

# Phase Behavior of Hydrogen-light-hydrocarbon Systems

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The decreasing solubility of hydrogen in hydrocarbons with decreasing temperature continues down to the freezing point of the hydrocarbons, around  $-300^{\circ}\text{F}$ . This behavior is shown to be an enlargement of phenomena exhibited by normal hydrocarbon mixtures. Methods of predicting equilibrium-phase compositions are presented for hydrogen in light-hydrocarbon systems. The correlations are satisfactory for binary and certain ternary systems, but are not reliable for complex mixtures.

The phase behavior of hydrogen-hydrocarbon systems is interesting because of the need for predicting their behavior in processing operations and because of the unusual region of reverse-order solubility described by Kay (11). This paper shows that the reverse-order solubility for hydrogen systems is different from that for hydrocarbon systems by only a matter of degree, no doubt because of the high volatility of the hydrogen. Methods of correlating vapor-liquid equilibria data (references in Table 1) are discussed for binary, ternary, and complex systems.

## REVERSE-ORDER AND NORMAL SOLUBILITY

In 1941 Kay (11) published some of the first results of a vapor-liquid-phase study of a hydrogen-hydrocarbon system, which show reverse-order solubility over a considerable range of temperatures and pressures. Reverse-order solubility is defined as the phenomenon occurring when the solubility of a constituent decreases with a decrease in temperature while all other variables are held constant.

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Aroyan (1) has shown that the hydrogen-hydrocarbon systems differ from normal phase behavior in degree but not in kind.

The ethane-*n*-heptane binary system (12) which may be taken as typical of many hydrocarbon systems, may be said to exhibit normal behavior. Reverse-order solubility occurs in the cross-hatched area (Figure 1) where the bubble-point portion of the phase envelope has a negative slope.

Figure 2 contains both the experimental pressure-temperature behavior of the hydrogen-methane system (3 and 4) and a hypothetical continuation of the phase envelopes drawn by comparison with the normal-type phase behavior. This figure shows that the region of negative slopes for bubble-point curves has been enlarged and reaches down to a temperature where the hydrocarbon separates as a solid phase. No vapor-liquid equilibria can be obtained in that portion of the phase envelope which would have a positive slope owing to the appearance of the solid phase. Thus hydrogen-hydrocarbon systems are different only to the extent that they have an enlarged region where reverse-order solubility occurs.

## GENERALIZED CORRELATION OF BINARY SYSTEMS

An expression first used by Krichevsky and Kasarnovsky (15) for extrapolating the solubility data of slightly soluble gases in liquids has been used to describe the solubility of hydrogen in light-hydrocarbon solvents. The expression as modified by Kobayashi and Katz (14) and applied in this work contains the assumption that the molal volume does not change with pressure and the approximation that the fugacity of a mixture of a liquid and a slightly soluble gas is predicted by a pseudo Henry's law constant,  $Q$

$$\log_{10} (f^{\circ}y/x)_2 = \log Q + \bar{V}_2 P / 2.303 RT \quad (1)$$

where

- $f_2^{\circ}$  = fugacity of hydrogen at  $T$  and  $P$
- $y_2$  = mole fraction of hydrogen in vapor phase
- $x_2$  = mole fraction of hydrogen in liquid phase
- $Q$  = modified Henry's-law constant at  $T$
- $\bar{V}_2$  = molal volume of hydrogen in liquid phase at  $T$
- $P$  = pressure of system
- $R$  = gas constant
- $T$  = temperature of system

This expression was used by Krichevsky and Kasarnovsky to predict the solubility of nitrogen in water up to 1,000 atm. pressure, by Wiebe and Gaddy (20) for carbon dioxide in water, and by Kobayashi and Katz (14) for hydrocarbons in water. Fastowsky and Gonikberg (9) used this expression for the description of their hydrogen-methane system.

An idealized description of the solubility behavior of a slightly soluble substance is shown in the sketch in Figure 3, which is a three-dimensional plot of the logarithm of  $f^{\circ}y/x$  as a function of  $P/2.303 RT$  and the temperature. The idealized case shown is for a substance displaying a molal volume which is a function of temperature only and which has a modified Henry's-law

TABLE 1. SOURCES OF HYDROGEN-HYDROCARBON EQUILIBRIUM DATA

System	Reference	Temperature range, $^{\circ}\text{F}$ .
Hydrogen-methane	(16)	-140 to -175
Hydrogen-methane	(9)	-230 to -298
Hydrogen-methane	(10)	-295 to -310
Hydrogen-methane	(3, 4)	-150 to -250
Hydrogen-ethylene	(17)	-120 to -175
Hydrogen-ethylene	(21, 22)	0 to -250
Hydrogen-ethane	(16)	-120 to -175
Hydrogen-ethane	(21, 22)	50 to -275
Hydrogen-propylene	(21, 22)	75 to -275
Hydrogen-propane	(21, 22)	75 to -300
Hydrogen-propane	(5)	40 to 190
Hydrogen-isobutane	(6)	100 to 250
Hydrogen- <i>n</i> -butane	(1, 2)	75 to -200
Hydrogen- <i>n</i> -butane	(18)	75 to 240
Hydrogen-methane-ethylene	(17)	-120 to -175
Hydrogen-methane-ethane	(16)	-120 to -175
Hydrogen-methane-propylene	(3, 4)	-100
Hydrogen-methane-propane	(3, 4)	0 to -200
Hydrogen-methane-ethylene-ethane-propylene-propane	(3, 4)	0 to -100

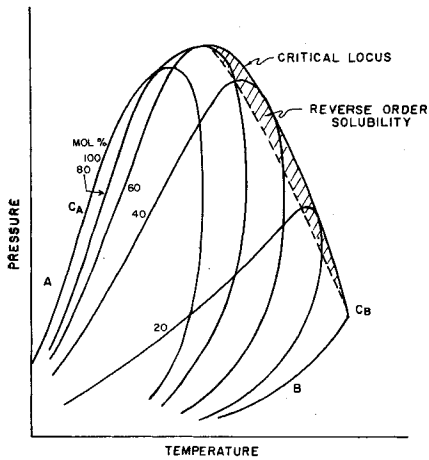


Fig. 1. Pressure-temperature phase behavior for the ethane-*n*-heptane system.

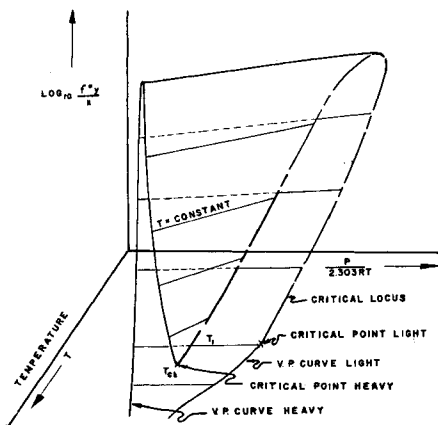


Fig. 3. Idealized behavior of a slightly soluble substance.

constant as is a function of temperature only. With these limitations Figure 3 would contain a family of straight lines having parameters of constant temperature, which in the three-dimensional figure result in a curved surface extending from the critical temperature of the heavy component down to lower limit of the coexistence of vapor and liquid for the particular system. At low temperatures (temperatures below the critical temperature of the slightly soluble component) the line extends between the vapor pressure of the two substances and will have a positive slope. For a temperature  $T_1$  equal to the critical temperature of the slightly soluble substance, the line will exist between the vapor pressure of the solvent and the critical pressure of the solute. Most substances show an increase in molal volume with an increase in temperature; therefore, the constant temperature lines in Figure 3 exhibit greater positive slopes at the higher temperature. The preceding analogy may be extended to higher temperatures up to the limit of the critical temperature of the solvent  $T_{C_2}$ , where a single point would be shown.

**TABLE 2. FUGACITY OF HYDROGEN**  
Fugacity, lb./sq. in. abs., at

Pressure, lb./sq. in. abs.	0°F.	-50°F.	-100°F.	-150°F.	-200°F.	-250°F.	-275°F.	-300°F.
250	252.5	252.8	252.8	252.8	252.5	251.0	249.4	247.0
500	510.5	511.0	512.0	511.0	510.0	504.5	499.5	489.5
1,000	1,044	1,046	1,049	1,049	1,045	1,025	1,007	972
2,000	2,186	2,196	2,208	2,216	2,204	2,154	2,094	1,994
3,000	3,441	3,468	3,498	3,525	3,522	3,459	3,369	3,213
4,000	4,816	4,872	4,940	5,012	5,036	5,004	4,908	4,720
5,000	6,320	6,435	6,555	6,675	6,785			
6,000	7,974	8,148	8,352	8,592	8,814			
7,000	9,779	10,120	10,370	10,770	11,100			
8,000	11,750	12,140	12,620	13,240				
10,000	16,310	17,060	17,950					

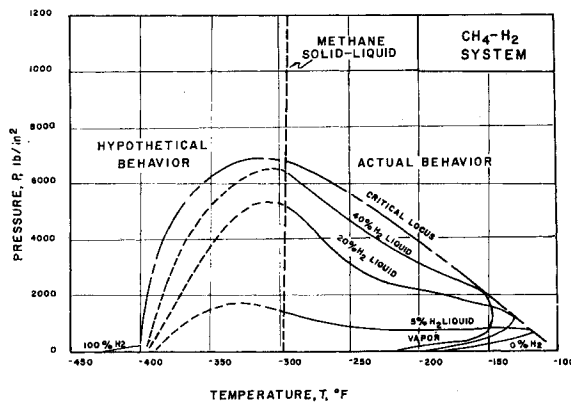


Fig. 2. Actual and hypothetical extension of pressure-temperature phase behavior for the hydrogen-methane system.

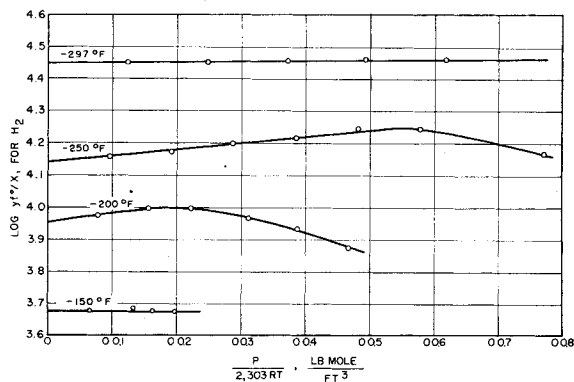


Fig. 4.  $K_f$  for hydrogen as a function of pressure for the hydrogen-methane system.

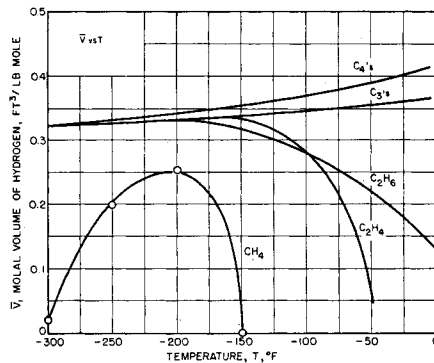


Fig. 5. Molal volume for hydrogen in the hydrogen-hydrocarbon system as a function of temperature.

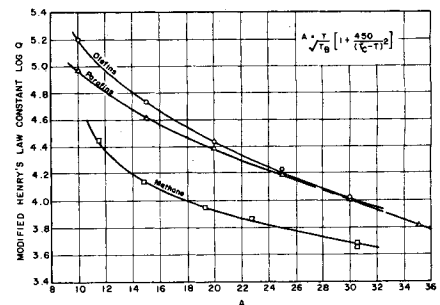


Fig. 6. Modified Henry's-law constant for hydrogen in the hydrogen-hydrocarbon system as a function of temperature.

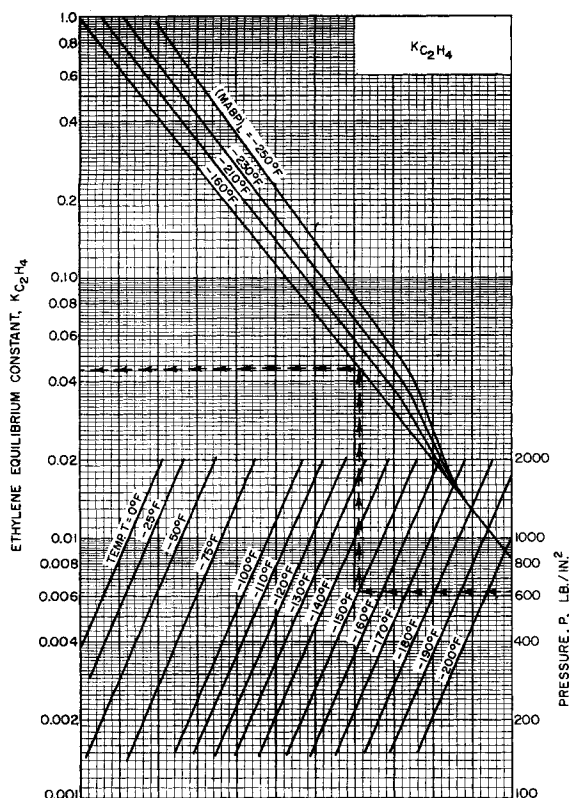


Fig. 7. Nomographic correlation of ethylene equilibrium constants in the hydrogen-methane-ethylene system.

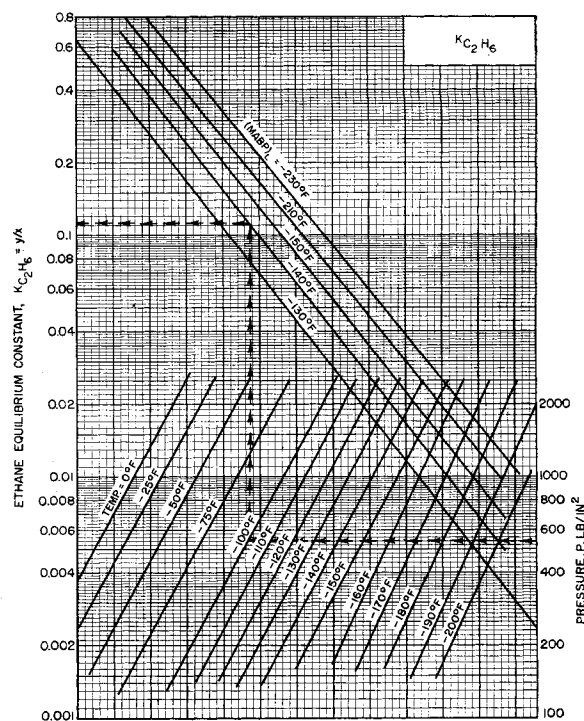


Fig. 8. Nomographic correlation of ethane equilibrium constants in the hydrogen-methane-ethane system.

Before the solubility relationship could be applied to hydrogen binary systems, it was necessary to have fugacity data for pure hydrogen. These data were obtained from Deming and Shupe (7) or were computed at low temperatures and high pressures (8, 21) from the compressibility data of Woolley et al. (23). Since these fugacity values do not appear to have been published elsewhere, they are given in Table 2.

From Equation (1) it may be seen that if one knows the fugacity, molal volume, and modified Henry's-law constant for the temperature, pressure, and system in question, the equilibrium constant ( $y/x$ ) for hydrogen may be calculated.

Figure 4 shows how the molal volume and the modified Henry's law-constant are evaluated. In these plots given for the hydrogen-methane systems the slope of the straight-line portion is equal to the molal volume of hydrogen and the intercept is equal to the modified Henry's-law constant. These molal volumes have been obtained for the available hydrogen-hydrocarbon binary systems and are shown as a function of temperature and solvent in Figure 5. Excluding methane, the limiting value of the molal average volume is about 0.32 cu. ft./mole near the freezing point of the light hydrocarbon solvent. The values of  $\bar{V}$  obtained here may not agree with experimentally determined values, owing to the previous assumptions used in obtaining Equation (1).

It was found that a plot of the logarithm of the modified Henry's-law constant as a function of an empirical temperature function gave a reasonably good grouping of the values of modified Henry's-law constant.

$$A = T/\sqrt{T_B}[1 + 450/(T_C - T)^2] \quad (2)$$

where

$T$  = temperature, °R.

$T_B$  = normal boiling point of the solvent, °R.

$T_C$  = critical temperature of the solvent, °R.

It will be seen in Figure 6 that the data are grouped principally into three lines representing the Henry's-law constant for hydrogen in paraffins, olefins, and methane, an indication of a different solubility dependence for hydrogen in each of these three types of solvents.

For systems containing more than one hydrocarbon, it is recommended that the solubility of hydrogen be calculated for each hydrocarbon as though it were present alone. The solubilities are then averaged in the ratio of the mole fraction of each hydrocarbon present.

An evaluation of the hydrogen binary systems reveals the following general characteristics. The equilibrium constant for hydrogen increases with a decrease in temperature at constant pressure except for a limited range of conditions close to the vapor-pressure curve for the hydro-

carbon solvent. A second characteristic is that the equilibrium constant for hydrogen increases as the hydrocarbon solvent is changed from methane to butane. A similar effect may be noted for the olefinic solvents. These observations would tend to indicate that the hydrogen equilibrium constant increases as the molecular weight of the solvent increases; however, consideration of both paraffinic and olefinic systems shows that neither the molecular weight nor the boiling point of the solvent are a good criterion for determining the effect of a different solvent. The equilibrium constant for hydrogen in propylene is sometimes greater than in propane, and likewise that in ethylene is sometimes greater than in ethane. Paraffinic and olefinic compounds are not interchangeable based on boiling point or molecular weight.

#### CORRELATION OF TERNARY SYSTEMS

According to the phase rule, a ternary system may be described in terms of three variables, such as temperature, pressure, and one concentration variable. Consideration of the available ternary-system data showed that the hydrogen systems definitely required the use of the phase-rule variables; i.e., consideration of data for a given temperature and pressure showed that the equilibrium constants for all three components varied as the composition of the liquid or vapor phase was changed.

A generalized correlation of equilibrium

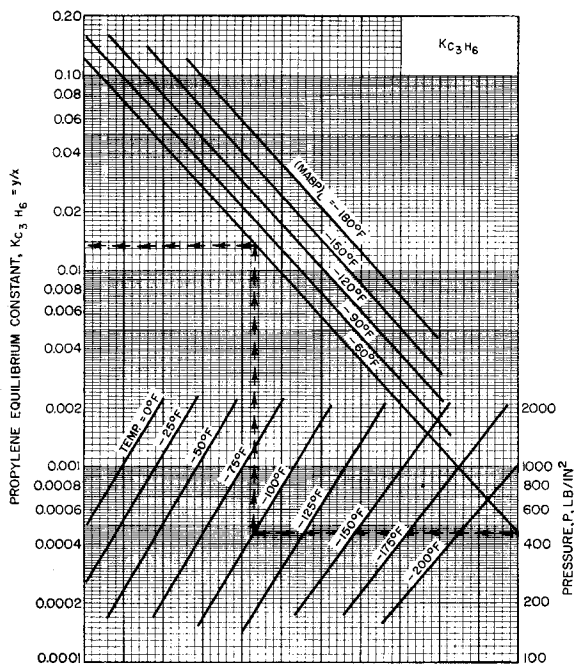


Fig. 9. Nomographic correlation of propylene equilibrium constants in the hydrogen-methylene-propylene system.

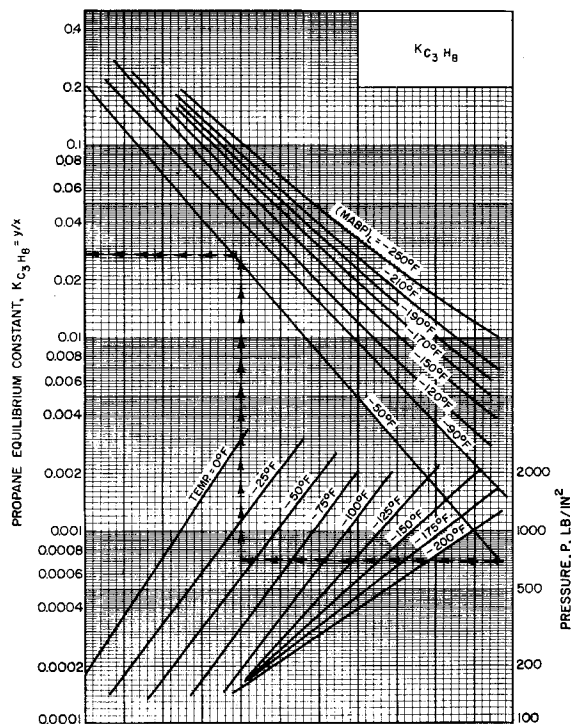


Fig. 10. Nomographic correlation of propane equilibrium constants in the hydrogen-methane-propane system.

constants 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 either phase would also be a universal property of hydrogen systems.

The hydrogen-methane ternary systems with ethylene, ethane, propylene, and propane were examined, and it was found that the equilibrium constants for the constituents could be correlated by use of the temperature, pressure, and a single generalized concentration variable such as the molal average boiling point of the liquid phase  $MABP_L$ .

Examination of the equilibrium constants for ethylene, ethane, propylene, and propane in the corresponding hydrogen-methane ternary systems revealed a regularity which was represented by nomographs as shown in Figures 7, 8, 9, and 10. These nomographs, which make use of the required number of phase-rule variables as represented by the temperature, pressure, and molal average boiling point of the liquid phase, represent the data for the hydrogen-hydrocarbon binary as well as for the corresponding hydrogen-methane-hydrocarbon ternary system. The nomographical correlations should not be expected to apply for conditions in the critical region.

#### TERNARY PAIR CORRELATIONS

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

The possibility of correlating the equilibrium constant for hydrogen in terms of the temperature, pressure, and the molal average boiling point of the liquid phase  $MABP_L$  was considered as a means of describing any hydrogen binary, ternary, or complex system. Figure 11 contains a semilogarithmic plot of the equilibrium constant for hydrogen in various systems as a function of  $MABP_L$  at  $-100^\circ\text{F}$ . and 500 and 1,000 lb./sq. in. This plot shows that use of those three variables is inadequate for the unique specification of the equilibrium constant for hydrogen in any binary, ternary, or complex system. The plot does show that these three variables are sufficient to describe any single hydrogen three-component system and also that there exists a simple straight-line relationship which describes the variation of the hydrogen equilibrium constant with  $MABP_L$  in a (hydrogen)-(saturated-hydrocarbon)-(corresponding-unsaturated-hydrocarbon) ternary system.

From the phase rule it may be shown that a four-component system may be described by use of four variables such as temperature, pressure, and two concentration variables. It follows that those

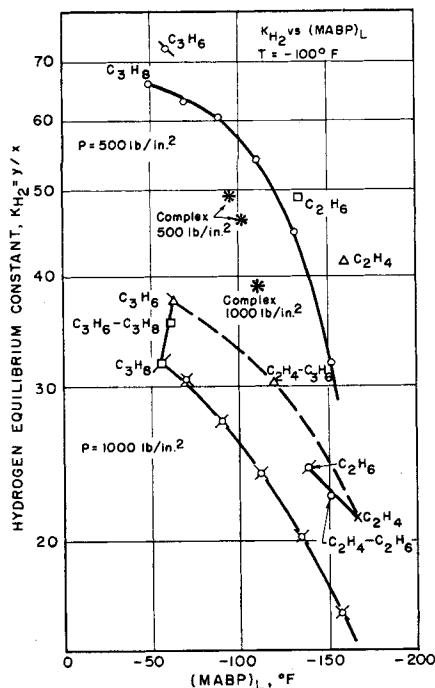


Fig. 11. Equilibrium constants for hydrogen at  $-100^{\circ}\text{F}$ . and 500 and 1,000 lb./sq. in. vs. the liquid molal average boiling point.

four variables should describe the behavior of the four possible ternary systems derived from the four components.

Methods of correlating the data from the ternary systems of both hydrogen-methane-ethylene and hydrogen-methane-propane in terms of two concentration variables in addition to the temperature and pressure were considered. Among those tried were two schemes which have proved useful for the correlation of paraffinic hydrocarbon systems.

The first method used was similar to that of the Kellogg (13) correlation of hydrocarbon equilibrium constants. From all the possible variables which could be used to correlate the hydrogen equilibrium constants the two which proved to be the best were  $MABP_L$  and the mole fraction of hydrogen in the vapor phase  $y_{H_2}$ . Figures 12, 13, and 14 contain the plots which predict the equilibrium constants for hydrogen in either the hydrogen-methane-ethylene system or in the hydrogen-methane-propane system. In Figure 12 the uncorrected equilibrium constant for hydrogen  $K_{H_2}$  has been plotted as a function of temperature for pressures of 500 and 1,000 lb./sq. in. and

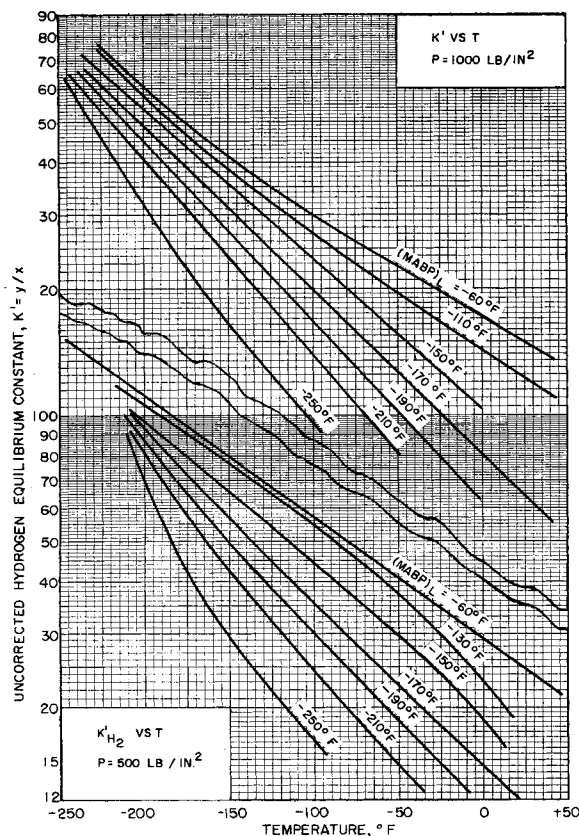


Fig. 12.  $(MABP)_L - y_{H_2}$  correlation for hydrogen equilibrium constants at 500 and 1,000 lb./sq. in.

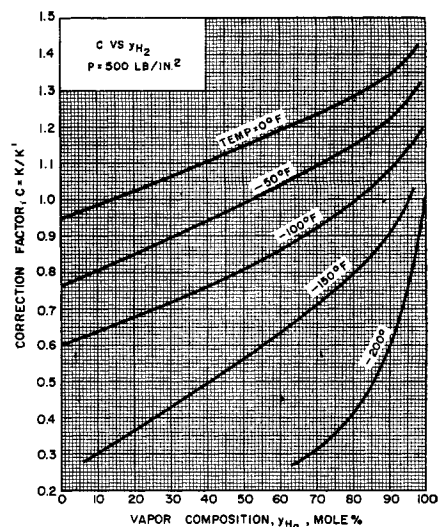


Fig. 13. Correction factor for Figure 14 at 500 lb./sq. in.

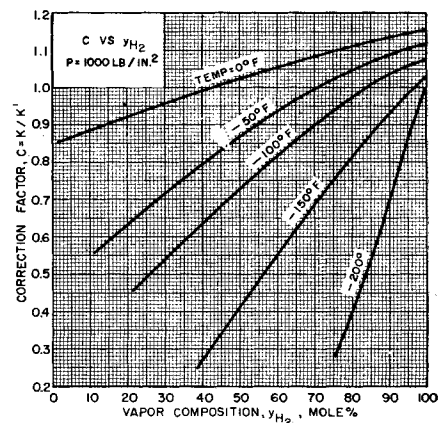


Fig. 14. Correction factor for Figure 12 at 1,000 lb./sq. in.

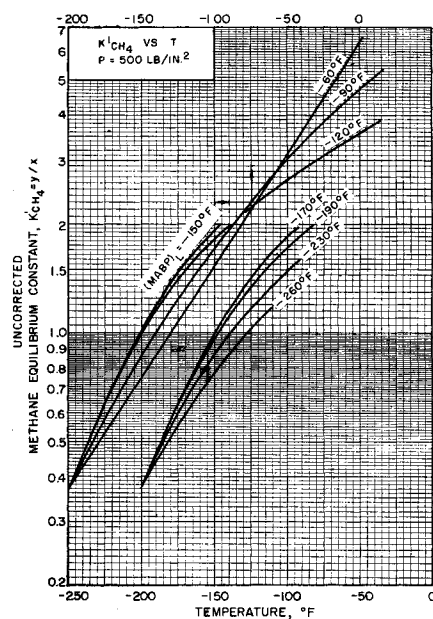


Fig. 15.  $(MABP)_L - (MABP)_V$  correlation for methane equilibrium constants at 500 lb./sq. in.

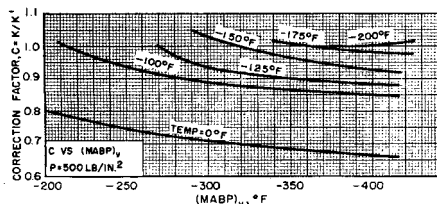


Fig. 16. Correction factor for Figure 17.

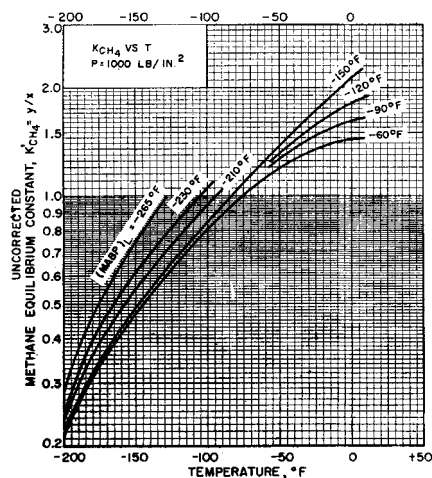


Fig. 17.  $(MABP)_L - (MABP)_V$  correlation for methane equilibrium constants at 1,000 lb./sq. in.

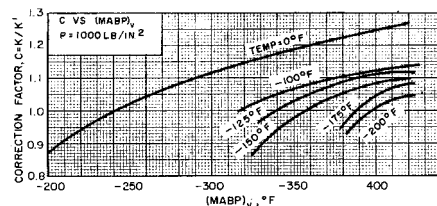


Fig. 18. Correction factor for Figure 17.

for  $MABP_L$ 's between values of  $-60^\circ$  to  $-250^\circ\text{F}$ . Figures 13 and 14 contain correction factors to be applied to  $K_{H_2}'$  which are shown as functions of the mole percentage of hydrogen in the vapor phase  $yH_2$ .

The methane equilibrium constants for the same systems have been correlated as functions of the temperature, pressure,  $MABP_L$ , and  $MABP_V$  as shown in Figures 15, 16, 17, and 18.

The correlations given for hydrogen and methane equilibrium constants were used to predict equilibrium constants for the hydrogen-methane-ethane and hydrogen-methane-propylene systems. A comparison with the actual data showed large deviations which implied that either the best correlation involving the use of four variables had not been found or that it was going to be necessary to use more variables.

The "convergence pressure method," used by Organick (19) to describe the equilibrium constants of the paraffinic hydrocarbons in terms of the temperature, pressure, and convergence pressure, was applied with little or no success.

#### COMPLEX SYSTEMS

A limited number of vapor-liquid data for a six-component system composed of hydrogen, methane, ethylene, ethane, propylene, and propane are available from which it was possible to consider the application of the foregoing correlations for ternary-system equilibrium constants. Three data points are shown in Figure 11 which demonstrate the inability of the three variables of pressure, temperature, and  $MABP_L$  to determine uniquely the equilibrium constant for hydrogen in a six-component system.

The  $MABP_L - yH_2$  correlation of hydrogen equilibrium constants was used to predict the constants for hydrogen in the six-component system and was found to give results which were in error from

3 to 35%. The  $MABP_L - MABP_V$  correlation of methane equilibrium constants was compared with the six-component data, and errors from 3 to 30% were obtained.

This lack of agreement shows the inability of four variables, including temperature, pressure, and two molal average properties, to predict six-component system behavior. Table 3 gives the comparison of the equilibrium constants in the two systems with almost identical values of the molal average of boiling points, molecular weights, critical temperatures, and critical pressures and at the same temperature and pressure. The comparison indicates that at least five variables and probably the full-phase-rule set of six variables is required to obtain an adequate correlation of a six-component system involving hydrogen and light hydrocarbons.

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TABLE 3. COMPARISON OF EQUILIBRIUM CONSTANTS IN A SIX-COMPONENT SYSTEM WITH THOSE IN A THREE-COMPONENT SYSTEM HAVING SIMILAR MOLAL AVERAGE PROPERTIES

(Temperature =  $-100^\circ\text{F}$ .; pressure = 500 lb./sq. in.)

	System	
	$\text{H}_2 - \text{CH}_4 - \text{C}_3\text{H}_8$	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./sq. in.	626	638
$(P_c)_V$ , lb./sq. in.	377	355
$K$ for $\text{H}_2 = y/x$	57.0	49.1
$K$ for $\text{CH}_4 = y/x$	1.50	2.05
$K$ for $\text{C}_3\text{H}_8 = y/x$	0.014	0.0136