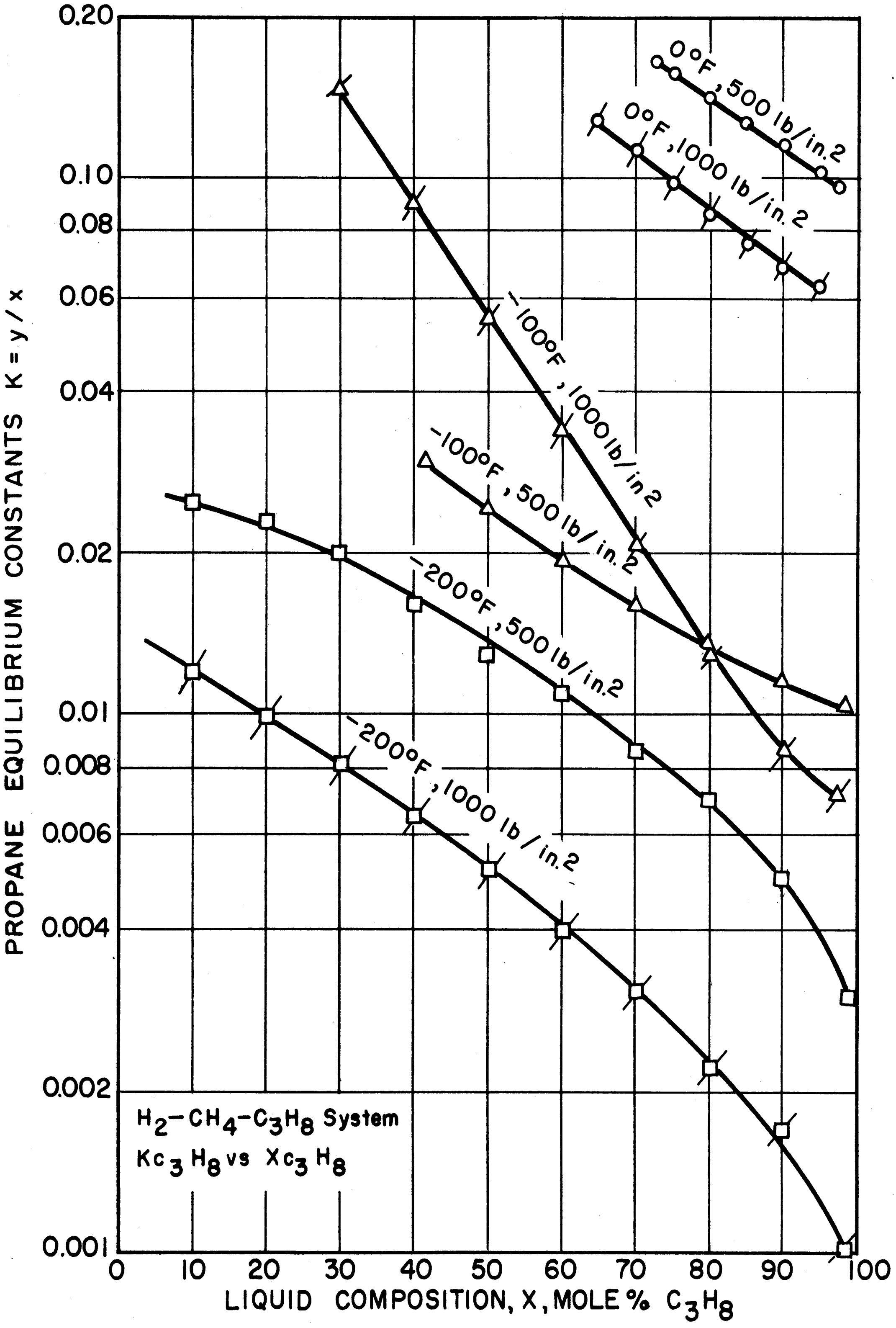

Figure 16. Equilibrium Constants for Propane in the Hydrogen-Methane-Propane System as a Function of Mole % Propane in the Liquid Phase.

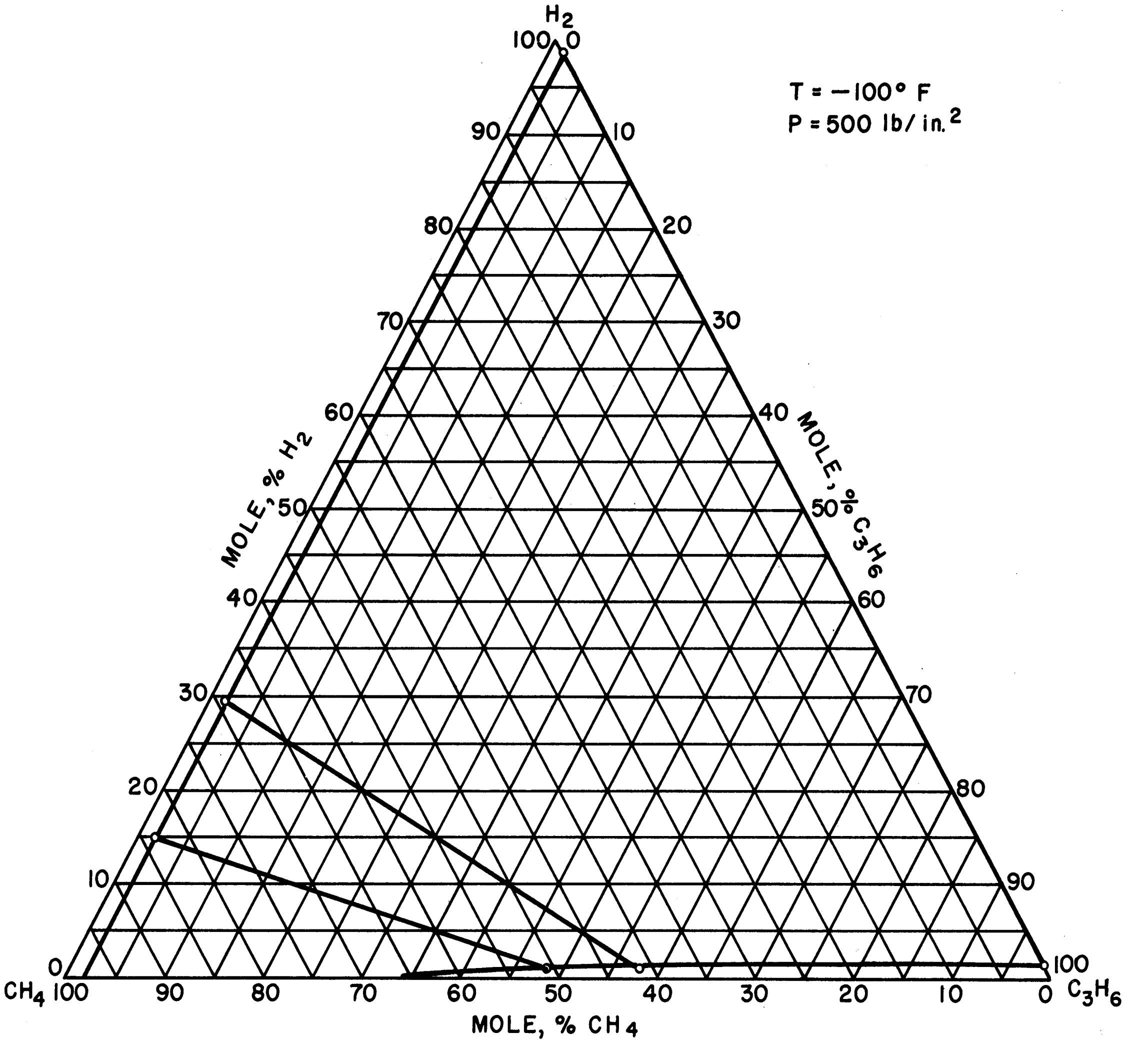

Figure 17. Triangular Composition Diagram for the Hydrogen-Methane-Propylene System at -100° F and 500 lb/in^2.

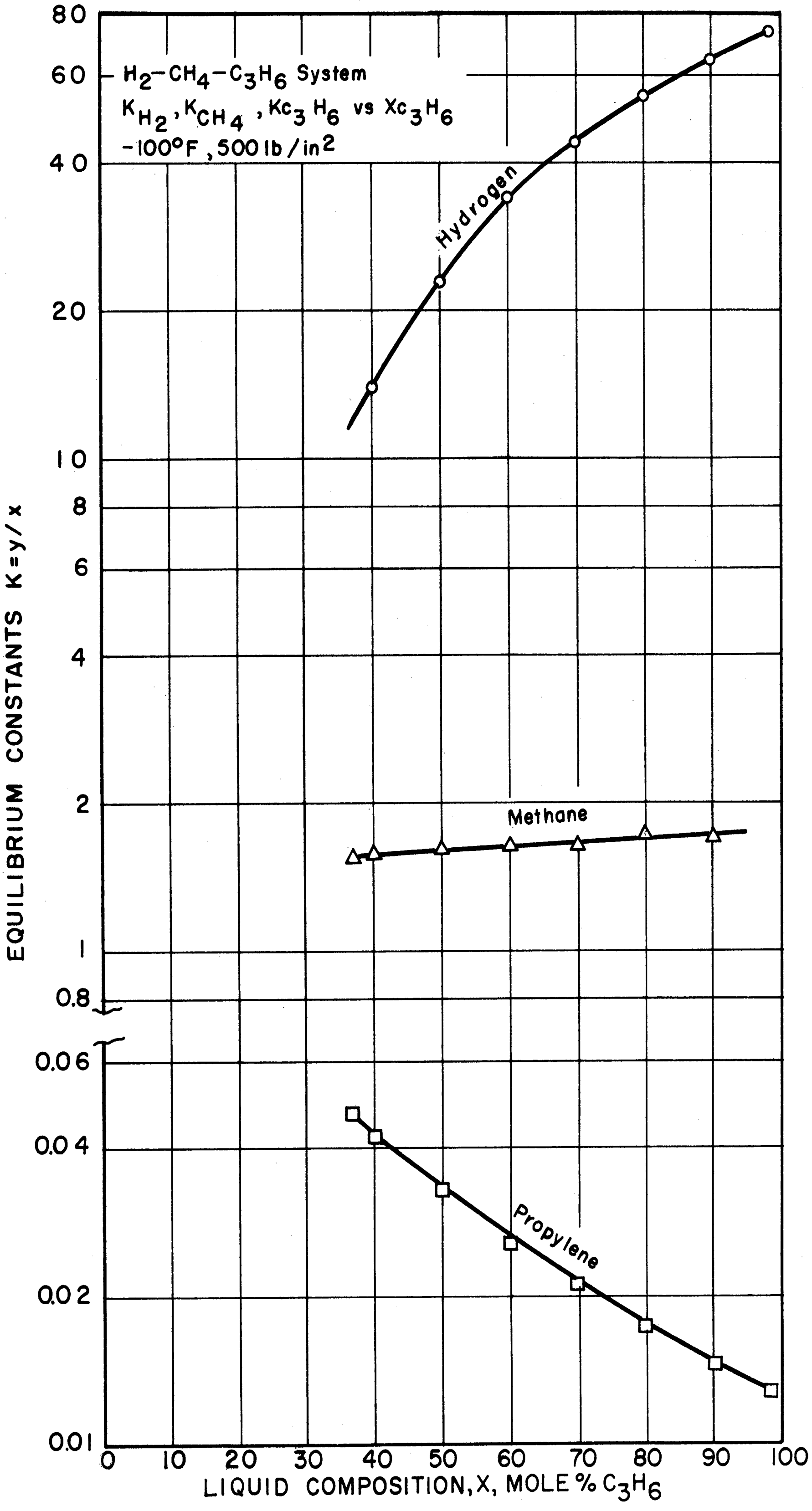

Figure 18. Hydrogen, Methane and Propylene Equilibrium Constants in the Hydrogen-Methane Propylene System as a Function of the Mole % Propylene in the Liquid Phase.

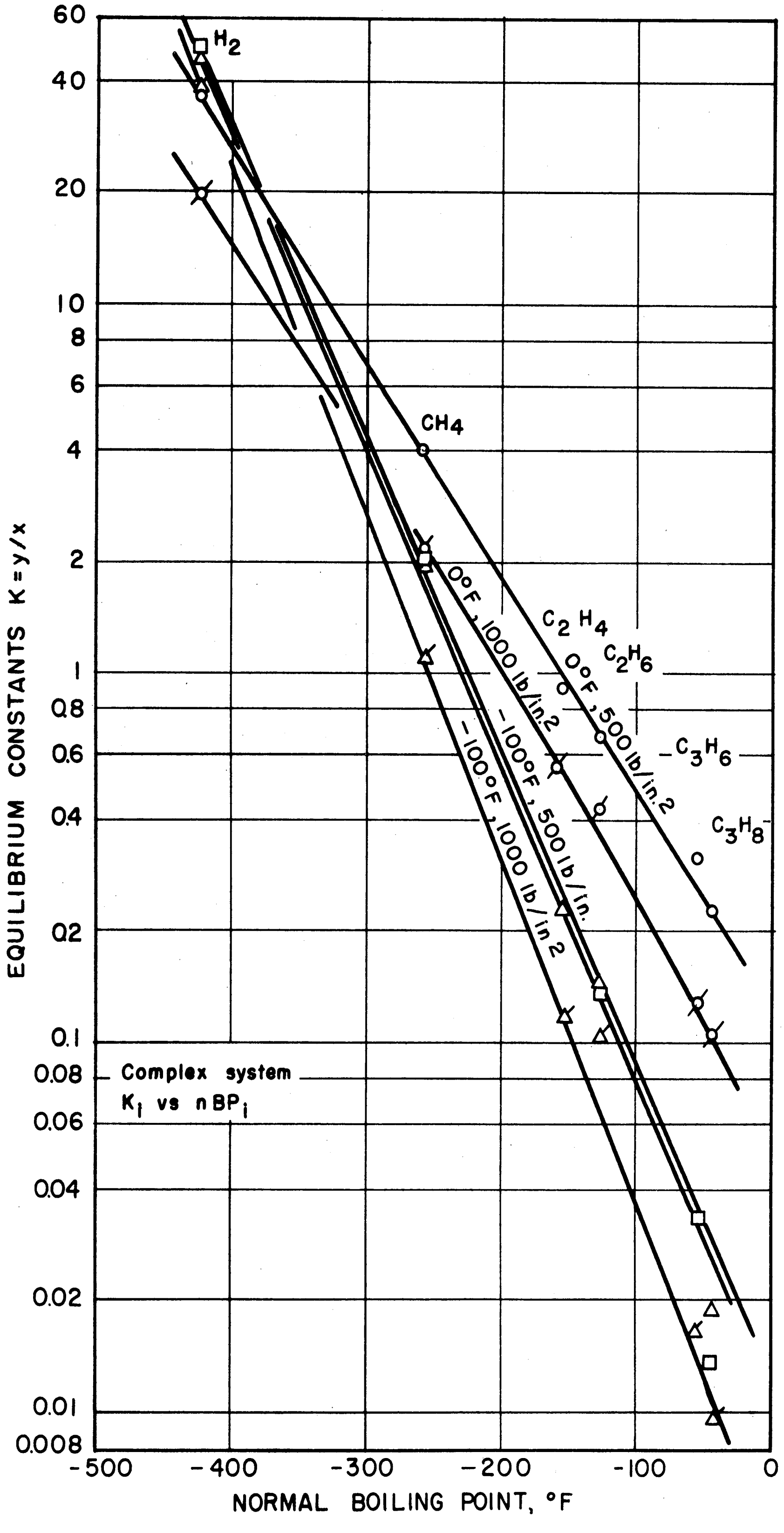

Figure 19. Constituent Equilibrium Constants in the Hydrogen-Methane-Ethylene-Ethane-Propylene-Propane System As a Function of the Normal Boiling Point.

The calibration of the thermocouples which indicated the temperature of the system has been described in detail in the Appendix. A. The reading accuracy of the temperature has been estimated at ±0.1°F at 0°F or ±0.25°F at -300°F. The temperature in the cell was kept within ±0.25°F of the desired temperature as indicated by the potentiometer.

The accuracy of the pressure measurement has been estimated to be ±2-1/2 lb/in.^{2} at 500 lb/in.^{2} ; ±5 lb/in.^{2} at 1000 lb/in.^{2}; and ±10 lb/in.^{2} at 2000 lb/in.^{2}. These figures would indicate that the pressure measurements are all accurate to ±0.5 per cent at all pressures.

The accuracy of the determination of composition depends upon the sampling technique and upon the method of analysis. It was found that the sampling technique and upon the method of analysis. It was found that the sampling technique was very important, as shown by a fluctuation in composition as successive samples were obtained from the cell and analyzed. It was determined that the important factor to be considered in sampling was the purging of the sample line. An estimate of the maximum error involved in sampling is roughly ±1/2 per cent of the composition of a given component. This is roughly of the same order of magnitude as the accuracy of the analysis.

Some of the phase compositions for the hydrogen-methane system were obtained from a gas gravity determination. Calculations indicate an accuracy of about ±1/2 per cent of the composition of a given component for the hydrogen-methane mixture.

A comparison of analyses which were obtained from the Mass Spectrometer with the known composition is given in Table XX, Appendix B.

III. CORRELATION

Correlations of the equilibrium constants are considered for four different kinds of systems: the binary, the ternary, ternary pairs, and multi-component.

A. Binary Correlations

In a doctorate thesis by Williams (44), a fugacity relationship (Eq. 4.8) was used for the correlation of the hydrogen equilibrium constants in the hydrogen binaries with ethylene, ethane, propylene and propane. This same correlation has been applied to the hydrogen-methane binary system data obtained in this investigation. The equation which is a basis of the correlation is:

$$\log f^o\, y/x = \log Q + (\overline{V}/2.303RT)\, P \,. \qquad (4.8)$$

Figure 20 shows a plot of log f^oK versus P/2.303RT for the hydrogen-methane system. y intercepts in this plot represent the modified Henry's law constant, Q, and the slopes represent the partial molal volume of hydrogen in the liquid. Figure 21 shows a plot which Williams developed for a correlation of the modified Henry's law constant, Q, for different hydrocarbons as a function of temperature as represented by

$$A = (T/\sqrt{TB})\,[1 + 450/(T_C - T)^2] \,. \qquad (24.1)$$

A curve for the hydrogen-methane data has been included in Figure 21. Figure 22 shows a plot of the partial molal volumes of hydrogen in the various hydrocarbons as a function of temperature. Table XII gives values of the modified Henry's law constant and of the partial molal volume of hydrogen for the hydrogen-methane system.

TABLE XII

VALUES OF THE MODIFIED HENRY'S LAW CONSTANT AND THE MOLAL VOLUME FOR HYDROGEN IN THE HYDROGEN-METHANE SYSTEM

Temp. T °F	Modified Henry's Law Constant Log Q	Molal Volume, $\bar{V}$ ft^3/lb mol
-150	3.675	0
-200	3.95	0.267
-250	4.14	0.200
-297 ( )	4.45	0.020

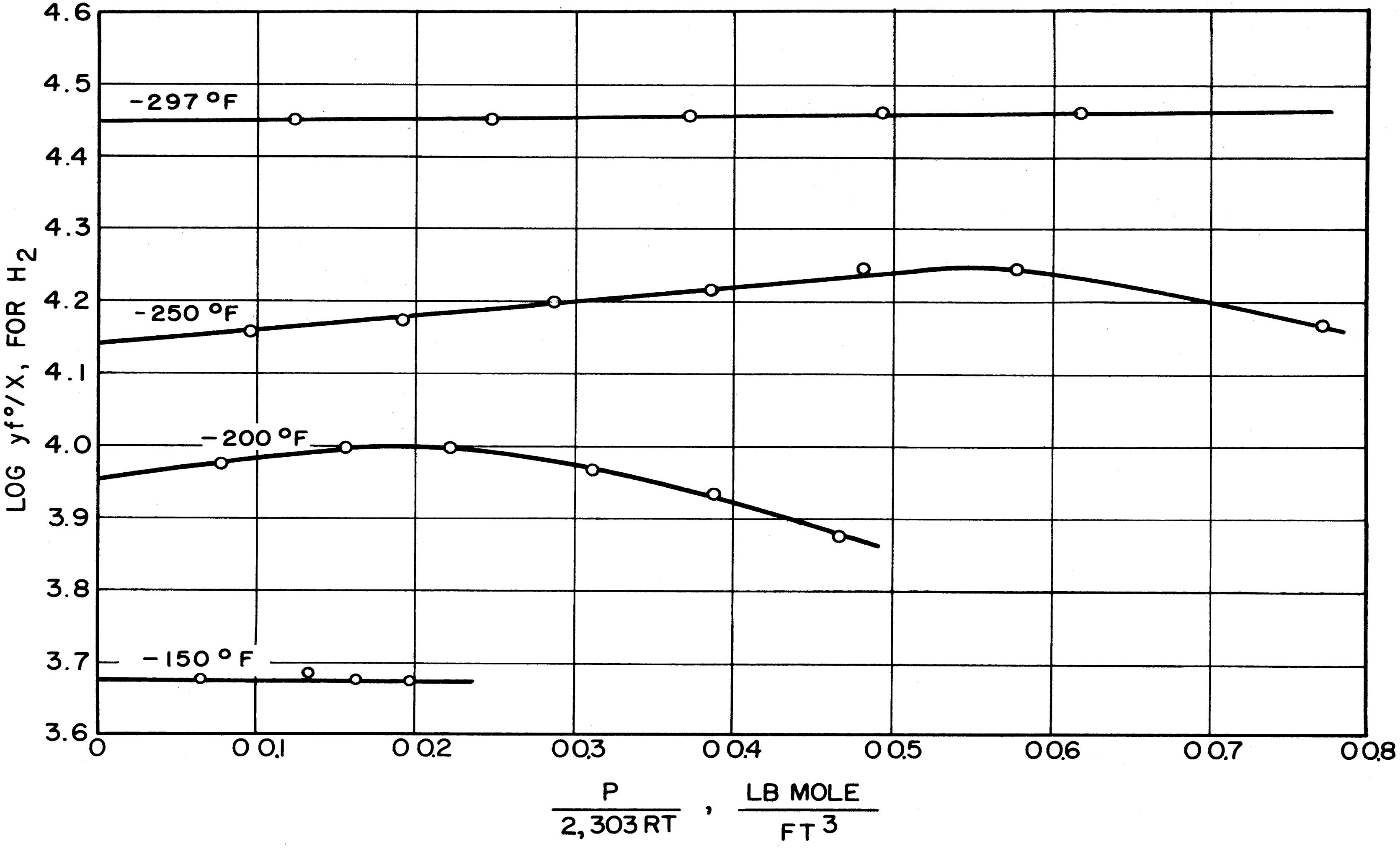

Figure 20. Kf^o for Hydrogen as a Function of Pressure for the Hydrogen-Methane System.

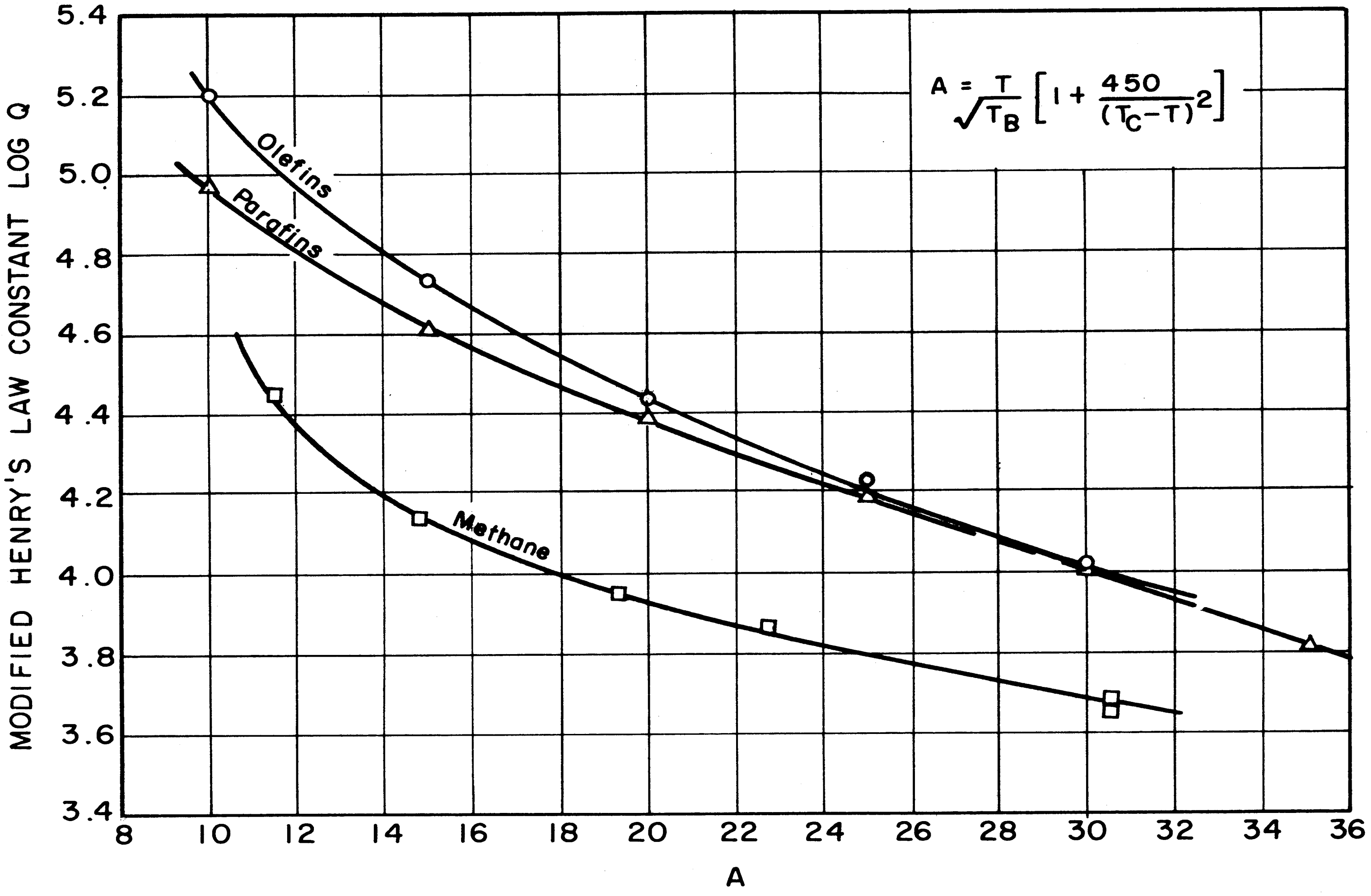

Figure 21. Modified Henry's Law Constant for Hydrogen in the Hydrogen-Methane System as a Function of Temperature.

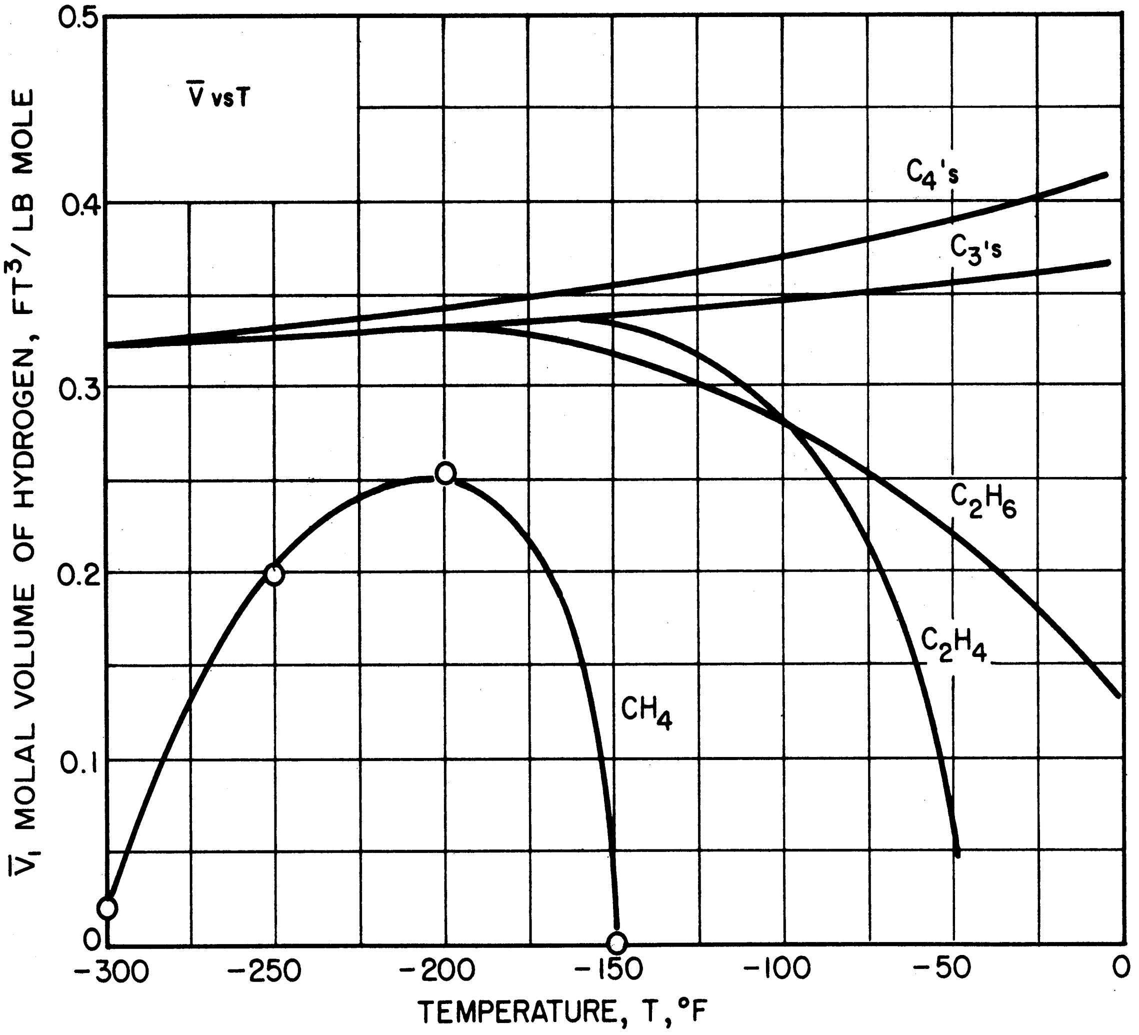

Figure 22. Molal Volume for Hydrogen in the Hydrogen-Methane System as a Function of Temperature.

B. Ternary Correlation

Data for all of the hydrogen-light hydrocarbon binaries and for the hydrogen-methane ternaries with ethylene, ethane, propylene and propane were available with the completion of the experimental work undertaken in this problem.

As described in the Results Section and as may be seen from consideration of other hydrogen ternary systems found in the literature, the equilibrium constants for the various constituents are definitely functions of the concentration as well as of the temperature and pressure.

A few general principles are evident from consideration of the data. We have found that the equilibrium constant for hydrogen increases with a decrease in temperature and that for a given pressure and temperature, the equilibrium constant for hydrogen increases as the solvent is changed from methane to ethane to propane to butane. In general, then it may be stated that the equilibrium constant for hydrogen increases as the temperature decreases and as the molecular weight of the hydrocarbon solvent increases. At the same time when we consider the unsaturated hydrocarbons, we find that the equilibrium constant for hydrogen increases as the solvent is changed from ethylene to propylene.

But when we consider both types of systems, we find that neither the molecular weight nor the boiling point is a good criterion for determining the effect of adding a heavier solvent. The equilibrium constant for hydrogen in propylene is sometimes greater than the equilibrium constant for hydrogen in propane, and likewise the equilibrium constant for hydrogen in ethylene is sometimes greater than the equilibrium constant for hydrogen in ethane. A difference in behavior of the solvents in the binaries may be seen by considering the correlations of binary systems.

Referring to Figure 21, it is seen that the modified Henry's law constant is represented by three curves--one for methane, one for saturated hydrocarbons, and one for unsaturated hydrocarbons. (Actually then the systems being considered contain components which may be classed according to their behavior as hydrogen, methane, saturated hydrocarbons and unsaturated hydrocarbons.)

A generalized correlation must contain variables which exist or may be obtained for any system regardless of its particular components or complexity. Some concentration variables which fulfill these requirements are the molal average properties of each phase such as the boiling points, molecular weights, critical temperatures and critical pressures. The mole fraction of hydrogen in the liquid or vapor phase would also be a universal property of hydrogen systems.

There were sufficient data available so that it was possible to consider solely the effect of composition.

According to the phase rule, a ternary system may be described in terms of three variables such as temperature, pressure, and one concentration variable. Calculations were made of the molal average boiling point of the liquid phase, and this property was used to represent the concentration variable. Plots have been made (Figures 23, 24, 25 and 26) of the logarithm of the equilibrium constant for hydrogen, methane and propane versus the temperature at constant pressures of 500 and 1000 lb/in.^{2} with parameters of liquid molal average boiling points.

Interpolations and extrapolation of the correlation for pressures other than 500 and 1000 lb/in.^{2} may best be made by drawing a straight line through the two points on a log-log plot of the equilibrium

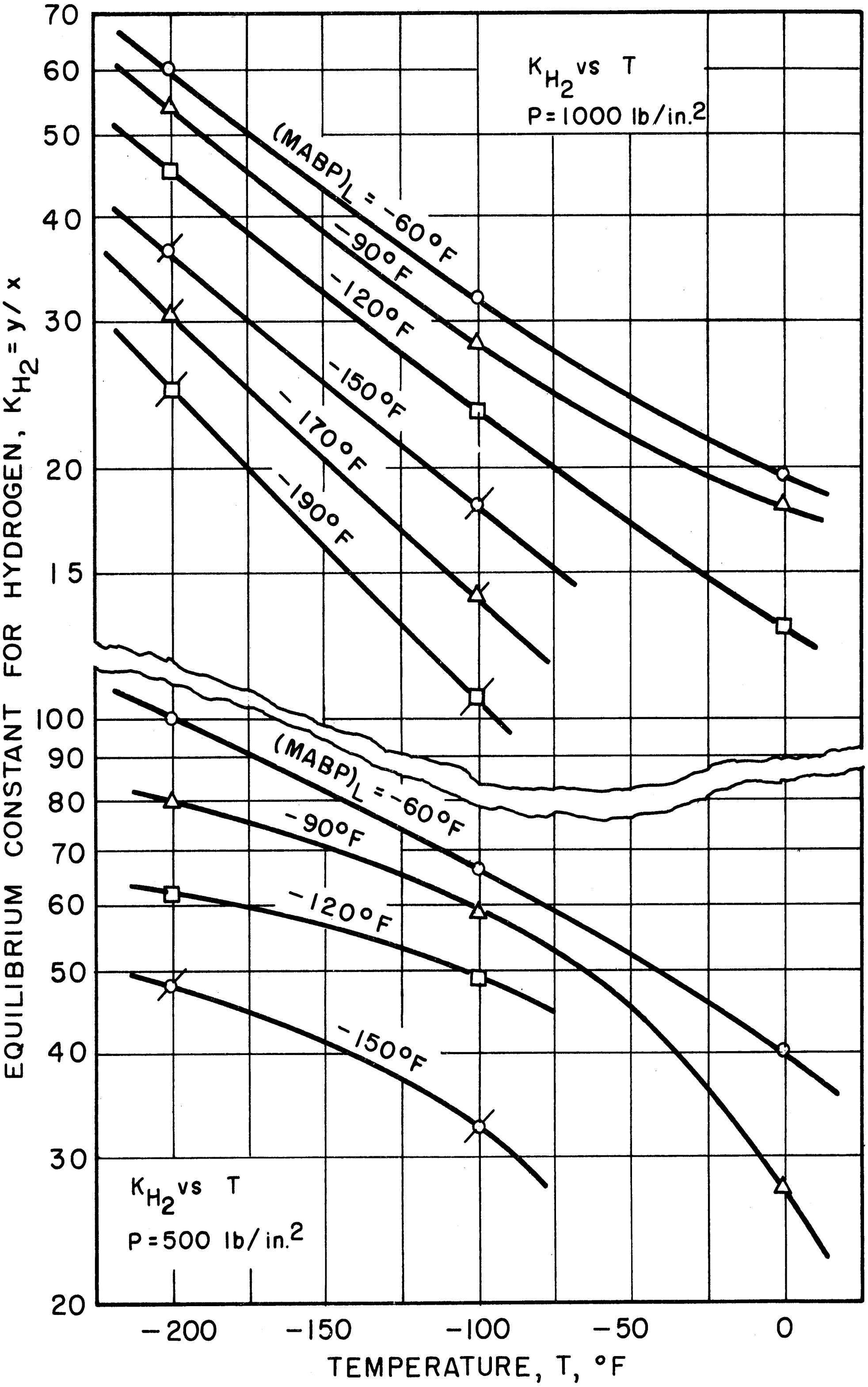

Figure 23. Equilibrium Constants for Hydrogen in the Hydrogen-Methane-Propane System as a Function of Temperature.

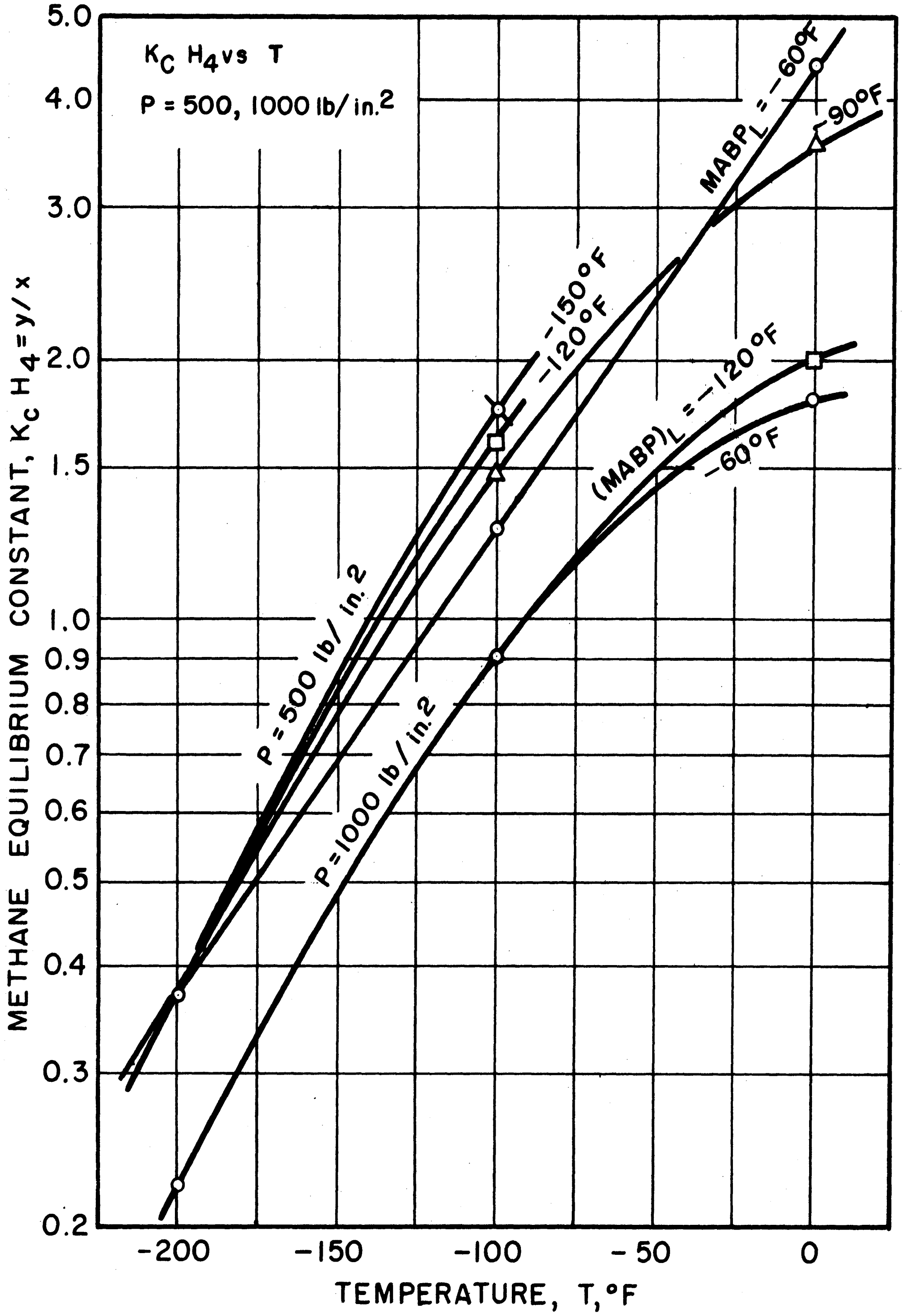

Figure 24. Equilibrium Constants for Methane in the Hydrogen-Methane-Propane System as a Function of Temperature.

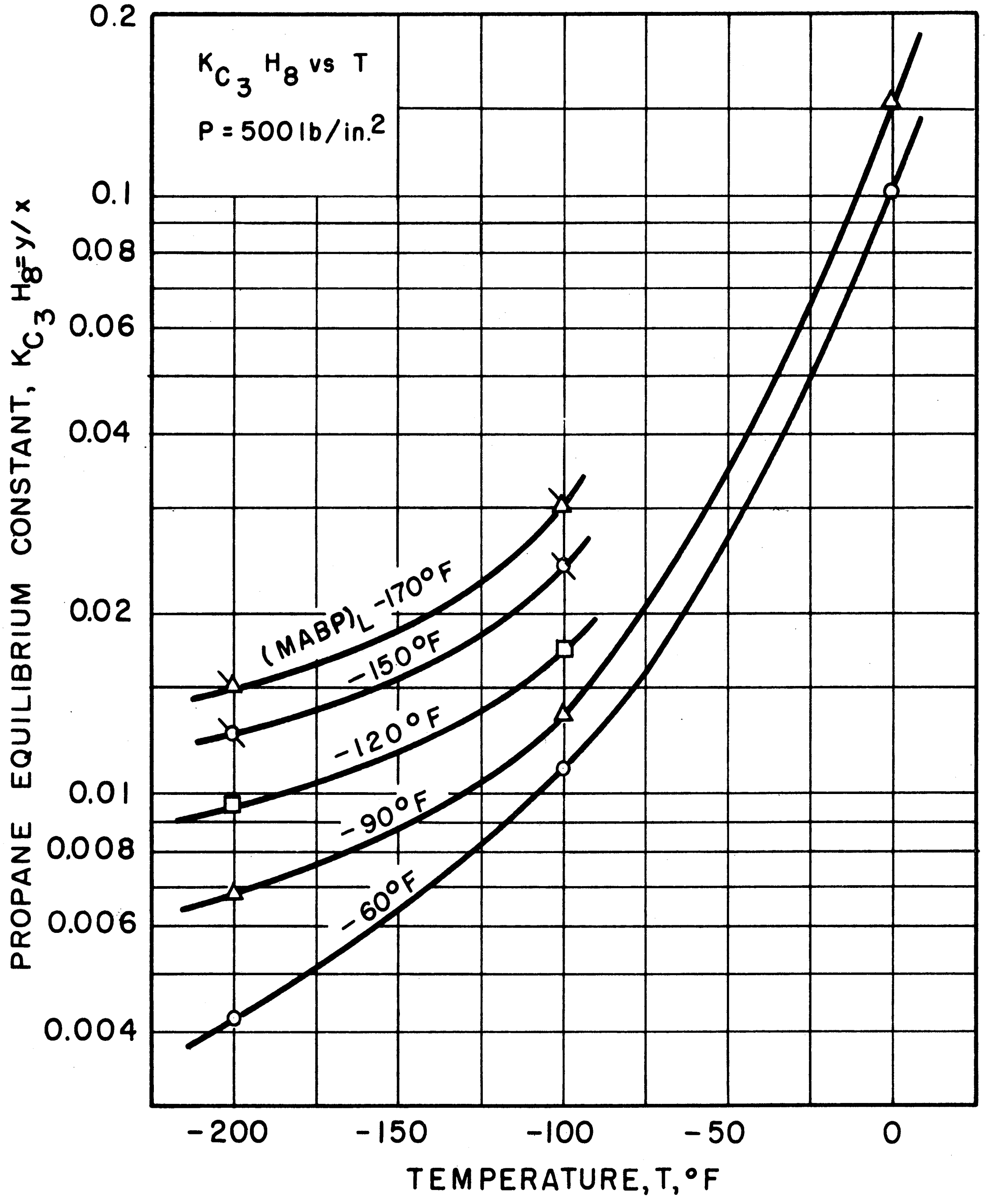

Figure 25. Equilibrium Constants for Propane in the Hydrogen-Methane-Propane System at 500 lb/in^2 as a Function of Temperature.

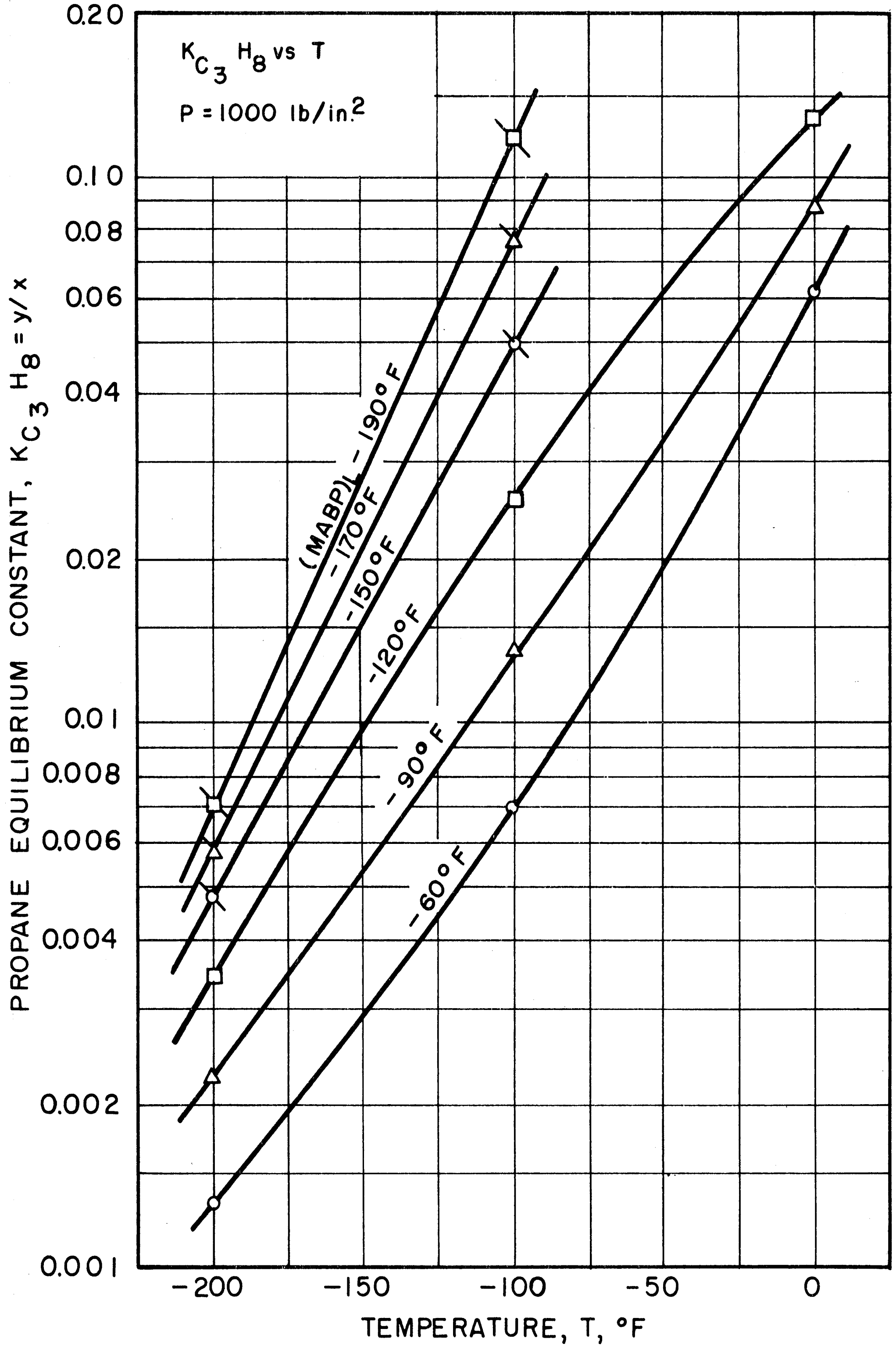

Figure 26. Equilibrium Constants for Propane in the Hydrogen-Methane-Propane System at 1000 lb/in.^{2} as a Function of Temperature.

constants versus pressure at constant temperature and liquid molal average boiling point.

The deviations in the correlations are small and they are due to the deviations in the data.

The equilibrium constants for ethylene, ethane, propylene and propane existing in their hydrogen-methane ternary systems have each been correlated with a sort of graphical nomogram, using the variables of temperature, pressure, and molal average boiling point of the liquid.

The description of the procedure used in constructing the nomographic correlation for ethylene contains the essential steps involved in deriving these correlations.

Referring to Figure 27, it can be seen that the nomograph covers a temperature range of 0 to -200°F and a pressure range of 100 to 2000 lb/in.^{2}. The hydrogen-ethylene data were smoothed, calculations of the molal average boiling point of the liquid phase were made, and the span of the equilibrium constants was noted. Semi-logarithmic graph paper was selected for the construction. The equilibrium constants were read from the left side of the plot and the pressure was indicated on the right-hand side of the plot. A straight line was drawn with a negative slope to cover the desired span of the ethylene equilibrium constants. This line was labeled by an average value of the molal average boiling points for the liquid phase for the hydrogen-ethylene system. Since hydrogen is only slightly soluble in ethylene, the values of the molal average boiling points at different temperatures and pressures don't deviate much from the mean value.

Next the constant temperature lines were drawn so that the hydrogen-ethylene binary results were predicted by reading across from the

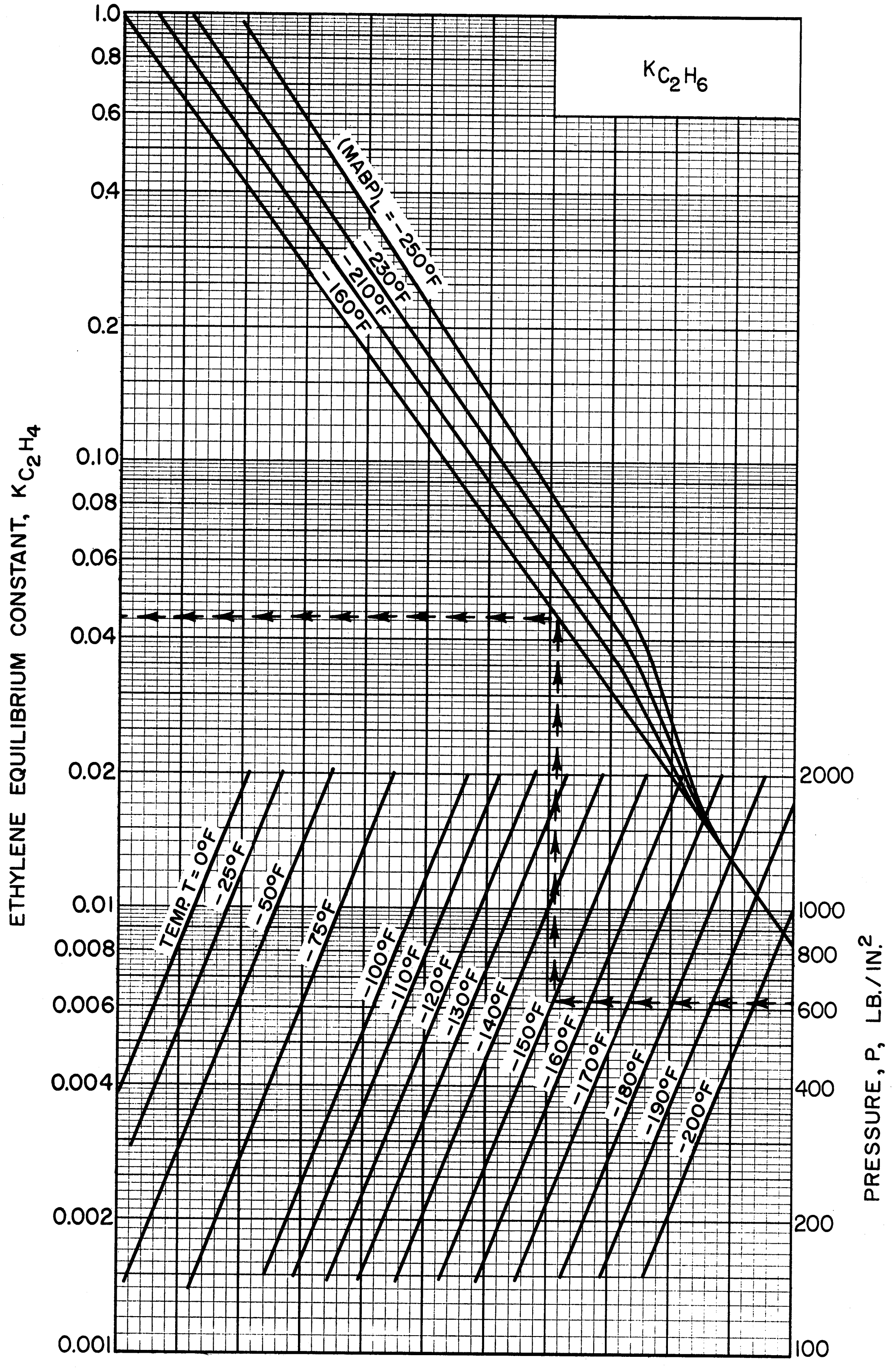

Figure 27. Nomographic Correlation of Ethylene Equilibrium Constants in the Hydrogen-Methane-Ethylene System.

pressure axis to the temperature line, then up to the molal average boiling point line and then across to the equilibrium constant axis. Now using the same temperature grid, other lines for constant values of the molal average boiling point of the liquid were drawn in the graph so that the equilibrium constants for ethylene in the hydrogen-methane-ethylene ternary system could be predicted.

If we compare the correlation of ethylene equilibrium constants with the original data for the hydrogen-methane-ethylene system we find an average percentage deviation of ±7.4% and a standard deviation of 0.0012.

Examination of the equilibrium constants for ethane revealed that the published data for the hydrogen-methane-ethane system is internally inconsistent and therefore probably incorrect. A nomographic correlation of the equilibrium constants for ethane is presented in Figure 28. The deviations from the published data are large.

A nomographic correlation of the propylene equilibrium constants in the hydrogen-methane-propylene system is presented in Figure 29. Only the set of conditions investigated in this work were available for deriving a correlation of propylene equilibrium constants. The correlation was made using this set of data by drawing the curves for constant molal average boiling point of the liquid phase similar in form to the curves shown by ethylene, ethane, and propane. Since the correlation was derived from only a single set of data, the only calculable deviation in this correlation is that which appears in that data.

A nomographic correlation of the equilibrium constants for propane is presented in Figure 30. Large negative deviations of the correlation from the experimental data were noted at -100°F and 1000 lb/in.^{2}.

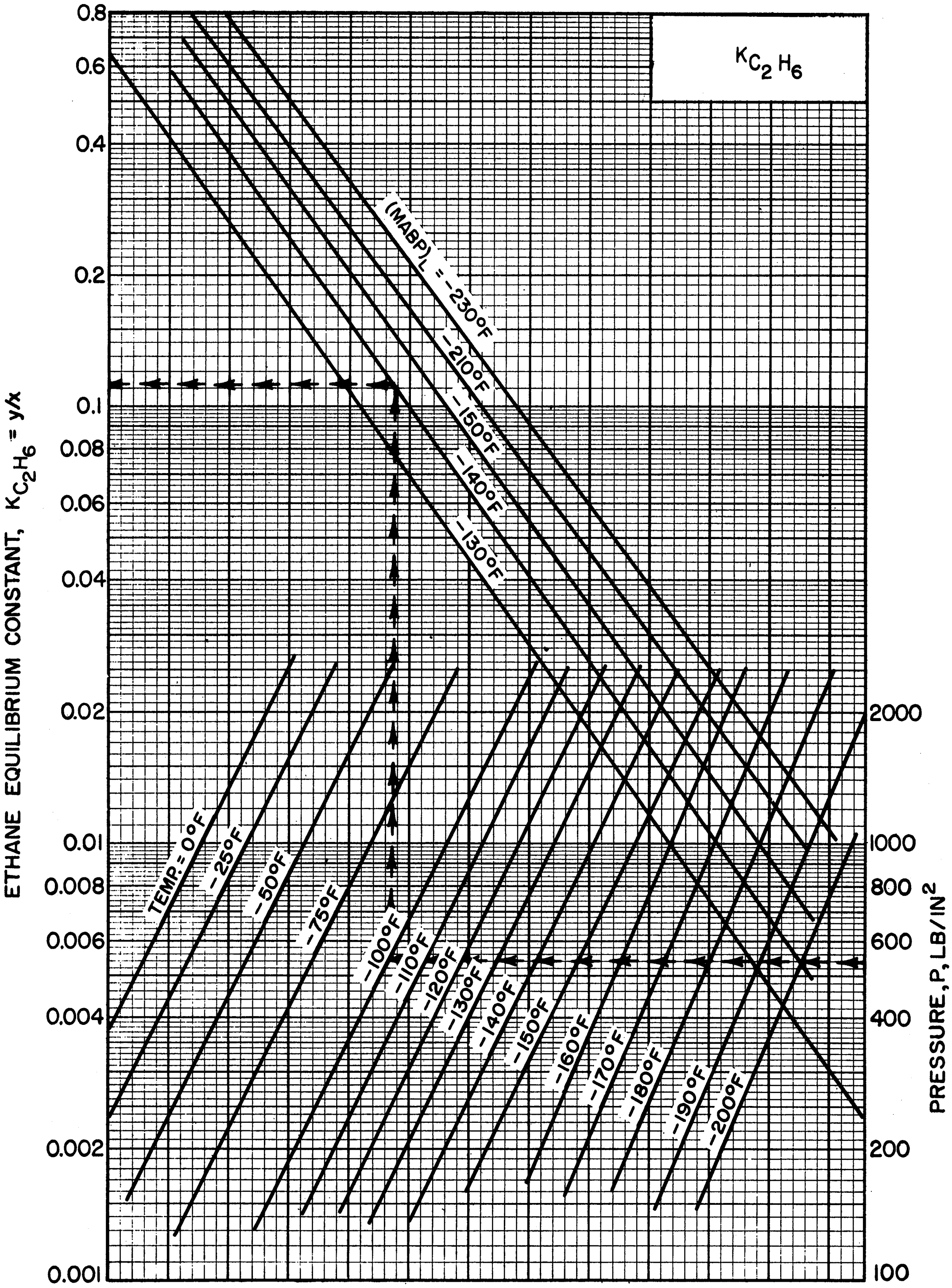

Figure 28. Nomographic Correlation of Ethane Equilibrium Constants in the Hydrogen-Methane-Ethane System.

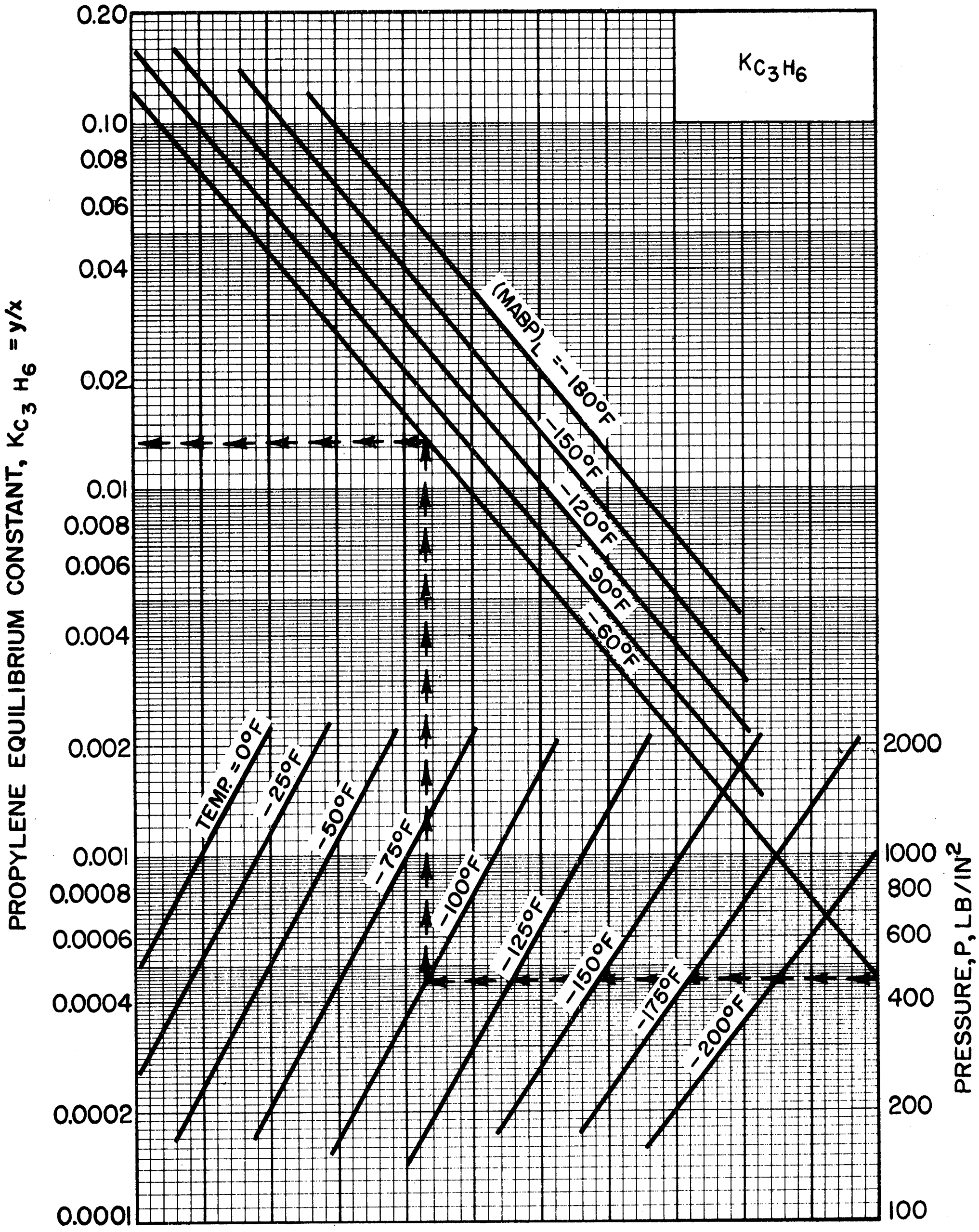

Figure 29. Nomographic Correlation of Propylene Equilibrium Constants in the Hydrogen-Methane-Propylene System.

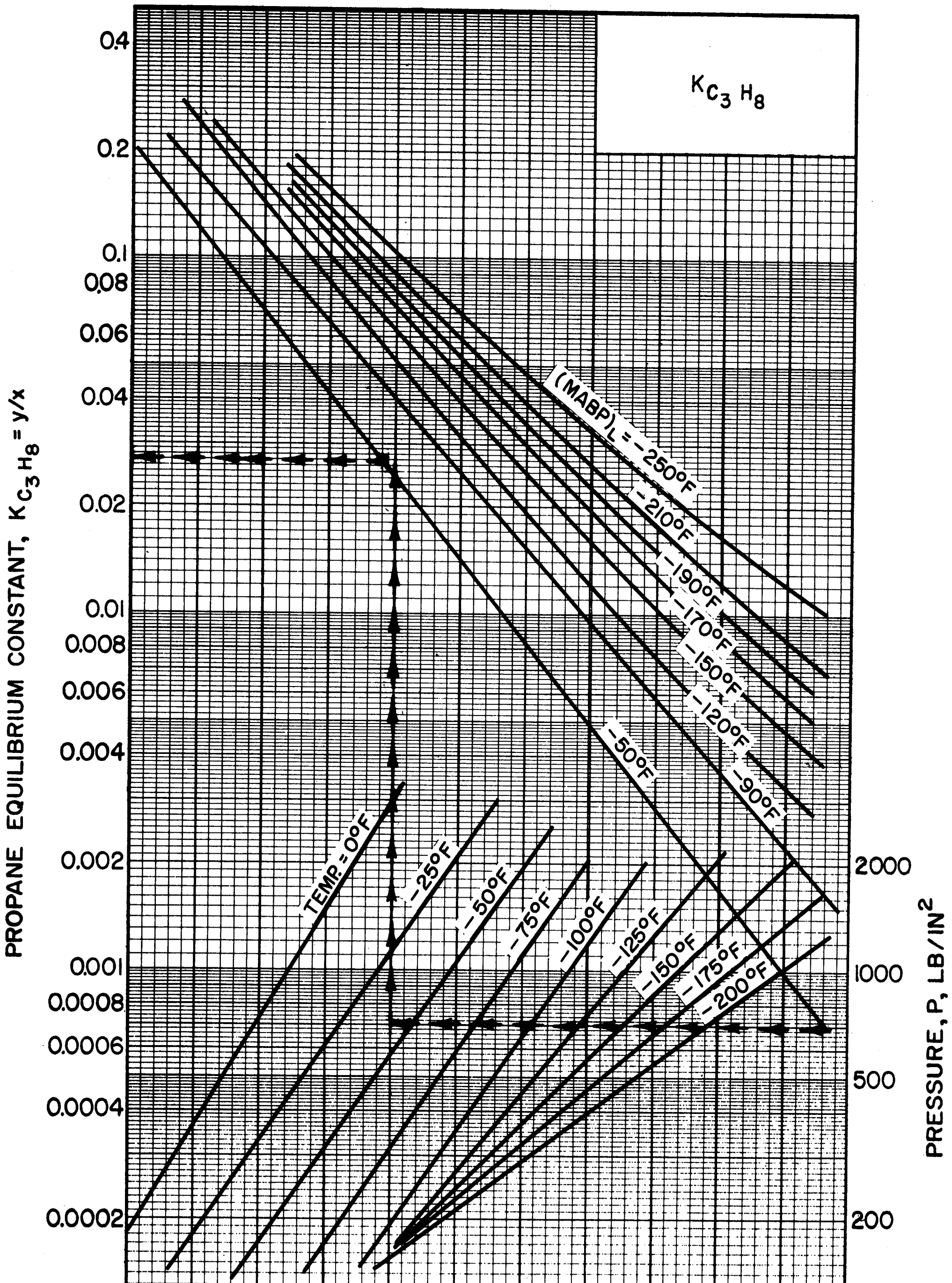

Figure 30. Nomographic Correlation of Propane Equilibrium Constants in the Hydrogen-Methane-Propane System.

By referring to Figure 12, a plot of the experimental data for hydrogen-methane-propane at -100°F and 1000 lb/in.^{2}, we find that these conditions lie within the critical region, and that a critical point exists in the diagram. From our discussion of theory, it may be recalled that as a system approaches the critical point, the equilibrium constants for the constituents approach unity. The equilibrium constants for propane, then, would increase as the critical point is approached. This would serve to explain why the correlation predicts equilibrium constants which are too low at -100° F and 1000 lb/in.^{2} It is recommended that the nomographic representation of the propane equilibrium constants be used only for those conditions of temperature and pressure lying outside of the critical region. Excluding the critical region data at -100°F and 1000 lb/in.^{2}, the nomographic correlation for propane gave an average deviation of ±4.6 and a standard deviation of 0.002 with most of the deviations occurring for the data at -100°F and 500 lb/in.^{2}. No explanation for this inconsistency is known.

C. Correlation of Ternary Pairs

Simple methods of correlating the equilibrium constants found in any hydrogen binary orternary system were considered. It was desirable to obtain a correlation involving the temperature, pressure and one or two concentration variables which could be used later for complex systems.

The correlation described previously for hydrogen in the hydrogen-methane-propane ternary system was considered as a means of describing the hydrogen equilibrium constants in the other binary and ternary systems. Figure 31 contains a semi-logarithmic plot of the

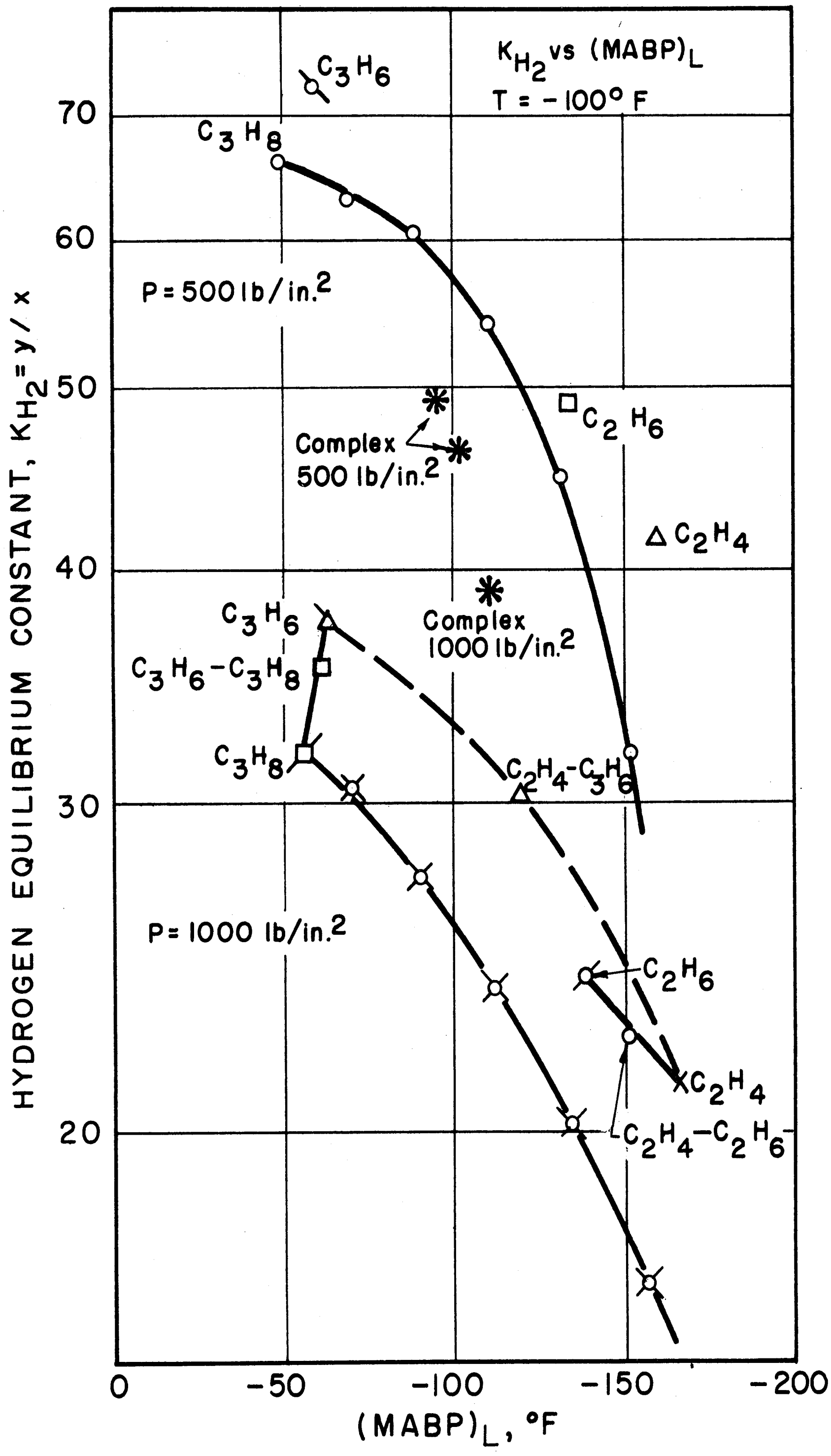

Figure 31. Equilibrium Constants for Hydrogen at -100° F and 500 and 1000 lb/in.² versus the Liquid Molal Average Boiling Point.

equilibrium constant for hydrogen as a function of the liquid molal average boiling point at -100°F and at 500 and 1000 lb/in.^{2}. Included in the plot are data points for the hydrogen binaries with ethylene, ethane, propylene and propane at 500 and 1000 lb/in.^{2}; for the hydrogen-methane-propane ternary system at 500 and 1000 lb/in.^{2} for the hydrogen-ethylene-ethane ternary system at 1000 lb/in.^{2} as obtained by Williams (44); also, for Williams' data for the hydrogen-ethylene-propylene ternary system at 1000 lb/in.^{2} and his data for the hydrogen-propylene-propane system at 1000 lb/in.^{2}. This plot clearly shows that use of the three variables of temperature, pressure and the molal average boiling point of the liquid does not result in the unique determination of the equilibrium constant for hydrogen in any binary of ternary light hydrocarbon system. The plot does show that these three variables are sufficient to describe any single hydrogen three-component system.

It is shown that there exists a simple straight line relationship which describes the variation of the hydrogen equilibrium constant with the liquid molal average boiling point in a (hydrogen)-(saturated hydrocarbon)-(corresponding unsaturated hydrocarbon) ternary system.

Methods of combining two concentration variables were considered. The first considerations were made using the schemes followed in the presentation of the Kellogg (6) correlation. In general, the correlation consists of two plots for each consistuent at a certain pressure. One plot, as shown for methane in Figure 32A, contains a semi-logarithmic representation of the equilibrium constant as a function of the temperature with parameters of constant liquid molal average boiling points. The second plot, as shown for methane in Figure 32B, gives a correction to the equilibrium constant from the first plot, Figure 32A, as a function of the vapor molal average boiling point with parameters of temperature.

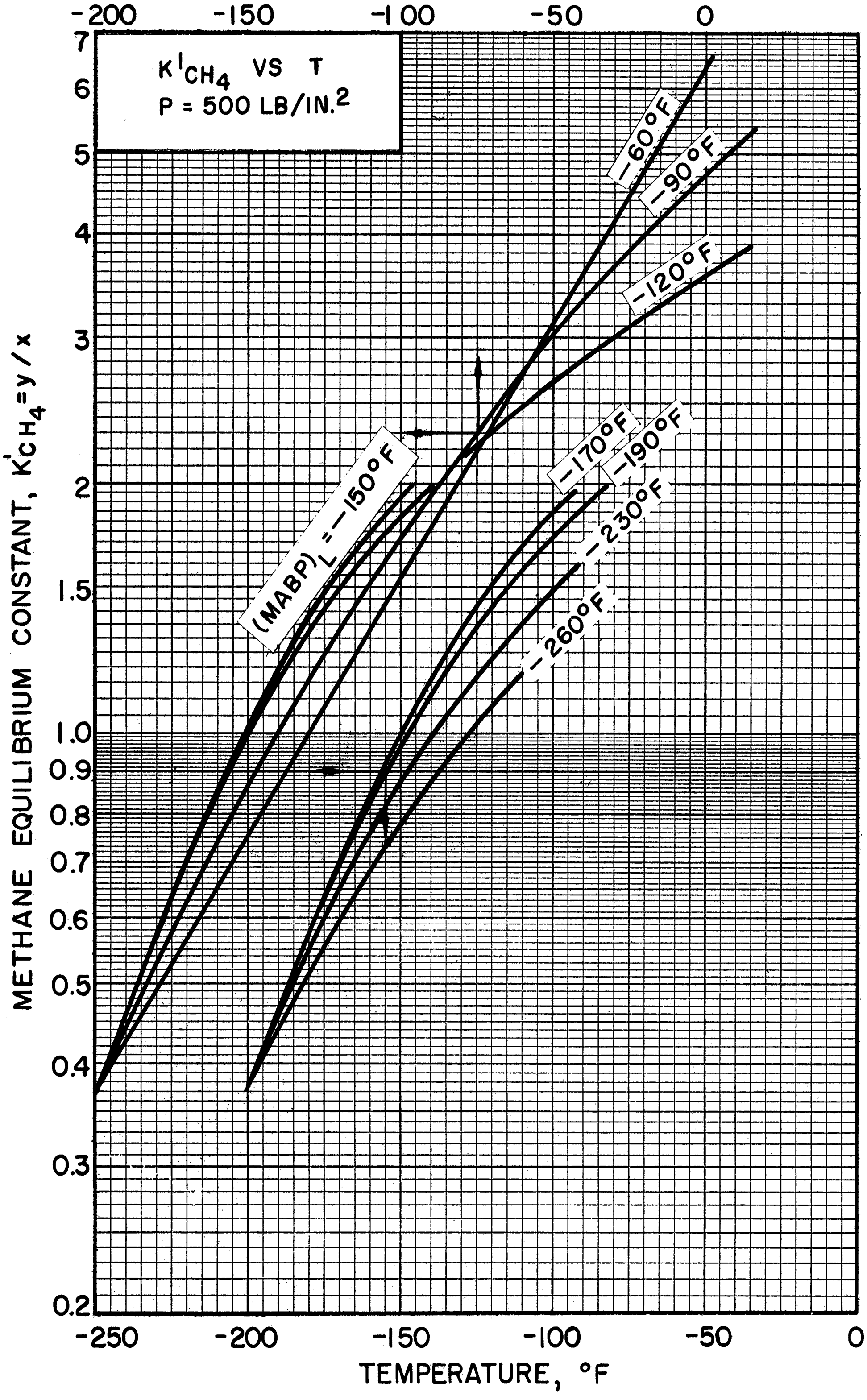

Figure 32A. $(MABP)_L$ - $(MABP)_V$ Correlation for Methane Equilibrium Constants at 500 lb/in.^{2}

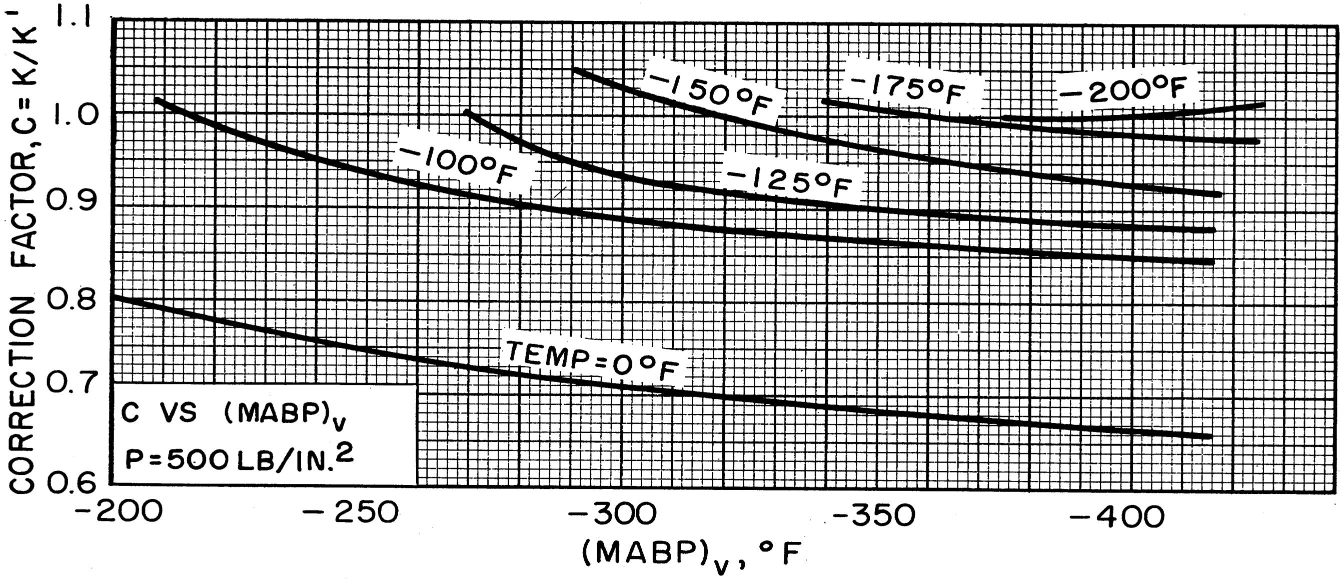

Figure 32B. Correction Factor for Figure 32A.

$$K \text{ actual} = C(K') \qquad (25.1)$$

C = correction factor

K' = equilibrium constant from correlation in first figure.

This correlation will hereafter be referred to as the $(MABP)_L - (MABP)_V$ correlation. The $(MABP)_L - (MABP)_V$ correlation was used as a means of correlating the hydrogen and methane equilibrium constants in the binary systems of hydrogen with methane, ethylene and propane along with the ternary systems of hydrogen-methane-ethylene and hydrogen-methane-propane. A description of the procedure used in constructing the correlation for methane will also give the essential elements involved in constructing the correlation for hydrogen. A description of this procedure is as follows.

The methane correlation given in Table XIII,* shown in Figures 32A, 32B, and 33A and 33B is based upon a correction factor of 1.0 for the methane equilibrium constant in the hydrogen-methane-propane system at a liquid molal average boiling point of -190°F and the temperature and pressure in question. A correction factor for the methane equilibrium constant found in the hydrogen-methane-ethylene system at these conditions was calculated and plotted on the correction factor plot for the vapor molal average boiling point of that system. Next, a straight line was drawn through these two points on the correction factor plot and correction factors were calculated for the two ternary systems for another set of liquid molal average boiling points and corresponding vapor molal average boiling point at the same temperature and pressure. These correction factors were used to calculate values of K', the equilibrium constant used in the first plot. Using an average value of K_c, new correction factors were calculated and plotted. The correction factor curve was then redrawn through the four points.

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*Presented in Appendix C.

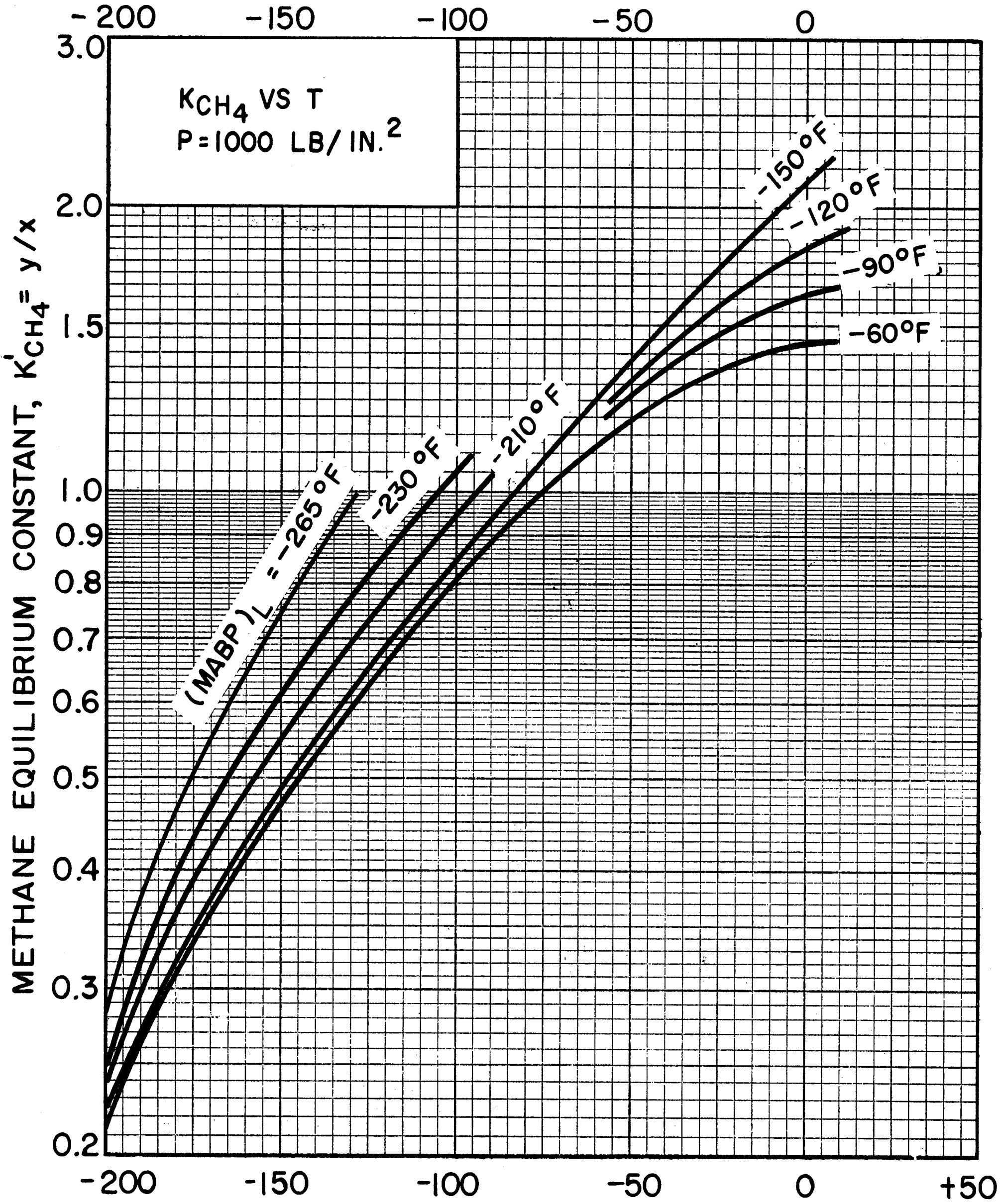

Figure 33A. $(MABP)_L$ - $(MABP)_V$ Correlation for Methane Equilibrium Constants at 1000 lb/in.^{2}

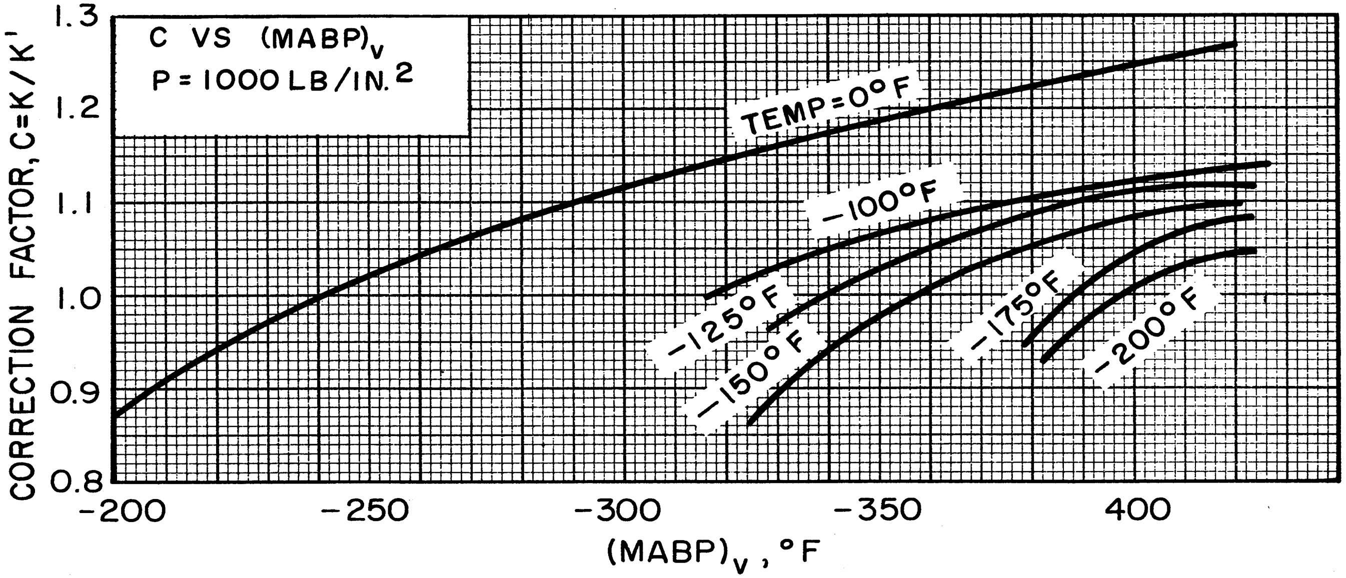

Figure 33B. Correction Factor for Figure 33A.

This procedure for constructing the methane correlation consisted then, of the following steps: (1) reading correction factors (C); (2) calculating (K')'s; (3) averaging the (K')'s; (4) recalculating correction factors (C); and (5) replotting the correction factor curve. This procedure was repeated until the entire range of liquid molal average boiling points was covered. This range extended from the lower limits of hydrogen-propane system to the upper limits of hydrogen-methane system. New conditions of temperatures and pressures were then used, and the correlation procedure was repeated.

The recommended procedure for interpolation or extrapolation of the correlation for other pressures is to obtain the equilibrium constant corresponding to the temperature, molal average boiling point and vapor phase concentration in question for the two pressures of 500 and 1000 lb/in.^{2}, and to then plot these constants as a straight line function of the pressure on a log-log plot.

A study was made of the deviations of the $(MABP)_L$ - $(MABP)_V$ correlation for methane equilibrium constants from the experimental data for the systems of hydrogen-methane-ethylene and hydrogen-methane-propane. The average percentage deviation was found to be ±6.8% and the standard deviation was 0.088.

A study was made of the deviations of the $(MABP)_L$ - $(MABP)_V$ correlation for hydrogen equilibrium constants from the experimental data for the hydrogen-methane-ethylene and hydrogen-methane-propane systems. The average percentage deviation was found to be ±5.4% and the standard deviation was 1.95%. A comparison of hydrogen equilibrium constants in the binary systems of hydrogen-ethane and hydrogen-propane with those predicted by the $(MABP)_L$ - $(MABP)_V$ correlation of the hydrogen-methane-propane and hydrogen-methane-ethylene systems, showed that the two concentration variables were still inadequate to describe simultaneously all these systems.

A second correlation for hydrogen equilibrium constants was made using the variables of temperature, pressure, liquid molal average boiling point and the mole percentage composition of hydrogen in the vapor phase, (Table XIV).* The mechanics of the correlation were patterened from the $(MABP)_L$ - $(MABP)_V$ correlation (Figures 34A, 34B, 34C, and 35). Pairs of plots have been given for pressures of 500 and 1000 lb/in.^{2}. One plot contains a semi-logarithmic representation of the equilibrium constant as a function of the temperature with parameters of liquid molal average boiling points. The second plot contains a correction factor as a function of the mole percentage of hydrogen in the vapor phase with parameters of temperature. This correlation will hereafter be referred to as the $(MABP)_L$- yH_2 correlation.

The procedure followed in constructing the $(MABP)_L$ - yH_2 correlation was the same as that for the $(MABP)_L$ - $(MABP)_V$ correlation described previously for methane with the exception that the hydrogen equilibrium constants in the hydrogen-ethylene system were used as a basis for a unity correction factor.

A study of the deviations of the hydrogen equilibrium constants predicted by the $(MABP)_L$ - yH_2 correlation from the experimental data was made, and an average percentage deviation of $\pm 3.3\%$ and a standard deviation of 1.4% were found.

A resume of the errors obtained from the above correlations is given in Table XV. A comparison of this correlation with the hydrogen

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*Presented in Appendix C.

TABLE XV

DEVIATION OF CORRELATIONS

Component	System	Correlation	% Dev.	Std. Dev.
H_2	H_2-CH_4-C_3H_8 and H_2-CH_4-C_2H_4	$(MABP)_L$-$(MABP)_V$	±5.4	1.95
H_2	H_2-CH_4-C_3H_8 and H_2-CH_4-C_2H_4	$(MABP)_L$-yH_2	±3.3	1.4
CH_4	H_2-CH_4-C_3H_8 and H_2-CH_4-C_2H_4	$(MABP)_L$-$(MABP)_V$	±6.8	0.088
C_2H_4	H_2-CH_4-C_2H_4	Nomographic	±7.4	0.0012
C_2H_6	H_2-CH_4-C_2H_6	Nomographic	--	--
C_3H_6	H_2-CH_4-C_3H_6	Nomographic	0	0
C_3H_8	H_2-CH_4-C_3H_8	Nomographic	±4.6	0.002

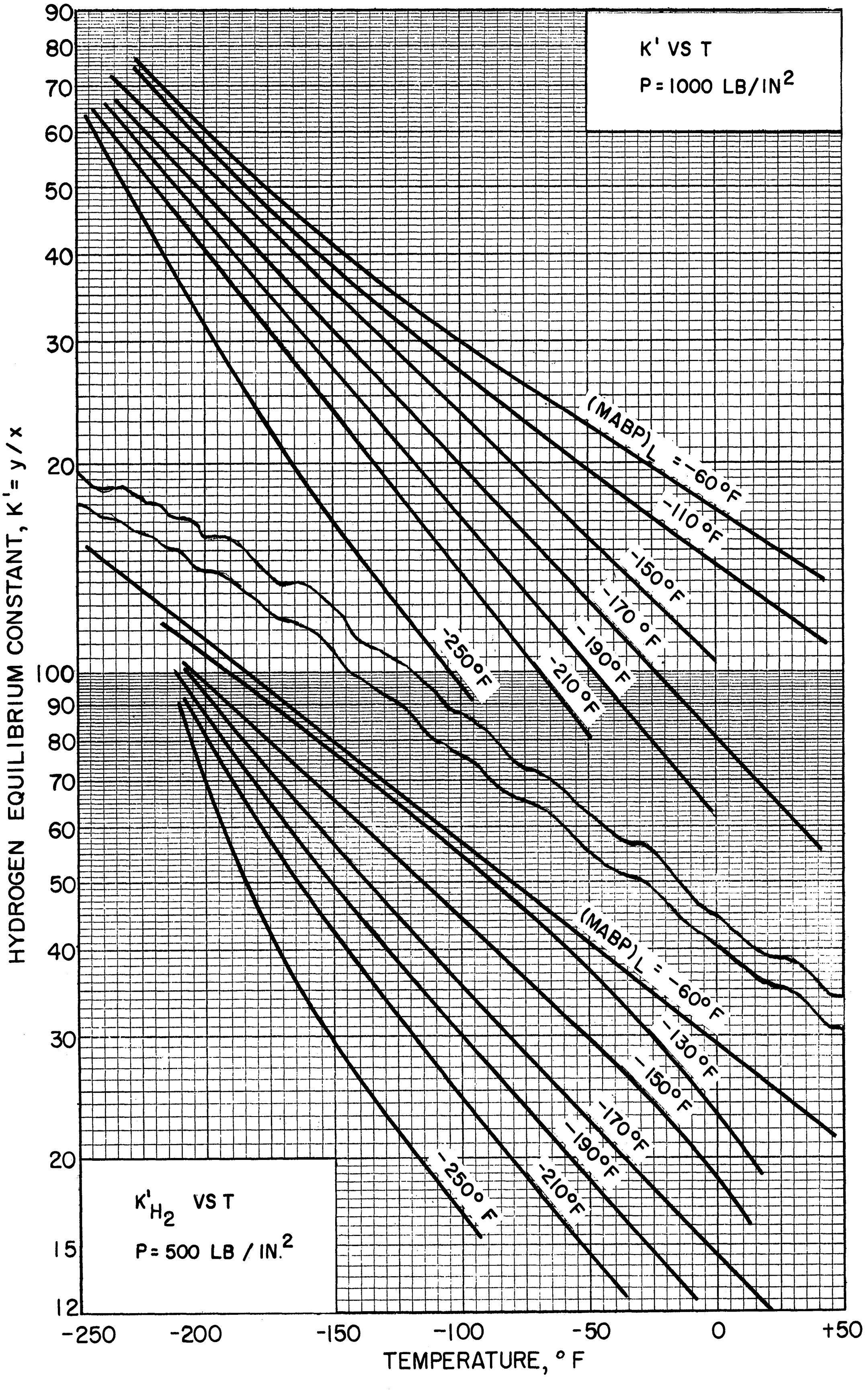

Figure 34A. $(MABP)_L$ - yH_2 Correlation for Hydrogen Equilibrium Constants at 500 and 1000 lb/in.^{2}

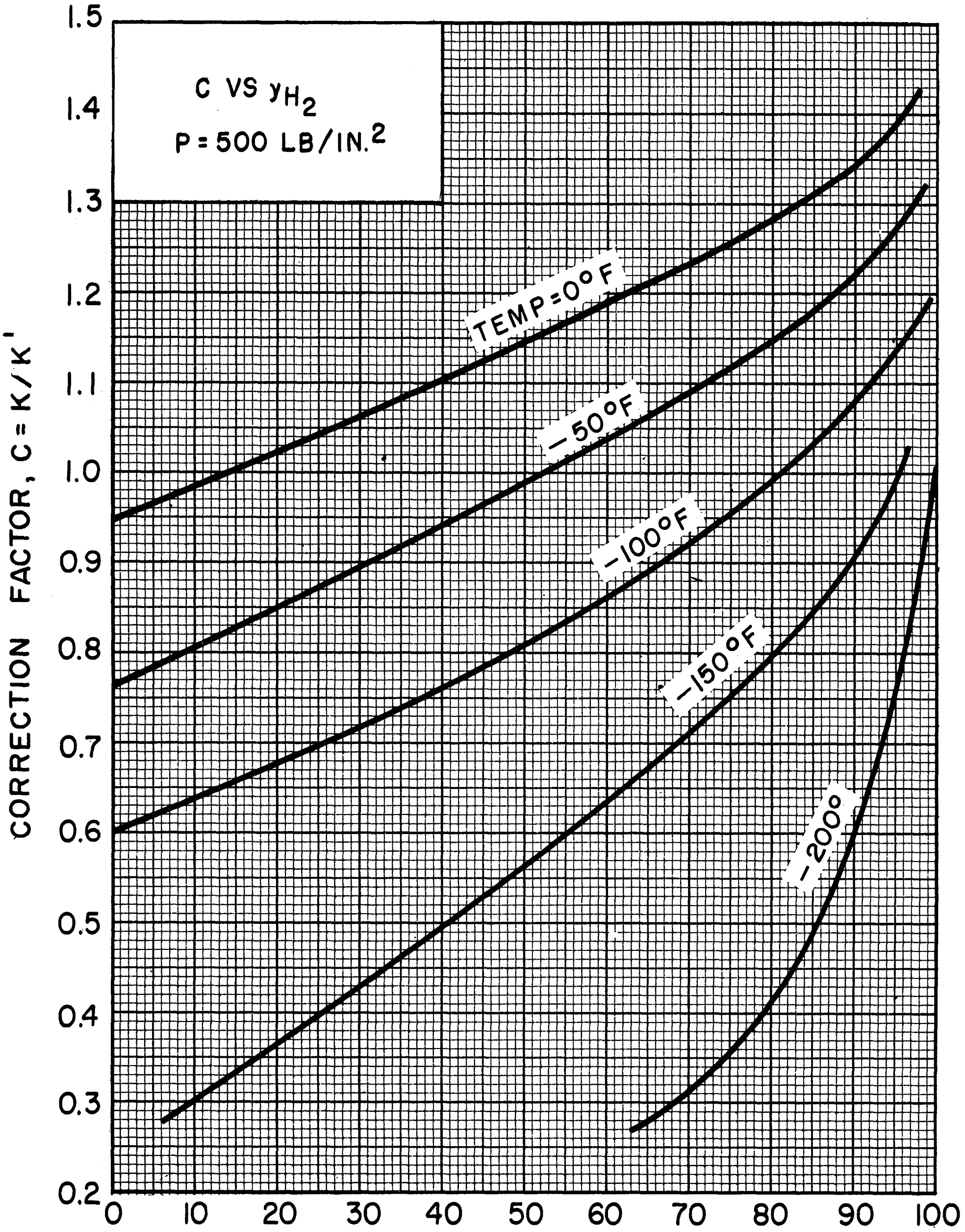

Figure 34B. Correction Factor for Figure 34A at 500 lb/in.^{2}

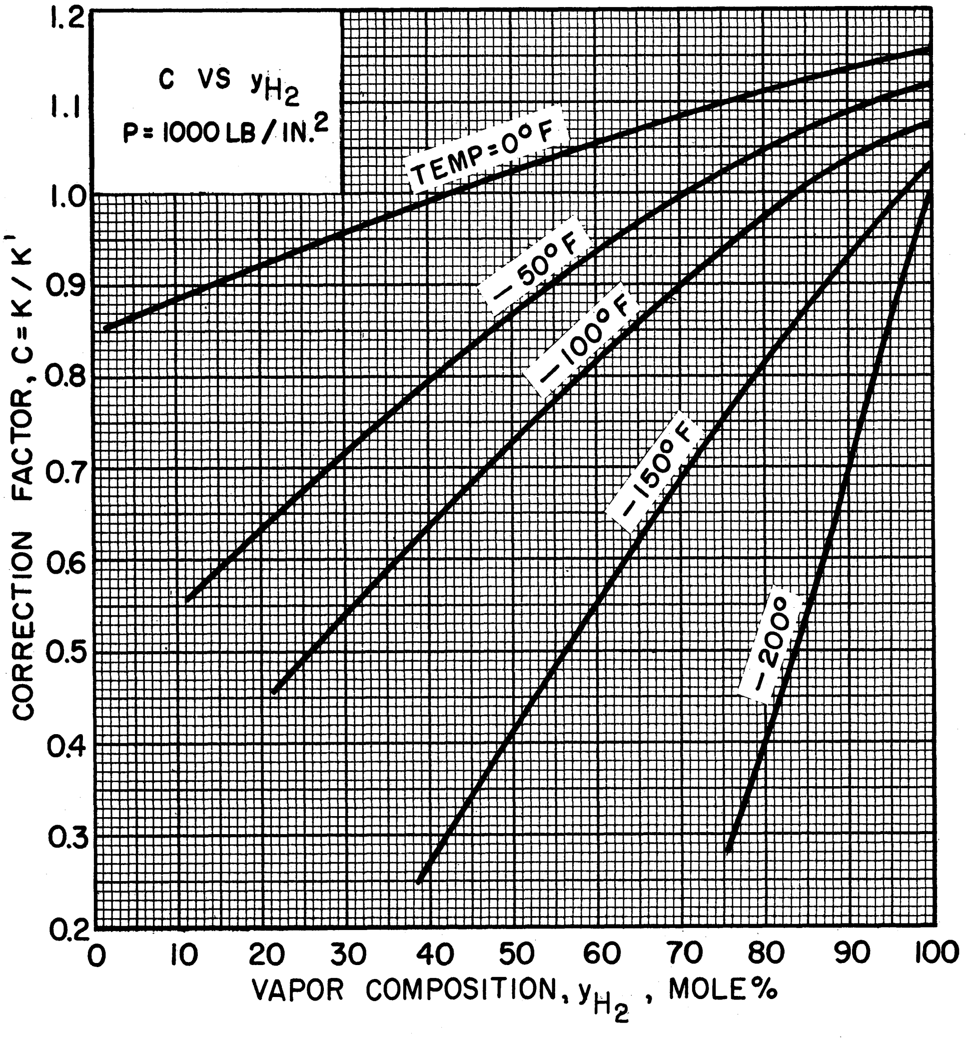

Figure 34C. Correction Factor for Figure 34A at 1000 lb/in.^{2}

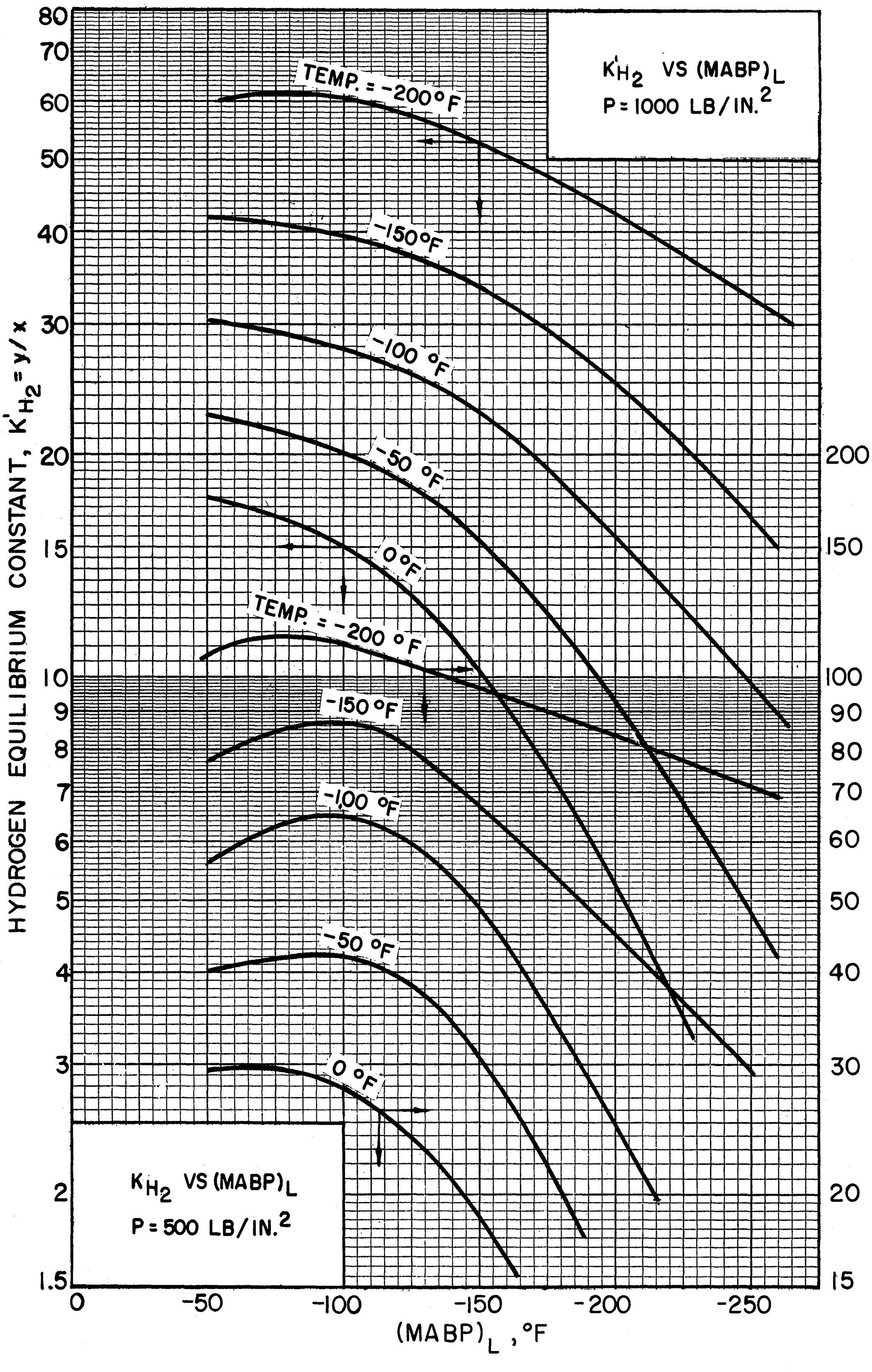

Figure 35. (MABP)$_L$ - yH_2 Correlation for Hydrogen Equilibrium Constants at 500 and 1000 lb/in.^{2}

ethane, hydrogen-propylene and hydrogen-methane-propylene data showed that the correlation was inadequate for the description of these systems; simultaneously with the hydrogen-methane-ethylene and hydrogen-methane-propane systems.

D. Complex System Correlation

Included with the results of this investigation are five data points for mixtures of hydrogen, methane, ethylene, ethane, propylene and propane, including temperatures of 0 and -100°F and pressures of 500 and 1000 lb/in.^{2}. These five isolated determinations were insufficient for the derivation of a correlation, but they were useful in testing whether any correlation derived from the study of binary and ternary systems could be applied to a six-component system.

Figure 31, a semi-logarithmic plot of the hydrogen equilibrium constants at -100°F versus the liquid molal average boiling points for pressures of 500 and 1000 lb/in.^{2}, contains three data points for the complex systems. This figure shows that at a fixed temperature and pressure, the equilibrium constant is not a single function of the liquid molal average boiling point.

The $(MABP)_L$- $(MABP)_V$ correlations for the hydrogen and methane equilibrium constants were used to predict equilibrium constants for the five complex system data points. Table XVI gives the results of this comparison along with a comparison of the equilibrium constants obtained by the $(MABP)_L$ - yH_2 correlation for hydrogen. Large deviations are found for both correlations which would indicate the inability of the variables used to describe both ternary and six-component systems.

TABLE XVI

COMPARISON OF HYDROGEN AND METHANE EQUILIBRIUM CONSTANTS IN A COMPLEX SYSTEM WITH CORRELATIONS

Run No.	Temp. T °F	Press. P	Equilibrium Constant K	K (Correlation)	% Deviation
			Hydrogen via $(MABP)_L$ - $(MABP)_V$ Correlation		
52	0	500	36.8	32.1	-13
53	-100	500	49.1	56.3	+15
54	-100	500	46.4	57.9	+25
55	0	1000	15.3	14.8	-3.3
56	-100	1000	39.2	24.6	-37
			Hydrogen via $(MABP)_L$ - yH_2 Correlation		
52	0	500	36.8	29.5	-20
53	-100	500	49.1	50.6	+3.0
54	-100	500	46.4	50.5	+8.9
55	0	1000	15.3	14.0	+8.0
56	-100	1000	39.2	25.5	-35
			Methane via $(MABP)_L$ - $(MABP)_V$ Correlation		
52	0	500	4.09	3.95	-3.4
53	-100	500	2.05	1.57	-24
54	-100	500	1.99	1.58	-20
55	0	1000	2.14	1.94	-9.4
56	-100	1000	1.10	0.77	-30

E. Re-examination of Methods of Correlation

Because the previously derived correlations could not be used to predict satisfactory equilibrium constants for the six-component complex system it was necessary to examine other methods of correlation.

First, methods of using a single concentration variable along with the temperature and pressure were examined. Figure 36 contains a semi-logarithmic plot of the equilibrium constant of hydrogen as a function of the molal average boiling point of the vapor phase at -100°F and 500 and 1000 lb/in.^{2}. Points are shown for the various hydrogen binaries, for the hydrogen-methane-propane system, and for the six-component system. The plot shows the inability of the vapor molal average boiling point to uniquely establish the equilibrium constant of hydrogen in any system. A second deficiency of the vapor molal average boiling point appears at low temperatures where the vapor phase is made up almost entirely of hydrogen, resulting in only a very small variation of the molal average boiling point of the vapor with the equilibrium constant. The dotted lines indicate a possible correlation of results using parameters of the composition of hydrogen in the liquid. Development of a complete grid for such a correlation would actually require four-component data since only a few scattered points are obtained from the binary and ternary systems. This correlation also contains a degeneracy at low temperatures where the vapor concentration of hydrogen approaches 100%. Since K is y/x then we get $K = 100/x$ at low temperature; thus by specifying x, K is specified.

Consideration of other molal average properties showed that none of them either singly or in pairs were capable of describing the vapor-liquid equilibrium results obtained for a six-component system. The inability of the molal average properties to predict complex behavior

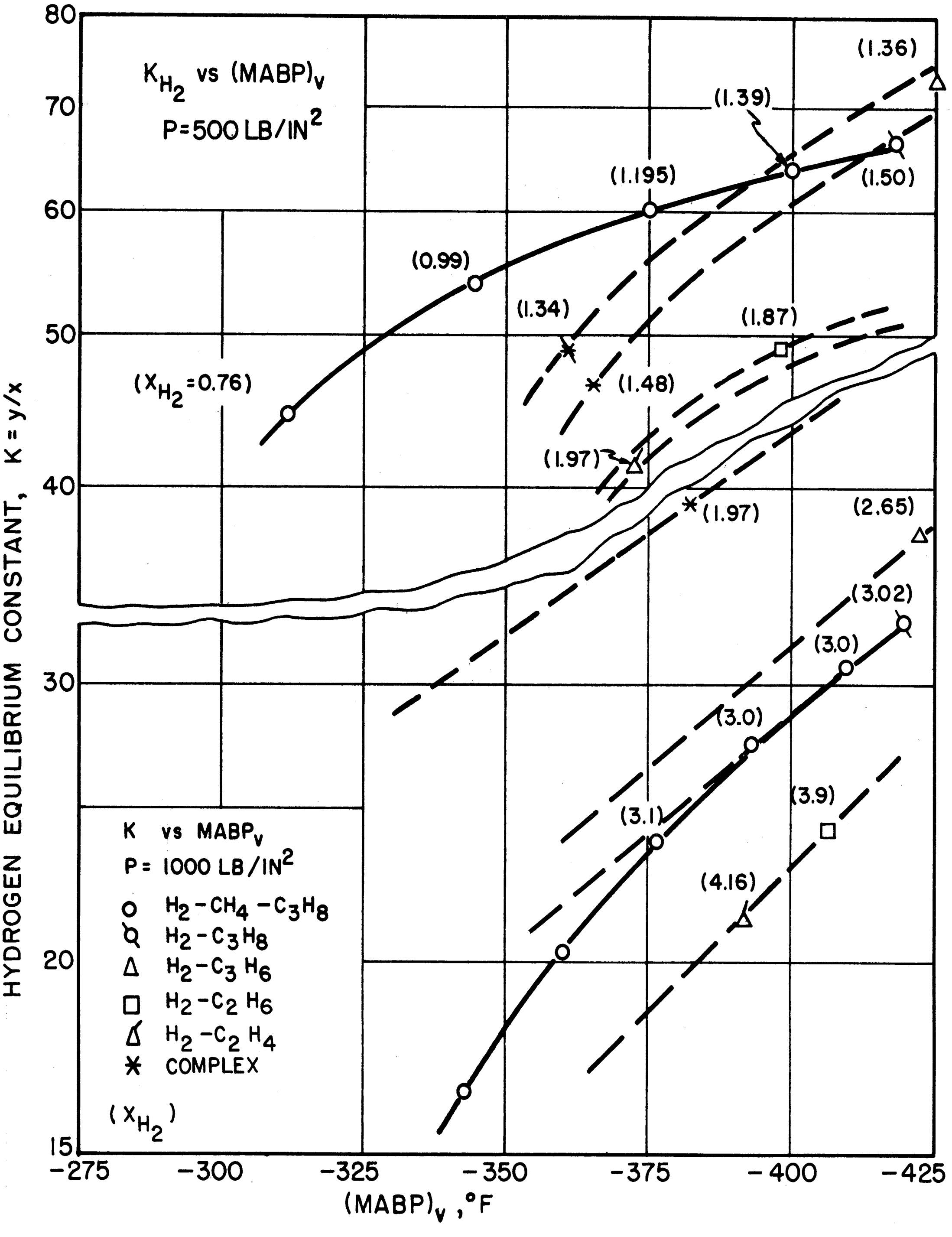

Figure 36. Equilibrium Constants for Hydrogen at -100° F and 500 and 1000 lb/in.^{2} as a function of the Vapor Molal Average Boiling Point.

for at least one condition is shown by the following comparison of results (Table XVII) for one of the six-component data points at -100°F and 500 lb/in.^{2} and a point for the hydrogen-methane-propane system at the same temperature and pressure.

TABLE XVII

COMPARISON OF EQUILIBRIUM CONSTANTS IN A SIX-COMPONENT SYSTEM
WITH THOSE IN A THREE-COMPONENT SYSTEM
HAVING SIMILAR MOLAL AVERAGE PROPERTIES

(Temperature = -100°F; Pressure = 500 lb/in.^{2})

	System	
	H_2-CH_4-C_3H_8	Six-Component
$(MABP)_L$, °F	-96	-96
$(MABP)_V$, °F	-362	-362
$(MW)_L$, lb/lb mole	37	37
$(MW)_V$, lb/lb mole	7.1	7.4
$(T'_c)_L$, °F	127	130
$(T'_c)_V$, °F	-300	-295
$(P'_c)_L$, lb/in.^{2}	626	638
$(P'_c)_V$, lb/in.^{2}	377	355
$K_{H_2} = y/x$	57.0	49.1
$K_{CH_4} = y/x$	1.50	2.05
$K_{C_3H_8} = y/x$	0.014	0.0136

A different approach to the prediction of vapor-liquid equilibrium constants has been used by Organick (39) for the description of hydro-carbon systems. His procedure, as described in the Theory Section, involved the specification of a correlating pressure in terms of the molal average boiling point of the vapor phase, the weight equivalent molecular weight of the liquid, and the pressure. This correlating pressure corresponded to the convergence pressure of a methane binary system having the same equilibrium constants at that temperature and pressure.

An attempt was made to correlate the hydrogen-light hydrocarbon systems in the same manner. The hydrogen binary systems data were plotted on a log-log plot where the equilibrium constant of hydrogen was plotted as a function of the pressure. Figure 37 shows the final result obtained by making the curves from the various binaries have a consistent form. The curves have been extrapolated to a convergence pressure.

The first attempt to correlate the convergence pressures as a function of concentration involved the consideration of hydrogen binaries existing at a certain temperature and pressure and the plotting of the convergence pressures as a function of the molal average boiling point of the liquid. Figure 38 shows the results of this correlation at -100°F and at 500 and 1000 lb/in.^{2}. The ternary data for the hydrogen-methane-propane system and the complex system data points have been included. As shown, there is a considerable error involved in this correlation. Errors of 22 to 40 per cent were estimated for the hydrogen equilibrium constants of complex systems as predicted by this type of correlation.

A second attempt at correlation is shown in Figure 39 where the convergence pressure was plotted as a function of the molal average boiling point of the vapor phase at a constant ratio of pressure to convergence pressure. The hydrogen binary systems seem to lie fairly close to a curve as shown. An exception is the hydrogen-methane system which lies well below the other data. The molecular weights have been shown on the plot and there is no basis for including lines of constant molecular weight. The data for two points for the ternary system of hydrogen-methane

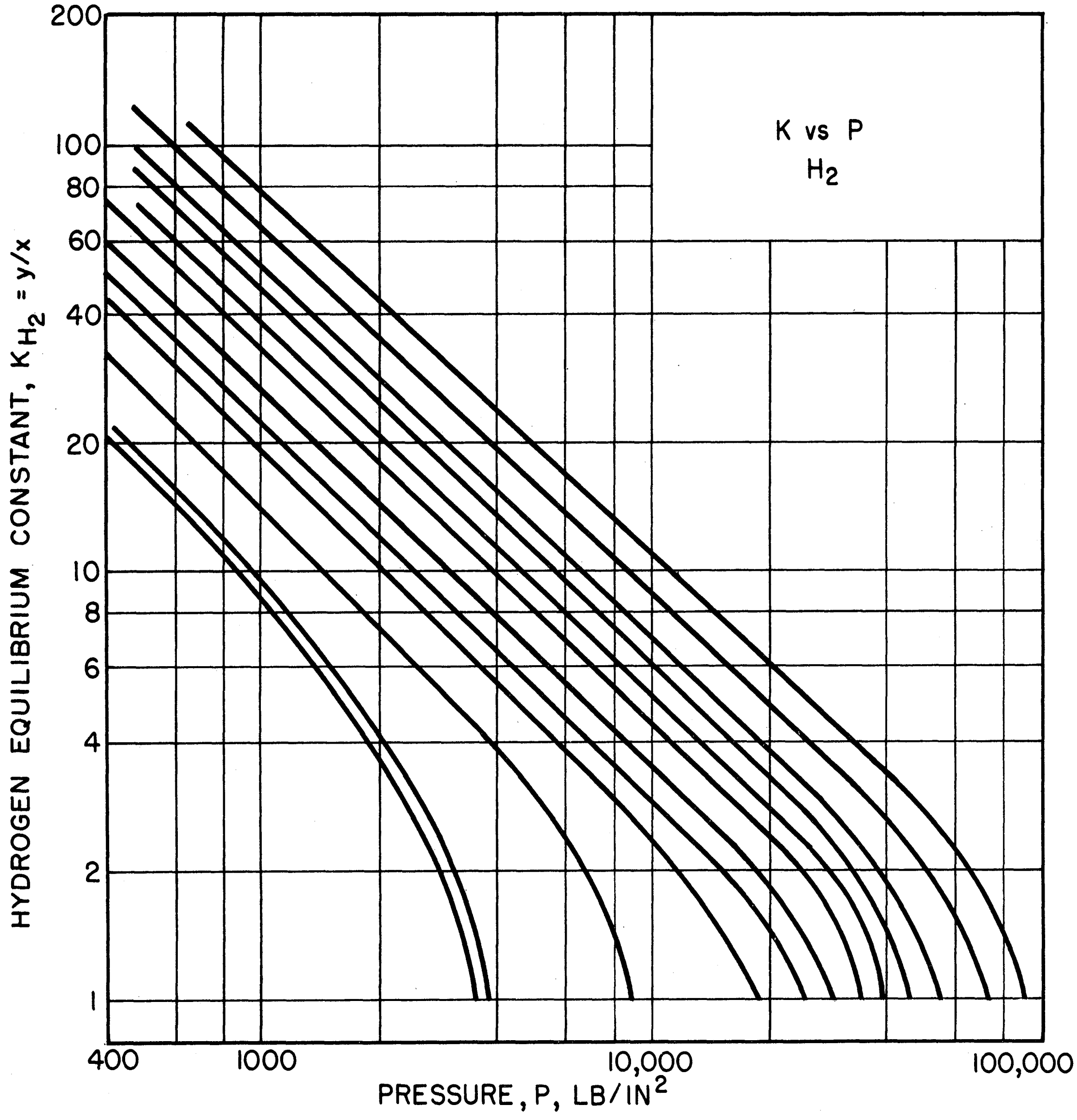

Figure 37. Log K versus log P Plot for Hydrogen in Binary Systems.

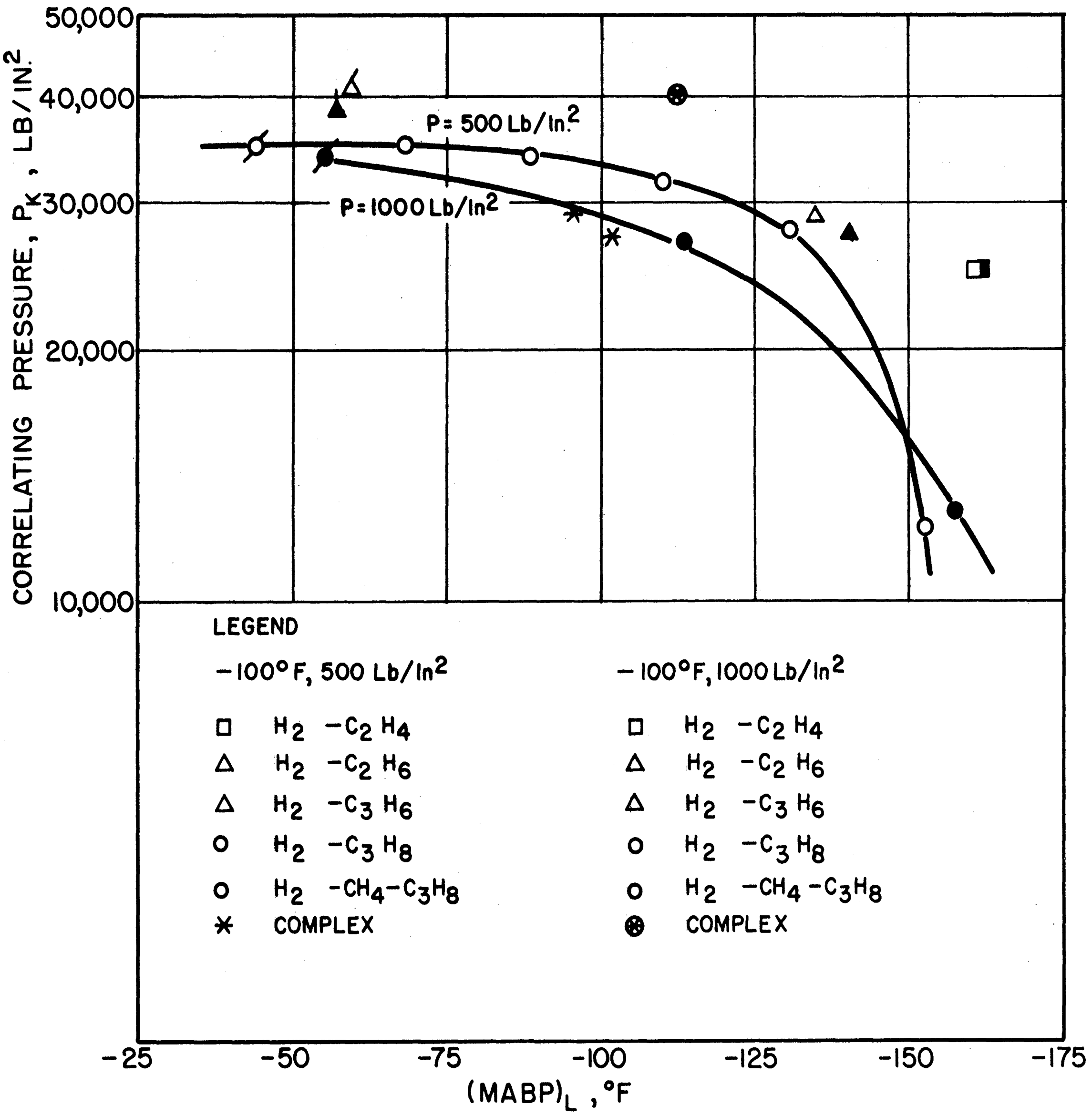

Figure 38. Convergence Pressure for Hydrogen-Light Hydrocarbon Systems as a Function of Liquid Molal Average Boiling Point.

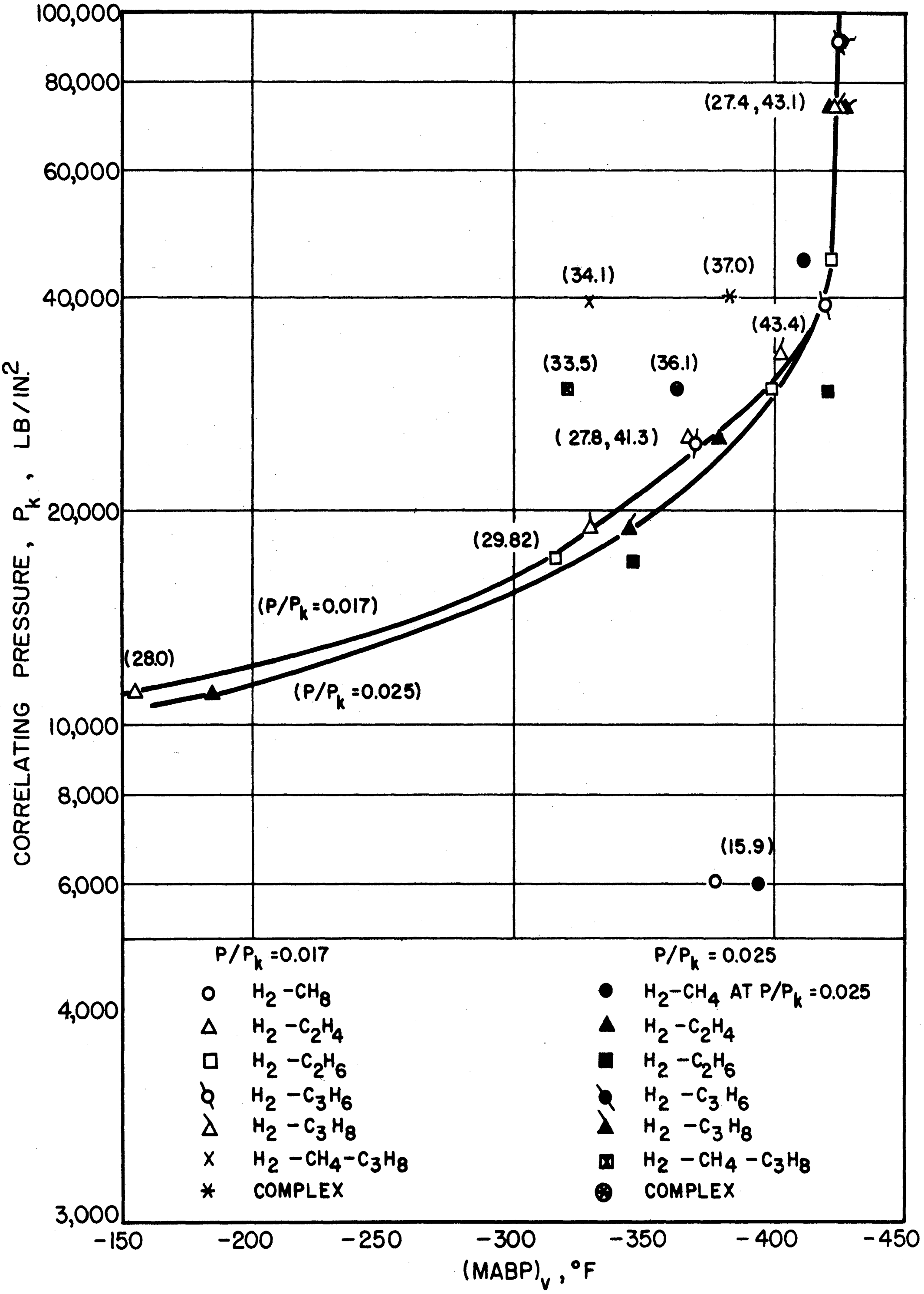

Figure 39. Convergence Pressure for Hydrogen-Light Hydrocarbon Systems as a Function of Vapor Molal Average Boiling Point.

propane and points for the complex systems have been included. The errors estimated for the prediction of the hydrogen equilibrium constant in complex systems were from 15 to 44 per cent.

Since a further examination of methods of correlation using the temperature, pressure, and two concentration variables did not uncover any satisfactory correlation of the results obtained from the six-component study with those obtained from the study of binary and ternary systems, it has been asserted that at least one and possibly two more phase rule variables will be required for a good correlation. In order to obtain a good correlation using five or six variables, more complex system data will be required. Examination of this new data may then reveal more about the feasibility of a generalized correlation involving fewer variables than required by the phase rule.

Since some good correlations using temperature, pressure, and two concentration variables have been made to describe paraffinic hydrocarbon systems, some explanation for the non-existence of a good correlation using these variables for the hydrogen-light hydrocarbon systems appears necessary. A partial explanation can be found in the fact that a dissimilarity of behavior exists in the components classed as hydrogen, methane, saturated hydrocarbons and unsaturated hydrocarbons.

IV. SUMMARY AND CONCLUSIONS

The following is a summary of investigations pursued and results or conclusions arrived at during the course of this study.

1. The hydrogen-methane system was studied experimentally at temperatures of -150, -200, and -250°F and at pressures from 500 to 4000 lb/in.^{2}. It was found that hydrogen exhibits reverse order solubility over the whole range of temperatures and pressures except near the vapor pressure of methane.

2. The hydrogen-methane-propane system was studied experimentally at temperatures of 0, -100, and -200°F and at pressures of 500 and 1000 lb/in.^{2}.

3. The hydrogen-methane-propylene system was studied experimentally at -100°F and 500 lb/in.^{2}.

4. Five data points were obtained for the complex system containing hydrogen, methane, ethylene, ethane, propylene and propane covering the conditions of 0 and -100°F and 500 and 1000 lb/in.^{2}.

5. The equilibrium constants for hydrogen in the hydrogen-methane system were correlated by a fugacity relationship used by Williams (44) to describe hydrogen-hydrocarbon binary systems.

6. The equilibrium constants for hydrogen, methane, and propane in the hydrogen-methane-propane system have been correlated as functions of the temperature, pressure, and the molal average boiling point of the liquid phase.

7. The equilibrium constants for ethylene, ethane, propylene and propane occurring in their hydrogen-methane ternary systems have been correlated by nomographs as functions of the temperature, pressure and molal average boiling point of the liquid phase.

8. A correlation involving the use of the temperature, pressure, molal average boiling point of the liquid and the mole per cent hydrogen in the vapor phase has been developed which describes the equilibrium

constants for hydrogen in the hydrogen-methane-propane system and in the hydrogen-methane-ethylene system with an average per cent deviation of ± 3.3% and a standard deviation of <u>1.4%</u>.

9. A correlation involving the use of the temperature, pressure, molal average boiling point of the liquid, and the molal average boiling point of the vapor has been developed which describes the equilibrium constants for methane in the hydrogen-methane-propane system and in the hydrogen-methane-ethylene system with an average deviation of ± 6.8% and a standard deviation of <u>0.088%</u>.

10. The six-component system made up of hydrogen, methane, ethylene, ethane, propylene and propane was not adequately described by the variables of temperature, pressure and the molal average boiling point of the liquid and vapor phases.

11. Since a further examination of methods of correlation using the temperature, pressure and two concentration variables did not uncover any satisfactory correlation of the six-component results with the binary and ternary systems' results, it has been asserted that at least one, and possibly two more, phase rule variables will be required. In order to obtain a good correlation using five or six variables, more complex system data will be required. Examination of this new data may then reveal more about the feasibility of a generalized correlation involving fewer variables than required by the phase rule.

12. Some explanation for the non-existence of a good correlation for the hydrogen-light hydrocarbon systems involving the use of temperature, pressure and two concentration variables appears necessary in view of some good correlations using the same variables for description of paraffinic hydrocarbon systems. A partial explanation is the dissimilarity of the behavior of the components which may be classed as hydrogen, methane, saturated hydrocarbons and unsaturated hydrocarbons.

APPENDIX A

PROCEDURE

A. Preparation

The first step in preparing the equipment for a run was to begin cooling the constant temperature bath and the equilibrium cell. Regardless of the desired final temperature, the first cooling was always done by placing crushed dry ice into the bath. The circulating fan was turned on. If temperatures below -100°F were to be investigated, then after a temperature of about -80°F was reached, liquid nitrogen was used to cool the bath. When the desired temperature was reached, the flow of liquid nitrogen was controlled by the Brown Recorder Controller to maintain the desired temperature. The cooling process normally took four to eight hours before the desired temperature could be obtained and maintained. During this time the cell could be flushed and evacuated and hydrocarbon could be put in for the next run.

B. Operation of Equipment

The equilibrium cell used for obtaining the data for this thesis was a blind cell. Since it was not possible to determine the location of the liquid level in the cell, it was necessary to make some preliminary assumptions about the solubilities and volatilities of the constituents and to put in a measured amount of hydrocarbon into the cell. The amount of hydrocarbon which was put into the cell was particularly critical in cases where the hydrocarbon was highly volatile such as is the case for the methane-hydrogen system. Before making a run, the system was alternately evacuated and flushed with the hydrocarbon that was to be used in that run. Two methods were used to measure the amount of hydrocarbon put into the system. When the vapor pressure of the hydrocarbon was less than about 150 lb/in.^{2}, the method used was to maintain the cell at some temperature less than room temperature, where condensation at some moderate pressure occurred, and put in hydrocarbon until the pressure in the system exceeded the vapor pressure expected at the cell temperature. When this occurred the cell was assumed to be completely full of liquid. Then the hydrocarbon was bled off through a wet test meter until a predetermined amount of it remained in the cell.

The second method involved measuring the hydrocarbon as a gas in the pressure generation equipment. The oil reservoir was calibrated in cubic centimeters so that by filling the cylinder C in Figure 1 with gas, and then carrying out the compression process and injecting the gas into the cell and circulation system, the amount of hydrocarbon added to the system could be calculated knowing the room temperature, the pressure in the compression cylinder at the beginning and end, and the volume of oil pumped into the compression system (this volume would be equivalent to the volume of gas transferred).

After the hydrocarbon had been transferred into the system, hydrogen was added until the desired pressure was obtained. Now the circulating pump was started so as to obtain a contacting of the vapor and liquid. As this occurred, the pressure usually dropped, and more hydrogen would have to be added to the system. The pumping rate was usually regulated at around 25 strokes/minute.

C. Equilibrium

The temperature and pressure were maintained over the period of time required to obtain equilibrium between the liquid and vapor. It was determined that constancy of pressure was not a good criterion of equilibrium. In order to assure equilibrium between the liquid vapor, it was found necessary to obtain samples at successive intervals of time and to obtain an analysis of them. When successive samples showed nearly identical analysis, it was assumed that equilibrium had been reached. It was further found that the liquid phase approached the equilibrium composition much slower than the vapor phase. The amount of time required to obtain equilibrium varied from two to eight hours. The criterion of equilibrium was taken as that of the consistency of the analytical procedure. This was usually around 1/2 per cent.

D. Sampling

The following procedure was used to obtain liquid samples for analysis:

a. The sampling system was evacuated to about one mm of Hg pressure.

b. The sample valve was opened slightly until the sampling system including the sample bulbs was filled to one atmosphere pressure with sample and was then closed.

c. The valve leading to the vacuum pump was opened and the system was evacuated.

A sample was taken only after this procedure had been carried out five times, thus insuring a complete flushing of the sampling lines.

The procedure for taking a vapor sample varied from that for liquid only in the number of flushings required. The bulbs were filled only once for a vapor sample and then were re-evacuated and filled for analysis.

E. Analysis

Analysis of the binary system hydrogen-methane was carried out in three different ways. A semi-quantitative analysis was made using the Gow-Mac thermal-conductivity meter. This method was used only as a check on equilibrium. The reference side of the conductivity cell was purged with pure methane at a rate of about 200 cc/min while the other side of the cell was filled to one atmosphere with the sample. The current through the bridge was adjusted to 200 ma and after allowing the instruments to stabilize, the unbalance in the bridge was read on a Leeds-Northrup potentiometer. The thermo-conductivity meter proved to be very useful for indicating the equilibrium for binary systems, but it was found to be unreliable for indicating the equilibrium of ternary mixtures.

A second method of analysis for the binary system was by density determination. The procedure for doing this has been adequately described by Aroyan (3).

The majority of the analyses for this work were carried out using the CEC 21-103B analytical mass spectrometer.

F. Calibration of Instruments

Before any experimental data were obtained, the three pressure gages were calibrated using a dead-weight tester. The calibrations are given in Table XVIII.

The three-junction thermocouple No. 6 used to indicate the temperature in the cell was calibrated previous to obtaining data. It was connected to a K-2 Leeds-Northrup potentiometer which had been calibrated by Bureau of Standards. The thermocouple was calibrated by comparison with a platinum resistance thermometer connected to a Mueller Bridge. The resistance thermometer had been previously calibrated by the Bureau of Standards and was described as having an accuracy of

TABLE XVIII

CALIBRATION OF PRESSURE GAGES

Actual Pressure lb/in.^{2}	Gage Reading lb/in.^{2}	
	Up	Down
Gage No. C2-467		
100	102	102
200	202	202
300	303	305
400	407	408
450	458	459
500	509	509
550	560	560
Gage No. C2-444		
500	505	515
750	750	760
1000	1005	1015
1250	1255	1265
1500	1505	1515
1750	1760	1770
2000	2020	2020
2250	2265	2270
2500	2510	2520
2750	2765	2770
Gage No. C2-529		
500	520	540
1000	975	1000
2000	1950	1970
3000	2925	2950
4000	3940	3980
5000	4950	4970
6000	5950	5960
7000	6960	6960

±0.02°F. Three temperatures were used for the calibration. They were approximately 32°F as produced by an ice-water mixture contained in a Dewar flask; -120°F as produced by a dry ice-acetone mixture; and -320°F as produced by boiling liquid nitrogen. The following table gives the exact temperatures as obtained from the resistance thermometer and the emf's as measured from the three-junction thermocouple.

Temperature, °F, Platinum Resistance Thermometer	emf mv	emf Tables	Δ(emf)
+32.06	0.0000	0.0009	0.0009
-119.29	8.6560	8.6553	+0.0107
-109.93	8.1945	8.1843	+0.0107
-320.44	16.520	16.418	+0.102

A plot of the voltage difference, ΔE, between the thermocouple value and the standard value (2) is shown in Figure 40 as a function of E. This plot was then used to obtain the emf for intermediate temperatures.

The potentiometer which was used to measure the emf of the thermocouples was calibrated against the K-2 potentiometer mentioned above. It did not give any measurable error.

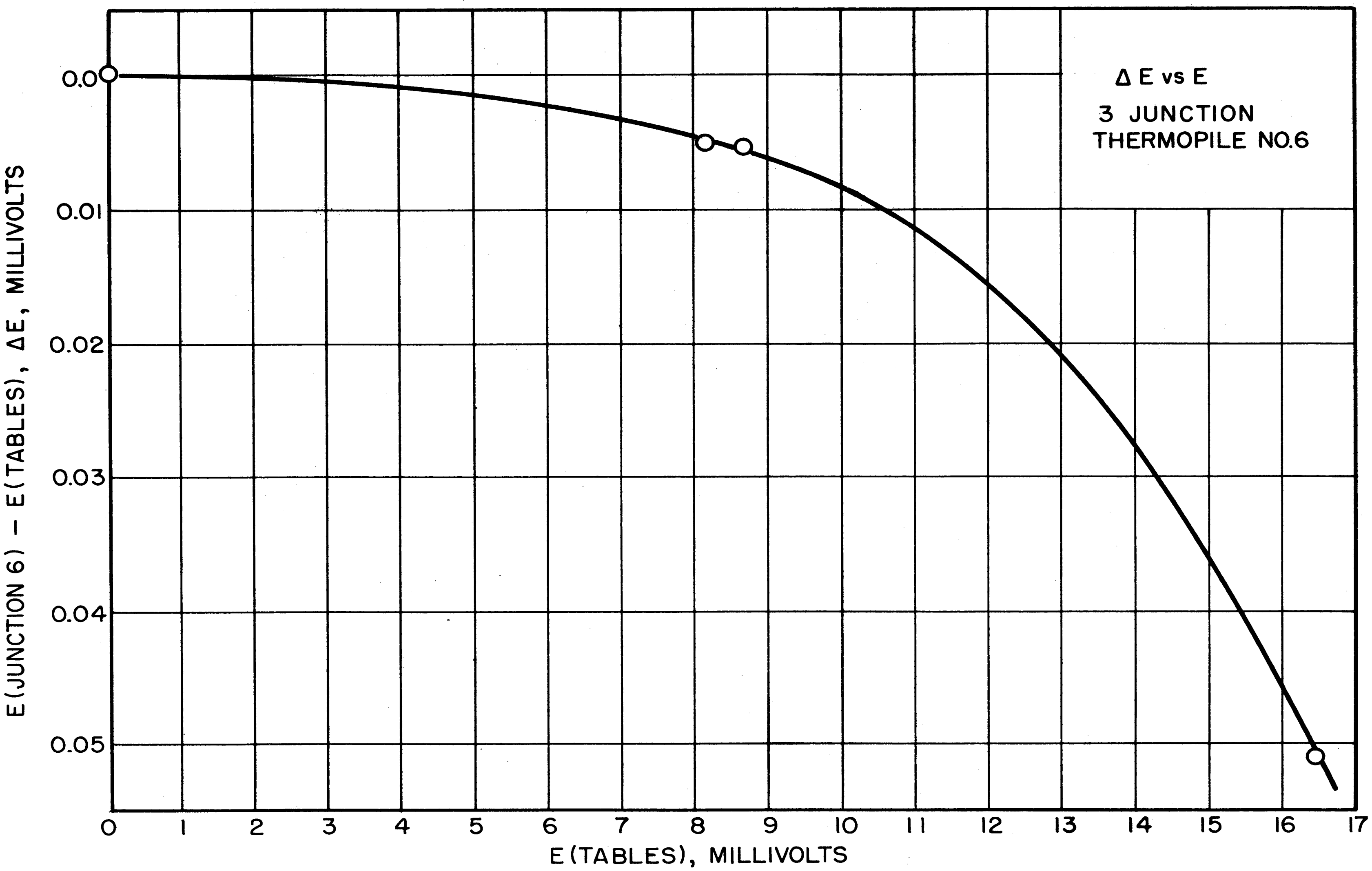

Figure 40. Error in emf for Thermopile No. 6

APPENDIX B

ANALYSIS USING THE MASS SPECTROMETER

A mass spectrometer is an instrument in which gaseous molecules at low pressure are first fragmented, ionized, and sorted into groups according to their mass to charge ratios (m/e) and are then measured according to their relative abundance.

The molecules are fragmented and ionized positively by a stream of electrons, and the ions are then accelerated by an electrostatic force and deflected in a magnetic field where they are caused to pass through a circular path with a five-inch radius. For a given accelerating voltage and magnetic field, only those ions possessing a very small range of m/e will traverse the five-inch radius; the rest will be grounded on the side of the tube. The ions which traverse the five-inch bend in the analyser tube are collected on a plate where they give up their charge. The current obtained from the collector is a measure of the abundance of these ions. This current is amplified and recorded. A whole spectrum of the ions may be obtained by varying the accelerating voltage from a high value down to a low one, maintaining a constant magnetic field.

The CEC 21-103B mass spectrometer requires only about 0.3 cc of gas at standard conditions for analysis. This gas is put into a three liter volume from which it passes into the analyzer tube assembly through a small leak. A very sensitive micromanometer is used to obtain the pressure of the gas sample in the inlet sample volume. The inlet pressure is commonly from 30 to 50 microns. The abundance of ions of a certain m/e as indicated in the recorder system, is in direct proportion to the pressure in the inlet volume.

From this result, we can make the following definition: that the abundance of a certain m/e, as indicated by the recording system, divided by the partial pressure of the pure substance in the inlet system yielding that m/e, is defined as the sensitivity of that substance for that value of m/e.

A photographic record of the relative abundance of ions with certain mass to charge ratios (m/e) is obtained from the CEC 21-103B mass spectrometer. An example of this record is given in Figure 41. The relative heights of the peaks representing abundance of a certain m/e compared to any one of the peaks selected as a reference is called the cracking pattern. For each pure substance there is a unique cracking pattern which serves to distinguish it from any other substance. Even different molecules having the same molecular weight may be distinguished by their individual cracking patterns. An m/e equal to the molecular weight of a substance represents the molecule with a single positive charge. Typical cracking patterns for some light hydrocarbons are given in Table XIX.

The mass spectrometer is constructed in such a way that the cracking pattern for a certain molecular species does not change if it exists in a mixture with a different specie. Also the sensitivity of a given m/e for a given molecular species does not change if it exists in a mixture. Using this information, we can analyze a mixture of substances.

For an example of the calculation of the analysis of a mixture, let us consider a mixture of three substances, A, B, and C. These substances have been previously run in the mass spectrometer and were found to have the following cracking patterns and sensitivities:

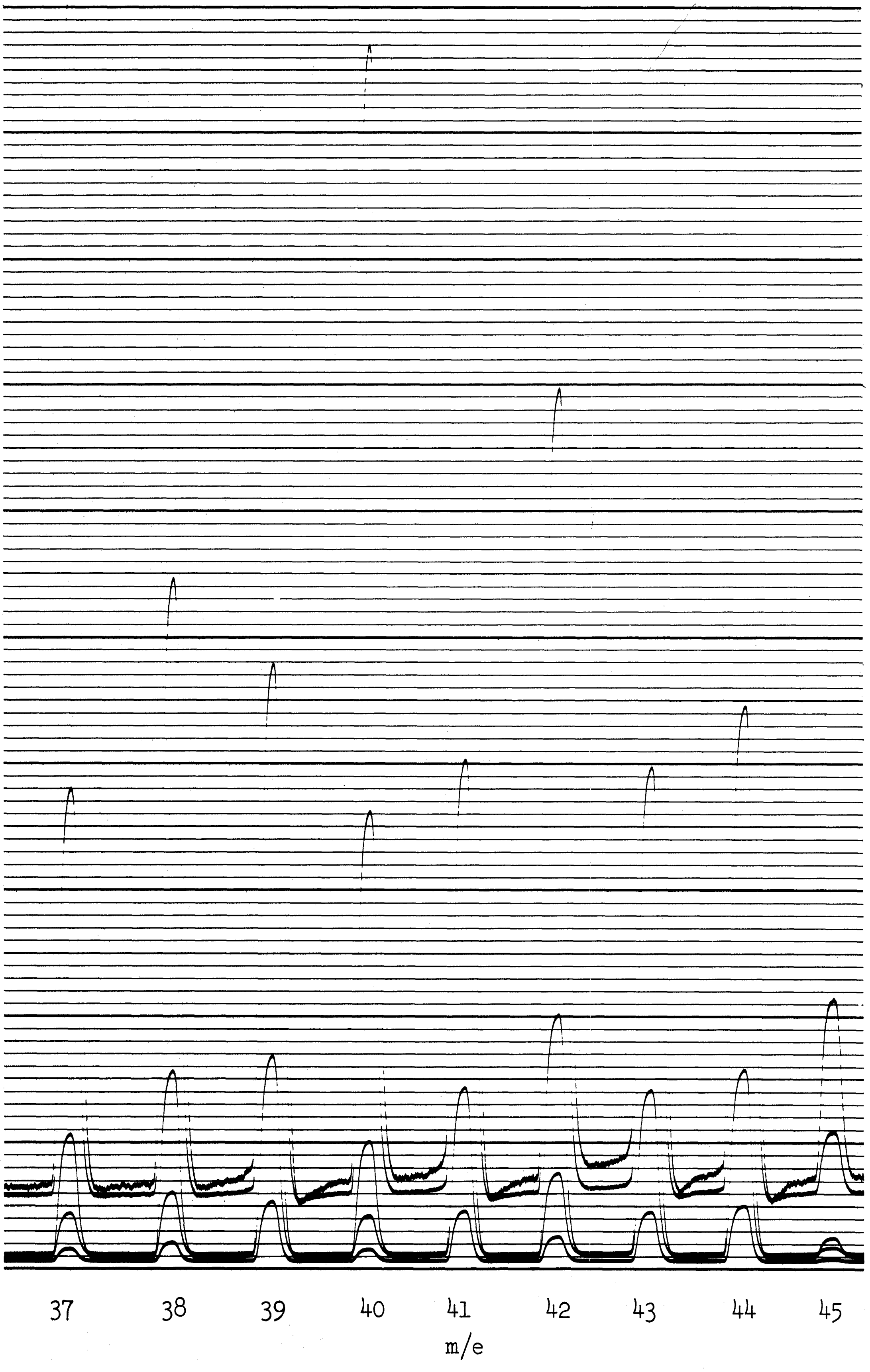

Figure 41. Example of a Mass Spectrometer Photographic Record.

TABLE XIX

CRACKING PATTERNS OBTAINED FROM MASS SPECTROMETER

m/e	H_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
2	1.0	0.002	0.005	0.003	0.004	0.0014
15		0.86	0.0056	0.0457	0.054	0.0619
16		1.00		0.0008	0.0016	0.0015
26			0.623	0.23	0.105	0.0859
28			1.00	1.00	0.0134	0.591
29			0.0222	0.217		1.00
30				0.262		0.022
41					1.00	0.127
42					0.677	0.0582
44					0.0003	0.290

m/e	A	B	C
2	0.1	0.04	1.0
16	0.2	1.0	0.0
44	1.0	0.0	0.0

Sensitivity of A for m/e of 44 is 15
Sensitivity of B for m/e of 16 is 50
Sensitivity of C for m/e of 2 is 20

We obtain the following results from the mass spectrometer for a mixture of the three:

m/e	Peak
2	545
16	780
44	150

Substances A, B, and C all contribute to the peak of m/e = 2. It is assumed that their effects are additive so that we may write the following equation for the peak value where P_A, P_B and P_C are respectively the partial pressures of A, B, and C, in the inlet volume.

$$545 = P_A S_A\ 0.1 + P_B S_B\ 0.04 + P_C S_C\ 1.0 \tag{26.1}$$

or

$$545 = P_A\ (15)(0.1) + P_B\ (50)(0.04) + P_C\ (20)(1.0). \tag{26.2}$$

Also for the 16 peak

$$780 = P_A\ (15)(0.2) + P_B\ (50)(1.0) + P_C\ (20)(0.0)\ , \tag{26.3}$$

and for the 44 peak,

$$150 = P_A\ (15)(1.0) + P_B\ (50)(0.0) + P_C\ (20)(0.0)\ . \tag{26.4}$$

$$545 = 1.5P_A + 2P_B + 20P_C \ , \qquad (26.5)$$

$$780 = 3P_A + 50P_B \ , \qquad (26.6)$$

$$150 = 15P_A \ . \qquad (26.7)$$

Solving these equations simultaneously, we get the following results:

P_A	=	10 microns or	20 mol per cent
P_B	=	15 "	30 "
P_C	=	25 "	50 "
		$\overline{50}$	$\overline{100}$.

The accuracy of the analysis depends upon the stability of the instrument and the purity of the standards. The limiting accuracy of the instrument has been calculated as 0.2 per cent of component composition, but in practice a prohibitive amount of work may be required to obtain such accuracy.

Extra care was taken in obtaining the analysis for this work. A standard mixture of the gases to be analyzed was made up, and this mixture was analyzed each time a number of samples were analyzed. This information was used to correct for the changes in sensitivity which sometimes occurred daily. The following samples (Table XX) were made up and analyzed during the course of this investigation, and it is believed that they represent the accuracy obtained in the analysis of results.

TABLE XX

CHECK OF ANALYSIS BY MASS SPECTROMETER

	Actual Composition mol %	Composition by M.S. mol %
Mix A		
H_2	61.51	61.31
CH_4	22.69	22.82
C_3H_8	15.80	15.88
Mix B		
H_2	1.30	1.29
CH_4	46.05	46.03
C_3H_8	52.65	52.69
Mix C		
H_2	42.88	42.59
CH_4	15.73	15.85
C_2H_4	30.19	30.22
C_3H_8	11.30	11.34

APPENDIX C

EXHIBITS

TABLE IX

SMOOTHED DATA FOR HYDROGEN-METHANE DATA

Temp. °F	Press. lb/in.^{2}	Phase Compositions		Equlib. Constants K = y/x	
		Vapor Mole % H_2	Liquid Mole % H_2	H_2	CH_4
-150	500	17.9	1.69	9.32	0.857
-150	1000	40.6	8.76	4.64	0.651
-150	1250	43.0	11.7	3.66	0.616
-150	1500	46.8	16.2	2.88	0.636
-200	500	63.9	3.43	18.6	0.372
-200	1000	76.2	7.81	9.75	0.258
-200	1500	79.5	13.0	6.11	0.239
-200	2000	71.0	21.1	4.22	0.265
-200	2500	76.0	25.4	3.00	0.324
-200	3000	74.6	35.0	2.14	0.392
-250	250	90.1	1.60	56.5	0.100
-250	500	93.2	3.26	28.6	0.0730
-250	1000	94.9	6.49	14.6	0.057
-250	1500	94.6	9.50	9.96	0.0586
-250	2000	94.1	12.4	7.62	0.0655
-250	2500	93.6	15.0	6.22	0.0760
-250	3000	92.8	17.9	5.19	0.0856
-250	4000	92.9	31.7	2.93	0.104

TABLE X

SMOOTHED DATA FOR HYDROGEN-METHANE-PROPANE SYSTEM

Composition Liquid Phase mol %			Composition Vapor Phase mol %			Equilibrium Constants K = y/x			MABP$_L$ °F
H_2	CH_4	C_3H_8	H_2	CH_4	C_3H_8	H_2	CH_4	C_3H_8	
Temperature = 0°F, Pressure = 500 lb/in.^{2}									
0.00	27.2	72.8	0.00	88.0	12.0	--	3.24	0.165	-102
0.21	24.8	75.0	6.0	82.2	11.8	28.4	3.31	0.158	-98
0.70	19.3	80.0	20.0	68.7	11.3	28.6	3.56	0.141	-88
1.18	13.8	85.0	36.5	52.8	10.7	30.9	3.82	0.126	-78
1.62	8.38	90.0	55.2	34.6	10.2	34.1	4.13	0.113	-68
2.08	2.92	95.0	78.0	12.4	9.6	37.5	4.25	0.101	-58
2.30	0.00	97.7	90.7	0.0	9.3	39.5	--	0.095	-53
Temperature = -100°F, Pressure = 500 lb/in.^{2}									
0.00	58.2	41.8	0.0	98.8	1.24	--	1.69	0.0297	-169
0.47	49.5	50.0	14.9	83.9	1.21	31.7	1.69	0.0241	-152
0.76	39.2	60.0	33.9	64.9	1.16	44.6	1.65	0.0194	-131
0.99	29.0	70.0	53.2	45.7	1.12	54.0	1.57	0.0160	-110
1.20	18.8	80.0	72.0	26.9	1.08	60.2	1.43	0.0135	-89
1.39	8.64	90.0	87.5	11.5	1.04	63.0	1.33	0.0115	-68
1.50	0.00	98.5	99.0	0.0	1.0	66.0	--	0.0102	-49
Temperature = -200°F, Pressure = 500 lb/in.^{2}									
3.43	96.57	0.0	63.9	36.1	0.0	18.6	0.374	--	-265
3.12	86.9	10.0	67.0	32.8	0.25	21.5	0.377	0.025	-243
2.8	77.2	20.0	70.6	29.0	0.45	25.2	0.375	0.023	-221
2.5	67.5	30.0	74.2	25.2	0.60	29.7	0.374	0.020	-199
2.2	57.8	40.0	78.0	21.4	0.65	35.4	0.370	0.016	-177
1.9	48.1	50.0	81.6	17.8	0.65	43.0	0.369	0.013	-155
1.65	38.4	60.0	85.2	14.2	0.65	51.6	0.369	0.011	-133
1.4	28.6	70.0	89.0	10.4	0.60	63.5	0.364	0.0086	-111
1.2	18.8	80.0	92.6	6.85	0.55	77.1	0.364	0.0070	-89
1.0	9.0	90.0	96.2	3.35	0.45	96.2	0.372	0.0050	-67
0.86	0.0	99.14	99.7	0.0	0.30	116.0	---	0.0030	-47

TABLE X (cont.)

Composition Liquid Phase mol %			Composition Vapor Phase mol %			Equilibrium Constants K = y/x			MABP$_L$ °F
H_2	CH_4	C_3H_8	H_2	CH_4	C_3H_8	H_2	CH_4	C_3H_8	
Temperature = 0°F, Pressure = 1000 lb/in.^{2}									
2.0	33.0	65.0	25.6	66.1	8.35	12.8	2.00	0.129	-122
2.48	27.5	70.0	38.2	54.0	7.79	15.4	1.96	0.111	-112
2.90	22.1	75.0	50.1	42.6	7.28	17.3	1.93	0.097	-102
3.38	16.6	80.0	61.3	31.9	6.80	18.1	1.92	0.085	-92
3.83	11.2	85.0	72.6	21.0	6.42	19.0	1.88	0.076	-82
4.30	5.7	90.0	83.7	10.2	6.11	19.5	1.79	0.068	-72
4.75	0.0	95.25	94.1	0.0	5.92	19.8	--	0.062	-62
Temperature = -100°F, Pressure = 1000 lb/in.^{2}									
4.00	66.0	30.0	35.8	59.7	4.48	8.95	0.905	0.149	-201
3.55	56.5	40.0	45.1	51.3	3.6	12.7	0.909	0.090	-179
3.32	46.7	50.0	54.6	42.6	2.78	16.5	0.912	0.056	-157
3.20	36.8	60.0	64.2	33.7	2.06	20.2	0.916	0.034	-135
3.10	26.9	70.0	73.9	24.6	1.48	23.8	0.916	0.021	-113
3.03	17.0	80.0	83.2	15.8	1.02	27.5	0.930	0.013	-92
3.02	7.0	90.0	93.0	6.24	0.76	30.8	0.895	0.0085	-70
3.02	0.0	96.98	99.3	0.0	0.69	32.8	--	0.0071	-55
Temperature = -200°F, Pressure = 1000 lb/in.^{2}									
7.81	92.19	0.0	76.2	23.8	0.0	9.75	0.259	--	-272
6.22	83.8	10.0	79.0	20.9	0.12	12.7	0.250	0.012	-248
4.88	75.1	20.0	82.0	17.8	0.20	16.8	0.237	0.01	-224
3.80	66.2	30.0	84.6	15.2	0.25	22.3	0.229	0.0083	-201
3.00	57.0	40.0	87.0	12.7	0.26	29.0	0.224	0.0065	-178
2.53	47.5	50.0	89.2	10.5	0.26	35.2	0.222	0.0052	-156
2.22	37.8	60.0	91.4	8.36	0.24	41.1	0.222	0.0040	-134
1.98	28.0	70.0	93.6	6.18	0.22	47.3	0.22	0.0031	-112
1.80	18.2	80.0	95.8	4.02	0.18	53.2	0.221	0.0022	-90
1.68	8.32	90.0	98.0	1.85	0.15	58.3	0.222	0.0017	-68
1.63	0.0	98.37	99.9	0.0	0.1	61.3	--	0.0010	-50

TABLE XI

SMOOTHED DATA FOR HYDROGEN-METHANE-PROPYLENE SYSTEM

Composition Liquid Phase mol %			Composition Vapor Phase mol %			Equilibrium Constants K = y/x		
H_2	CH_4	C_3H_6	H_2	CH_4	C_3H_6	H_2	CH_4	C_3H_6
Temperature = -100°F, Pressure = 500 lb/in.^{2}								
0.30	59.7	40.0	4.2	94.1	1.70	14.0	1.58	0.043
0.80	49.2	50.0	18.3	80.0	1.65	22.8	1.63	0.033
1.01	39.0	60.0	33.8	64.6	1.56	33.5	1.66	0.026
1.14	28.9	70.0	50.0	48.1	1.49	43.9	1.66	0.021
1.23	18.7	80.0	66.5	32.1	1.40	54.1	1.72	0.018
1.30	8.7	90.0	83.8	14.9	1.33	64.5	1.71	0.015
1.36	0.0	98.64	98.72	0.0	1.28	72.6	--	0.013

TABLE XIII

(MABP)$_L$ - (MABP)$_V$ CORRELATION OF METHANE EQUILIBRIUM CONSTANTS

	0°F	-100°F	-125°F	-150°F	-175°F	-200°F
(MABP)$_L$ °F	Equilibrium Constants, K' = y/x at T Pressure = 500 lb/in.^{2}					
-60	6.5	1.50	1.09	0.75	0.54	0.365
-90	4.8	1.71	1.24	0.876	0.58	0.366
-120	3.6	1.85	1.40	0.99	0.63	0.367
-150		1.94	1.46	1.005	0.65	0.368
-170		1.87	1.424	1.001	0.65	0.370
-190		1.75	1.34	0.965	0.64	0.372
-210		1.63	1.29	0.919	0.63	0.373
-230		1.50	1.175	0.872	0.61	0.375
(MABP)$_V$ °F	Correction Factors, C = K/K' at T Pressure = 500 lb/in.^{2}					
-200	0.805					
-225	0.75	0.98				
-250	0.71	0.94				
-275	0.682	0.91	0.99			
-300	0.668	0.892	0.939	1.03		
-325		0.88	0.91	0.99		
-350		0.865	0.899	0.96	1.006	
-375		0.855	0.889	0.94	0.99	1.00
-400		0.850	0.88	0.925	0.98	1.00
-425			0.875	0.915	0.975	1.012

TABLE XIII (cont.)

	0°F	-100°F	-125°F	-150°F	-175°F	-200°F
$(\text{MABP})_L$ °F	Equilibrium Constant, K' = y/x at T Pressure = 1000 lb/in.^{2}					
-60	1.45	0.80	0.60	0.476	0.329	0.213
-90	1.62	0.809	0.612	0.48	0.331	
-120	1.82	0.823	0.625	0.485	0.339	
-150		0.846	0.648	0.49	0.348	0.22
-170		0.868	0.652	0.498	0.355	
-190		0.905	0.685	0.515	0.370	
-210		0.950	0.739	0.55	0.396	0.235
-230		1.05	0.819	0.61	0.43	0.242
$(\text{MABP})_V$ °F	Correction Factor, C = K/K' at T Pressure = 1000 lb/in.^{2}					
-200	0.875					
-300	1.115					
-320		1.005				
-340		1.05	1.01			
-360		1.08	1.05	1.01		
-380		1.105	1.08	1.05	0.955	0.91
-400	1.25	1.12	1.10	1.082	1.045	1.005
-420		1.135	1.11	1.098	1.08	1.042

TABLE XIV

(MABP)$_L$ - yH_2 CORRELATION OF HYDROGEN EQUILIBRIUM CONSTANTS

(MABP)$_L$ °F	0°F	-50°F	-100°F	-150°F	-200°F
Equilibrium Constant, $K'H_2$ = y/x at T					
Pressure = 500 lb/in.^{2}					
-60	29.5	41.0	59.0	80	111
-90	28.8	42.0	65.0	86	113
-120	25.0	39.5	60.0	82.5	105
-150	18.5	31.0	48.5	67.0	97.0
-170		23.8	38.0	57.5	92.0
-190			29.0	49.0	86.5
-210			21.5	41.5	81.5
-250				29.5	71.5
Correction Factor, C = K/K' at T					
yH_2 mol % H_2 — Pressure = 500 lb/in.^{2}					
0	0.95	0.76	0.60	0.24	
20	1.02	0.85	0.68	0.37	
40	1.10	0.94	0.76	0.50	
60	1.19	1.04	0.86	0.64	
80	1.28	1.15	0.99	0.80	0.42
90	1.34	1.22	1.08	0.91	0.61
95	1.39	1.28	1.14	0.99	0.77
100					1.02

TABLE XIV (cont.)

$(MABP)_L$ °F	0°F	-50°F	-100°F	-150°F	-200°F
Equilibrium Constant, K'_{H_2} = y/x at T					
Pressure = 1000 lb/in.^{2}					
-60	17.0	22.0	30.0	41.5	60.5
-90	15.6	20.8	28.5	40.0	61.0
-120	13.3	18.5	26.0	37.5	58.0
-150	10.2	15.2	23.0	33.5	52.5
-170	8.0	12.6	19.8	30.2	48.5
-190	6.1	10.2	16.8	26.8	44.0
-210			14.0	23.0	40.0
-250			9.8	16.5	32.3
Correction Factor, C = K/K' at T					
y_{H_2} Pressure = 1000 lb/in.^{2} mol % H_2					
0	0.85				
20	0.92	0.63	0.45		
40	0.99	0.80	0.64	0.27	
60	1.05	0.93	0.81	0.55	
80	1.11	1.05	0.97	0.81	0.40
90					0.70
95					0.86
100	1.16	1.12	1.08	1.03	1.01

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