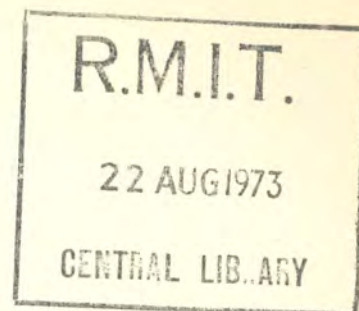




APPLIED THERMODYNAMICS

F. J. VAN ANTWERPEN, *Editor*

WAYNE C. EDMISTER, *Symposium Chairman*

Carroll O. Bennett

J. W. Brydon

Lawrence N. Canjar

C. L. DePriester

Leo Friend

Stuart T. Hadden

Dysart E. Holcomb

Kun Li

G. V. Michael

J. M. Nelson

A. Papadopoulos

R. L. Pigford

F. C. Schiller

H. W. Schnaible

J. M. Smith

George Thodos

C. C. Tsao

N. Walen

660.2
C517
7
1

Chemical Engineering Progress Symposium Series

No. 7

1953

Vol. 49

R.M.I.T. CENTRAL LIBRARY

Accession No.

081243 /

Published by

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

120 East 41 Street

New York 17, N. Y.

SCOUT and CHEVRON EXHIBIT 1021

Page 1

Copyright 1953
by
AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

Lithoprinted in U.S.A.
Edwards Brothers, Inc.
Ann Arbor, Michigan
Varityping by
Strumpf Associates
New York

LIGHT-HYDROCARBON VAPOR-LIQUID DISTRIBUTION COEFFICIENTS

Pressure-Temperature-Composition Charts and Pressure-Temperature Nomographs

C. L. DePRIESTER

Experimental distribution coefficients were determined for thirty-three mixtures of light hydrocarbons at temperatures from -60° to 300°F . Variations up to 30% were found for individual components in a series of mixtures investigated at the same temperature and pressure.

Pressure-temperature-composition (P.T.C.) charts were developed for predicting fugacity relations of light hydrocarbons as functions of temperature, pressure, and molal average boiling point of phase. The distribution coefficient was obtained as the product of vapor- and liquid-phase fugacity functions.

A generalized correlation of distribution coefficients is presented, also, on pressure-temperature nomographs for temperatures from -100° to 400°F . and pressures from 14.7 to 800 lb./sq. in. abs.

Calculation procedures that combine use of the two correlations lead to accurate results from reasonable expenditure of engineering time. The generalized correlation is used in preliminary calculations to estimate phase compositions and other unknown variables, and the P.T.C. charts are used to make final calculations.

THIS paper presents the results of an extensive study of vapor-liquid equilibrium relations of light-hydrocarbon systems. The study was prompted by the lack of experimental data in the low-temperature range and the inconsistencies among the available correlations of equilibrium relations both in the low- and medium-temperature ranges. Stutzman and Brown (38) investigated a natural-gas system at temperatures from -130° to -240°F ., but there are few published experimental data on light-hydrocarbon systems for temperatures from 100° to -100°F . Several correlations of vapor-liquid distribution coefficients, $K = y/x$, for light hydrocarbons include this temperature range, but agreement between available correlations is poor, and critical evaluation is difficult in the absence of experimental data.

An experimental investigation was made to provide multicomponent vapor-liquid equilibrium data and to evaluate, in part, the effects of phase composition on distribution coefficients. Experimental data are reported for temperatures from -60° to 300°F . and for pressures from 100 to 800 lb./sq. in. abs. Experimental measurements on five multicomponent mixtures at 20°F . and 200 lb./sq. in. abs. indicated variations in K for a given component of 30% or more, and similar composition effects were found at other temperatures and pressures.

Experimental results on ternary and multicomponent systems reported in the literature (1, 8, 10,

12, 17, 28, 30) show that phase-composition effects must be considered to obtain an accurate representation of equilibrium data. The suitability of various methods for correlating the effects of composition changes on the distribution coefficient was investigated, and the Kellogg Equilibrium Charts, developed by Benedict and co-workers (6, 7, 22) from the Benedict equation for thermodynamic properties of hydrocarbons (2, 3, 4, 5), were selected as the most promising approach to a useful presentation of accurate equilibrium data.

Two correlations of distribution coefficients are presented. The pressure-temperature-composition (P.T.C.) charts show K as the product of vapor- and liquid-phase fugacity functions for temperatures from -100° to 400°F ., pressures up to 1000 lb./sq. in. abs., and a range of phase compositions. Distribution coefficients for twelve light hydrocarbons are shown on twenty-four charts for the entire range of conditions covered, and interpolation for the effect of all variables is continuous. The Kellogg correlation (22), which was used in developing the P.T.C. charts, is presented on 192 charts, each chart consisting of two separate graphs, for essentially the same range of variables.

The generalized correlation is presented on two nomographs, one for temperatures from -100° to 70°F . and the other for temperatures from 20° to 400°F . The nomographs show K as a function of temperature and pressure only and were developed for use in preliminary calculations.

Experimental Vapor-Liquid Equilibrium Data

Apparatus. The experimental data were determined in a batch equilibrium cell fitted with a sliding piston and heads with built-in valves. Figure 1 is a schematic diagram showing the cell and arrangement of major parts. The cell was wrapped with copper tubing for circulation of heat-transfer fluid, insulated, enclosed in a steel outer shell, and mounted for rocking.

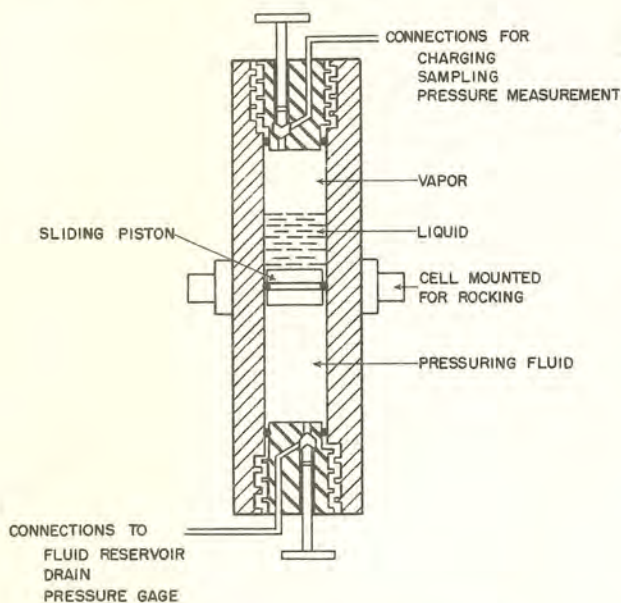


Fig. 1. Schematic diagram of equilibrium cell.

Cell temperature was maintained by pumping heat-transfer fluid through coils in a constant-temperature bath and through the copper tubing wrapped around the cell. A by-pass was installed around the constant-temperature bath, and suitable valves were provided for accurate manual control of cell temperature. The constant-temperature bath was filled with a dry-ice-*n*-butanol mixture for cell temperatures below 100°F., and with oil for cell temperatures of 100°F. and above. Electric immersion heaters were used for heating the bath. Temperatures were measured by use of copper-constantan thermocouples with a portable precision potentiometer, which were calibrated at the solid carbon dioxide sublimation temperature, the boiling point of propane, and the boiling point of water.

Cell pressure was controlled by controlling pressure on a hydraulic fluid, ethyl alcohol or mercury, in the lower chamber of the cell. Change in hydraulic pressure caused a change in position of the sliding piston and a corresponding change in volume of the hydrocarbon mixture. Pressure on the hydraulic chamber was nearly equal to pressure on the hydrocarbon mixture and was indicated at all times on a Bourdon-tube gauge. Equilibrium pressure of the hydrocarbon mixture was measured at the time of sampling on a Bourdon-tube gauge that was calibrated against a dead-weight tester prior to each run.

Procedure. Synthetic mixtures of high-purity hydrocarbons were charged into the cell and brought to equilibrium at the desired temperature and pressure. The mixtures were calculated to yield equal volumes of vapor and liquid sufficient to provide samples for three equilibrium runs,

and the hydrocarbons were measured and displaced into the cell as liquid or vapor. After charging was completed, temperature and pressure were adjusted to the desired conditions, and the rocking mechanism was started. Additional adjustments were made until pressure became constant at the desired conditions, and the cell was rocked at least twenty minutes at constant temperature and pressure before either phase was sampled.

The vapor phase was sampled with the cell in the position shown in Figure 1, and liquid samples were obtained with the cell inverted. As samples were withdrawn, pressure was held constant by forcing fluid into the hydraulic chamber. The sample line was evacuated, flushed with sample, and again evacuated before each sample was removed.

With a few exceptions, two runs were made on each mixture at the same temperature and approximately the same pressure. All liquid samples and four vapor samples were analyzed in low-temperature fractionating columns, and all other vapor samples were analyzed by mass spectrometer.

Experimental Results. The objective of the experimental investigation was to provide representative equilibrium data on multicomponent systems throughout the range of temperatures and pressures to be included in the two correlations of distribution coefficients. To assist in planning the work, suitable investigations (1, 8, 10, 12, 17, 19, 28, 30) reported in the literature were noted on a pressure-temperature diagram similar to Figure 2. Conditions to be investigated were then selected to complement

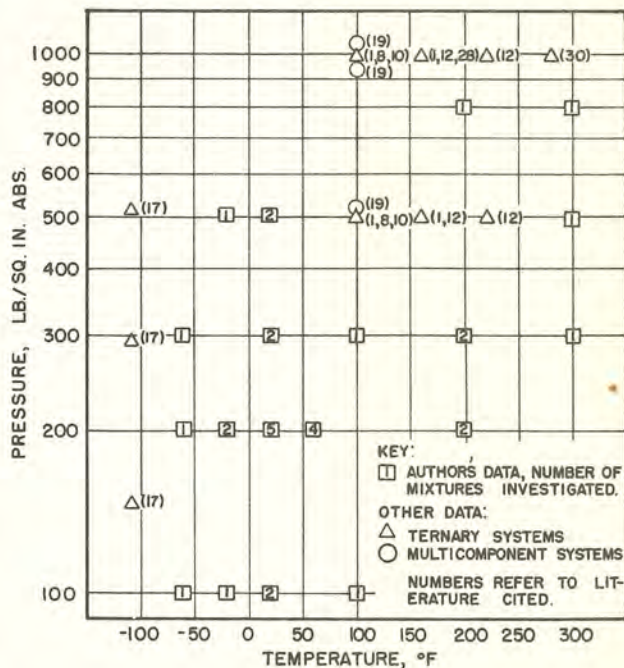


Fig. 2. Pressure-temperature distribution of experimental data.

TABLE 1
EXPERIMENTAL RESULTS*

Component	1 -60 °F. $p = 115^\dagger$				2 -60 °F. $p = 109$			
	y	x	K_e	K_s	y	x	K_e	K_s
Methane	0.869	0.085	10.2	10.2	0.912	0.091	10.0	10.0
Ethane	0.057	0.085	0.67	0.67	0.049	0.074	0.66	0.66
Propane	0.057	0.393	0.145	0.145	0.035	0.394	0.089	0.096
<i>n</i> -butane	0.017	0.249	0.068	0.068	0.004	0.253	0.016	0.013
2-Methyl pentane		0.188				0.188		
	1.000	1.000			1.000	1.000		

	3 -60 °F. $p = 204$				4 -60 °F. $p = 288$			
	y	x	K_e	K_s	y	x	K_e	K_s
Methane	0.852	0.160	5.33	5.33	0.874	0.234	3.74	3.74
Ethane	0.080	0.188	0.425	0.425	0.060	0.178	0.337	0.337
Propane	0.063	0.583	0.108	0.108	0.059	0.527	0.112	0.115
<i>n</i> -butane	0.005	0.069	0.072		0.007	0.061	0.115	
	1.000	1.000			1.000	1.000		

	5-1 -20 °F. $p = 100$			5-2 -20 °F. $p = 100$			K_s
	y	x	K_e	y	x	K_e	$p = 100$
Methane	0.865	0.055	15.7	0.863	0.064	16.0	15.8
Ethane	0.041	0.031	1.32	0.045	0.031	1.45	1.42
Propane	0.053	0.188	0.282	0.055	0.190	0.290	0.280
<i>n</i> -butane	0.038	0.634	0.060	0.035	0.632	0.055	0.058
<i>n</i> -pentane	0.003	0.092	0.033	0.002	0.093	0.022	
	1.000	1.000		1.000	1.000		

	6-1 -20 °F. $p = 200$			6-2 -20 °F. $p = 202$			K_s
	y	x	K_e	y	x	K_e	$p = 201$
Methane	0.758	0.079	9.60	0.758	0.101	7.50	7.50
Ethane	0.187	0.197	0.95	0.185	0.230	0.804	0.804
Propane	0.028	0.160	0.175	0.028	0.160	0.175	0.175
<i>i</i> -butane	0.027	0.564	0.048	0.029	0.509	0.057	0.057
	1.000	1.000		1.000	1.000		

*The complete table is on file as Document 4014 with A.D.I. Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C. Copies may be secured by remitting \$1.25 for photoprints or \$1.25 for 35mm. microfilm to Chief, Photoduplication Service, Library of Congress.

$\dagger$ 1 -60 °F. $p = 115$, etc. — Run number, equilibrium temperature and pressure.

y = mole fraction in vapor.

x = mole fraction in liquid.

$K_e = y/x$, experimental distribution coefficient.

K_s = smoothed distribution coefficient.

p = pressure, lb./sq. in. abs.

previously reported data. Figure 2 shows pressure-temperature distribution of the author's data and ternary- and multicomponent-system data reported from other investigations.

At the time this work was undertaken, no ternary or multicomponent light-hydrocarbon systems had

been reported in the temperature range from -100° to +100°F. The majority of the determinations were made in this region because of increased interest in low-temperature processes and the relatively large effect of temperature on the distribution coefficient. The remainder of the measurements were made at

temperatures and pressures selected to provide a reasonably consistent density of experimental data over the range of conditions covered by the two correlations.

Table 1 shows the experimental data arranged in order of increasing temperature and of increasing pressure for each temperature. The temperature, pressure, phase analyses, and experimental distribution coefficient, K_e , for each component of the system are shown for each experimental run. In addition, K_s , a smoothed value of the distribution coefficient, is shown. The smoothed values were read from the curve obtained by plotting data from all runs at similar conditions of temperature, pressure, and phase composition as $\log K_e$ vs. normal boiling point of hydrocarbon. Figure 3 is the smoothing curve drawn for runs 8-1 and 8-2. The pressure shown at the top

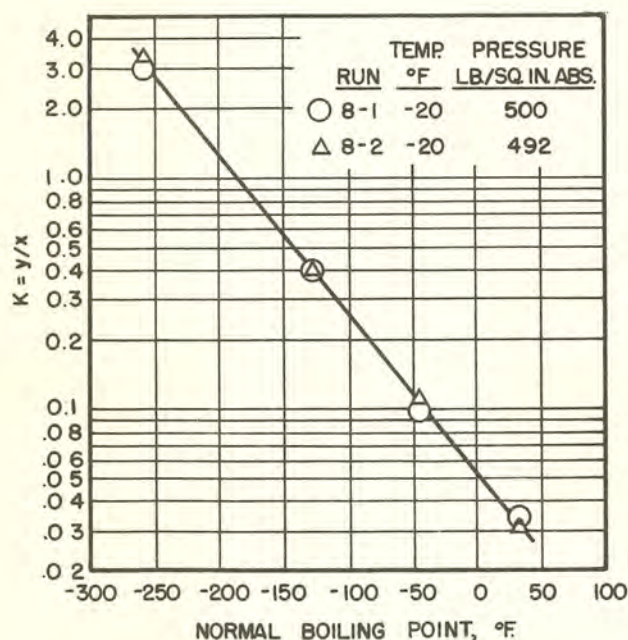


Fig. 3. Smoothing plot for runs 8-1 and 8-2.

of the K_s column is the arithmetic average pressure of the runs considered in smoothing the data. The smoothed distribution coefficients are considered to be the best values derivable from the actual experimental measurements. In some instances more weight was given to one run than to the other. This was done only if data from one of the runs did not yield a smooth $\log K$ -vs.-boiling-point curve, or if analysis of one of the samples was not compatible with the composition of the mixture originally charged into the cell.

The smoothing method used was selected because K and normal boiling point are both indices of volatility, and the method was tested with experimental data from a number of sources. The same plotting method was used by Winn (43) in developing a nomographic presentation of distribution coefficients. Distribution coefficients read from the Kellogg charts (22) yield a smooth $\log K$ -vs.-boiling-point curve with the exception of a few minor deviations which appear to be due to random error in the charts.

Experimental Uncertainties. The accuracy of temperature and pressure measurements was about the same for all runs. Estimated uncertainty in cell temperature is 0.5°F ., which corresponds to an uncertainty in the distribution coefficient ranging from about 0.1% for methane to about 0.35% for *n*-pentane and *n*-hexane, depending to some extent on the temperature, pressure, and mixture being investigated. The uncertainty in pressure measurement is approximately 2 lb./sq.in., and the corresponding uncertainty in K varies from about 2% for runs at 100 lb./sq.in. abs. to negligible uncertainty for some components heavier than methane at higher pressures. The uncertainty due to errors in pressure measurement is also a function of the temperature and equilibrium phase composition and is usually less than the uncertainty approximated by the ratio of the probable pressure error to the absolute pressure.

The most difficult measurement in an investigation of multicomponent vapor-liquid equilibria is analysis of the equilibrium phases. The effects of uncertainties in analysis were minimized by omitting isomers from experimental mixtures and, wherever possible, by adjusting mixture compositions to yield equilibrium phase compositions with easily analyzable component concentrations. For each component, one or both of the experimental mole fractions are in the range from 0.020 to 0.200 for most of the distribution coefficients reported. The uncertainty in low-temperature fractional analysis is approximately 0.001 mole fraction in this concentration range, and the accuracy of mass-spectrometer analysis is about the same for careful work. The uncertainty due to analysis errors can be estimated for a given experimental K by computing the effect of adding or subtracting 0.001 mole fraction of the component in both phases.

Suitable precautions were observed in sampling and transfer of samples to analysis apparatus, but there is a possibility that unknown uncertainties exist in the experimental results. The net uncertainty is shown to some extent by comparing analyses and experimental distribution coefficients for duplicate runs.

Discussion of Experimental Data. Equilibrium data for light-hydrocarbon systems are most frequently applied to mixtures of more than two or three components, whereas most of the experimental data re-

TABLE 2

EXPERIMENTAL DISTRIBUTION COEFFICIENTS
FOR FIVE MIXTURES AT 20° F. AND 200 LB./SQ. IN. ABS.*

Mixture	b_L , °F.	b_V , °F.	$K = y/x$			
			Methane	Ethane	Propane	Isobutane
11	-28	-219	9.51	1.22	0.318	0.111
12	-83	-148	8.39	1.33	0.352	0.123
13	-95	-121	—	1.31	0.354	0.142
14	-1	-214	10.2	1.36	0.338	0.123
15	+49	-229	11.0	1.27	0.324	

* K_s values from Table 1 adjusted to a pressure of 200 lb./sq. in. abs.

Maximum pressure adjustment was from 204 lb./sq. in. abs.

ported in the literature have been for binary and ternary systems. The data reported here should prove valuable in future studies because the mixtures investigated more nearly approach the characteristics of actual process streams, and many of the determinations were made at temperatures and pressures not covered by previous investigations. The experimental results provide information on the effects of phase composition on K , and measurements were made on more than one mixture at several conditions of temperature and pressure, as shown on Figure 2. Experimental pressures varied slightly from those indicated on Figure 2, but pressure adjustments can be estimated with sufficient accuracy to make the distribution coefficient data comparable.

To illustrate the significance of the effects of phase composition on distribution coefficients, experimental K 's for five different mixtures at 20°F. and 200 lb./sq.in.abs. are shown in Table 2. The equilibrium vapors from mixtures 11, 12, and 13 contained 82%, 21%, and 0% methane, respectively. Iso-

butane was the heaviest hydrocarbon in mixtures 11, 12, and 13. Mixture 14 contained *n*-pentane, and mixture 15 contained *n*-butane and *n*-heptane in addition to the components for which K 's are shown. Molal average boiling point of the liquid, b_L , and molal average boiling point of the vapor, b_V , are shown to characterize the equilibrium phase compositions. The distribution coefficients shown in Table 2 are smoothed data from Table 1 adjusted to a pressure of 200 lb./sq.in.abs. The variation in K with phase composition is significant for all components listed and is largest for methane and isobutane.

Similar comparisons could be drawn from data reported on other mixtures. Consideration of the variations found is important in regard to equilibrium data used in making equilibrium-flash-vaporization, dew-point, and bubble-point calculations. Depending on the conditions for which the calculation is to be made, errors in distribution coefficients can lead to significant errors in the calculated results.

TABLE 3

EXPERIMENTAL DATA FROM THE LITERATURE USED IN CHECKING CORRELATIONS

System	Literature cited	Temperature, °F.	Pressure, lb./sq. in. abs.
Methane, ethane, propane, <i>n</i> -butane, <i>n</i> -pentane	(19)	100	517; 946
Methane, ethane, propane, <i>n</i> -pentane, <i>n</i> -hexane	(19)	100	1046
Methane, ethylene, ethane	(17)	-108.3	147; 294; 515
Methane, ethylene, <i>i</i> -butane	(1)	100	500; 1000
		160	500; 1000
Methane, ethane, <i>n</i> -pentane	(8)	100	500; 1000
Methane, propane, <i>n</i> -pentane	(10)	100	500; 1000
	(12)	160	500; 1000
		220	500; 1000
Methane, <i>n</i> -butane, decane	(28)	160	1000
	(30)	280	1000

Correlation of Distribution Coefficients

Previous Methods. The distribution coefficient, K , used in calculating vapor-liquid equilibrium relations, is defined as the ratio of the fugacity coefficient in the liquid phase to the fugacity coefficient in the vapor phase:

$$K_i = \frac{y_i}{x_i} = \frac{f_i^L/x_i}{f_i^V/y_i} \quad (1)$$

In this equation, f_i^L is the fugacity of the i th component in the liquid phase, and f_i^V is the fugacity of the i th component in the vapor phase.

For ideal-solution behavior, the fugacity coefficients f^L/x and f^V/y are independent of phase composition, and the distribution coefficient was originally termed "equilibrium constant" (37). Many correlations have been presented for predicting K , and most of the generalized correlations currently in use are based on the correlations of Brown and associates (9) or Taylor and Parker (40). The K values in the original presentations of these authors were computed for ideal-solution behavior from pure-component fugacity data, and K is shown as a function of temperature and pressure. Other correlations have been developed from experimental data on crude-oil-natural-gas, absorption-oil-natural-gas, or other specialized systems (20, 31, 41).

Experimental investigations of Sage and Lacey, Kay, and others have shown that K varies with composition at constant temperature and pressure, and several methods for correlating composition effects have been proposed. Early investigations of composition effects led to use of the apparent-convergence pressure (14, 18, 42, 43) to correlate the effect of composition on K . Smith and Watson (35) presented a correlation of fugacity data and a series of activity coefficient charts for correcting fugacity for composition effects in the vapor and liquid phases. Benedict, Webb, and Rubin (2, 3, 4, 5) developed an empirical equation of state for light hydrocarbons that can be used to predict vapor-liquid equilibria.

The Benedict equation of state is the most accurate means available for predicting thermodynamic properties of light-hydrocarbon mixtures. The equation is too complex for direct use in calculation of vapor-liquid equilibria because a system of involved nonlinear equations must be solved by successive approximations to obtain a solution for a given set of conditions. Fugacity data calculated from the Benedict equation were used by Benedict, Webb, Rubin, and Friend (6, 7) in developing the Kellogg Equilibrium Charts (22). Two fugacity factors are shown on the Kellogg charts as functions of

temperature and molal average boiling point of vapor and liquid phases on a series of constant-pressure charts. The product of the factor for the liquid phase, f^L/px , and for the vapor phase, reciprocal of f^V/py , is the distribution coefficient, K , defined in Equation (1).

Distribution coefficients read from the Kellogg charts approach the accuracy of K 's calculated directly from the Benedict equation (7) and provide the best method previously available for predicting light-hydrocarbon vapor-liquid equilibria. The Kellogg charts have a number of disadvantages from the standpoint of practical use:

1. The data for each component are presented on sixteen constant-pressure charts covering the 14.7 to 1000 lb./sq.in.abs. range, which makes accurate interpolation for effect of pressure on the two factors tedious.
2. Interpolation for the effect of molal average boiling point of the liquid phase on the liquid factor is uncertain on many charts, and, in practice, part of the basic accuracy of the correlation is nullified by uncertainty in interpolation.
3. Solution of a given problem in phase equilibria is slow because K is a function of the equilibrium-phase compositions which must be established by successive approximation.

Use of the Kellogg charts for process calculations led to consideration of possible improvements in graphical presentation of the two factors and of calculation methods which might lead to more rapid solutions. Presented below are two correlations of distribution coefficients that were derived from the Kellogg charts. The P.T.C. charts show the same functions as the Kellogg correlation on two charts for each hydrocarbon. Interpolation for the effects of temperature, pressure, and phase composition is continuous for a wide range of variables. The generalized correlation is a set of two nomographs that show average values of K as functions of temperature and pressure. Distribution coefficients read from the nomographs are sufficiently accurate for preliminary estimates of phase compositions and liquid-vapor mole ratios for use in equilibrium calculations with the P.T.C. charts. When used together, the two correlations provide a method for computing phase-equilibrium relations that is accurate and comparatively rapid.

Pressure-Temperature-Composition Charts

Development of Correlation. The fugacity functions shown on the Kellogg charts were given the symbols A and B , and the distribution coefficient is the product of the two functions:

$$K = AB \quad (2)$$

$$\text{where } A = f^L/px \quad (3)$$

$$B = \frac{1}{f^V/p\gamma} \quad (4)$$

The liquid factor, A , is a function of temperature, pressure, and composition of the liquid phase. Similarly, the vapor factor, B , is a function of temperature, pressure, and composition of the vapor phase. The effects of composition on A and B are correlated with molal average boiling point of the liquid and vapor phases, respectively. The molal average boiling points, b_L and b_V , are defined as summation of mole fraction times normal boiling point for all components of the phase:

$$b_L = \sum_i x_i b_i \quad (5)$$

$$b_V = \sum_i y_i b_i \quad (6)$$

In these two equations, b_i is the normal boiling point of the i th component.

The fundamental problem in developing a simplified presentation of the Kellogg charts is to find linear, or nearly linear, relations between the two fugacity functions and pressure. Liquid factors at various values of temperature and b_L were read from the Kellogg charts and plotted vs. pressure on log-log charts. Smooth curves were obtained as shown by data for propane on Figure 4. A method was found for representing the effects of p , t , and b_L on A by use of a b_L - t coordinate system graphically related to a p - A coordinate system.

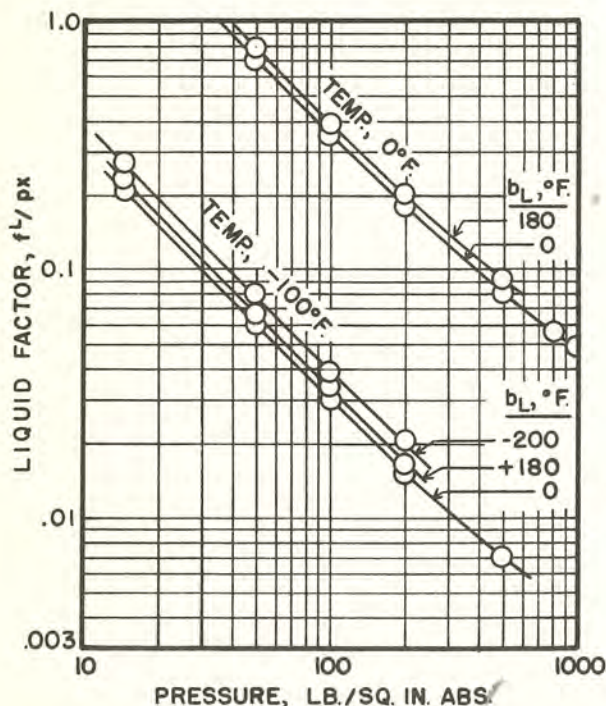


Fig. 4. Liquid factor for propane read from Kellogg charts (22).

To construct the charts, A values were read from the Kellogg charts at a series of temperatures and pressures for all b_L 's shown. Suitable scales were established for A and b_L and a straight line was drawn with the slope necessary to cover the range of A at 14.7 lb./sq.in.abs. Data for 14.7 lb./sq.in.abs. were used to locate temperature lines opposite the b_L scale by entering the chart with the values of A , going horizontally to the pressure line and vertically to the b_L lines. Temperature- b_L points established in this manner were used to locate the pressure line for the next higher pressure. Additional t - b_L points were located from the new pressure line. This procedure was continued until lines were established for pressures up to 1000 lb./sq.in.abs., and for temperatures from -100° to 400° F. All tabulated values of A were used to check location of temperature lines for the location of pressure lines and, again, to check location of pressure lines for final locations of temperature lines. Figure 7 shows A for methane as a function of molal average boiling point, temperature, and pressure, and A charts for other hydrocarbons are similar.

Characteristics of the vapor factor, B , differ from those for A , but a similar approach was used to find a simplified method for presenting the data. Plots of B for methane at constant t and b_V vs. pressure are straight or slightly curved lines. For all other hydrocarbons, plots of $\log B$ vs. pressure are straight or slightly curved lines. For all hydrocarbons, at all temperatures and b_V 's, $B = 1.0$ at $p = 0$. Figures 5 and 6 show B vs. pressure for methane and isobutane, respectively. The effects of all variables

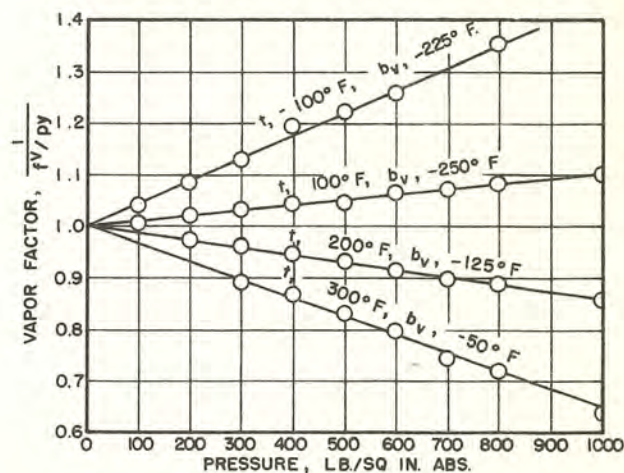


Fig. 5. Vapor factor for methane read from Kellogg charts (22).

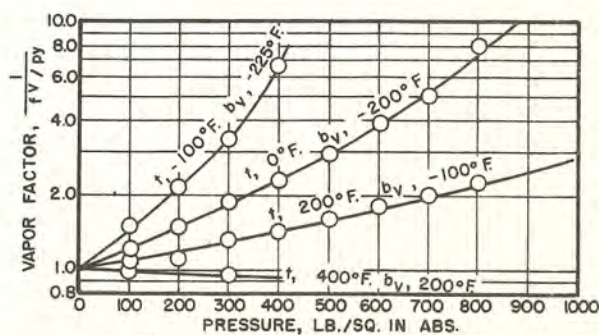


Fig. 6. Vapor factor for isobutane read from Kellogg charts (22).

are presented on the final charts by use of a t - b_V coordinate system graphically related to a p - B coordinate system. Values of the factor read from the Kellogg charts at a series of b_V 's were plotted vs. pressure for all temperatures shown. The linear portions of the lines at low pressures were extrapolated to higher pressures and intercepts read at 1000 lb./sq.in.abs. The 1000 lb./sq.in. intercepts were cross plotted - B vs. temperature at constant b_V , and B vs. b_V at constant temperature - for smoothing. Scales for B and b_V were laid out, and a 1000 lb./sq.in.abs. pressure line was drawn with slope to cover the range of B represented on the chart. The smoothed intercepts for 1000 lb./sq.in.abs. were used to establish temperature lines by entering the chart with the intercept on the B scale, moving horizontally to the 1000 lb./sq.in.abs. pressure line and vertically to the b_V scale. All tabulated values of B read from the Kellogg charts were used to locate points for pressure lines by entering the chart with b_V , moving horizontally to the established temperature lines, and vertically to B . Smooth curves were drawn through the plotted points. Locations of pressure and temperature lines were cross plotted for smoothing and for location of intermediate lines for interpolation. For methane, an arbitrary temperature scale was established, and lines of constant b_V were drawn to eliminate crossover of temperature lines that would occur with the scale arrangement used for other hydrocarbons. Figures 8 and 12 are the final charts for methane and ethane, respectively.

Adjustment of Charts. In order to check the accuracy of the charts as drawn, distribution coefficients were read from the charts for comparison with experimental data reported above and in the literature. Literature data used in checking the correlation are listed in Table 3, which shows the system, reference, and temperatures and pressures included in the comparison.

Agreement between observed and predicted K values was good, but there were consistent deviation trends in some ranges of experimental conditions. The development of the Benedict equation (2, 3, 4, 5) and preparation of the Kellogg charts (6, 7) were reviewed to see whether there was any basis for making empirical adjustments in the A or B charts to give better agreement of the correlation with experimental data. The equation is more accurate at high temperatures and low densities than at low temperatures and high densities. Thermodynamic properties of pure hydrocarbons calculated by the Benedict equation for the vapor state are more accurate than those calculated for the liquid state (4). The equation is less accurate for densities greater than 1.8 times the critical density, and special constants must be used for calculating vapor pressures less than 1 atm. The equation is not recommended for higher densities or lower temperatures than those for which the equation has been fitted.

These characteristics of the Benedict equation suggested a method of adjusting the charts. It was assumed that vapor factors and the positions of pressure lines on the A charts satisfactorily represented the data. Experimental points were then noted in the

b_L - t network on the liquid-factor charts by entering the chart with $A = K_e/B$, where K_e is the experimental distribution coefficient. By this procedure, all available data for a given component at one temperature could be used to determine a corrected temperature line in the b_L - t network. Adjustments were made by this procedure on liquid-factor charts for methane at temperatures from -100° to 300° F. and for ethane at temperatures from -100° to 100° F. For all other hydrocarbons, either the charts, as initially drawn, gave satisfactory agreement or the available experimental data were too few, or too inconsistent, to justify corrections.

Description of Charts. The correlation is shown in Figures 7 through 30. Two charts are included for each of twelve hydrocarbons from methane through n -heptane. For each hydrocarbon, one chart is used to read values of the liquid factor, A , as a function of b_L , t , and p , and the other shows values of the vapor factor, B , as a function of b_V , t , and p . The distribution coefficient is the product of A and B and the range of variables covered on the charts is $b_L = -210^\circ$ to 200° F., $b_V = -250^\circ$ to 200° F., $t = -100^\circ$ to 400° F., and $p = 14.7$ to 1000 lb./sq.in.abs. Guide lines drawn on the charts show how the charts are read. Accuracy of the correlation and its use in calculations are discussed in following sections.

Generalized Correlation

Development of Charts. Use of the P.T.C. charts involves trial-and-error procedures to establish b_L and b_V for estimation of distribution coefficients. Time consumed in using the correlation can be shortened if preliminary calculations are made with approximate K 's to estimate phase compositions and liquid-vapor mole ratios. Previously available correlations were considered for this purpose, but no one correlation met the requirements of range of variables, internal consistency, accuracy, and simplicity of form. After study of several presentation methods, the nomograph form developed by Scheibel and Jenny (34) was selected as most desirable because the presentation is compact and the attainable accuracy of the method is adequate for presentation of K as a function of temperature and pressure. Distribution coefficients derived from the Kellogg charts were used in developing the correlation, and the pressure and temperature scales were developed from fugacity data for pure n -butane (13, 23, 24, 27).

To construct the nomographs, an arbitrary series of K values was selected for each component. By use of average values of b_L and b_V , a series of pressure-temperature combinations was derived from the Kellogg charts for each K value selected. The pressure and temperature scales were drawn and pressure-temperature- K data were used to locate K scales for each hydrocarbon. After preliminary

scales were constructed, locations of the scale lines, and points along the lines, were smoothed by cross plots. Data for *n*-octane, *n*-nonane, and *n*-decane were developed by use of experimental data for *n*-decane (25, 38, 30) and interpolation on *K* vs. boiling-point curves.

For convenience in use, the correlation is shown on two nomographs with overlapping temperature ranges. There are unavoidable minor differences in *K* read from the two charts in the common temperature range, but *K*'s read from both nomographs are of comparable accuracy.

Description of Nomographs. The generalized correlation is shown on two nomographs (Figures 31 and 32) for fourteen hydrocarbons from methane through *n*-decane. Figure 31 shows *K* at temperatures from -100° to 70° F., and at pressures up to 800 lb./sq.in. abs. Figure 32 shows *K* at temperatures from 20° to 400° F. and at pressures up to 700 lb./sq.in. abs. Distribution coefficients are read from the nomographs by placing a straight edge at the desired temperature and pressure and reading *K*'s at intersections of the component lines with the straight edge.

Comparisons with Experimental Data

Pressure-Temperature-Composition Charts. The Kellogg correlation gives an average deviation from experimental data of 7.1% (7). The P.T.C. charts should have the same order of accuracy and may be more accurate because adjustments were made to give better agreement with experimental data, and

some smoothing was obtained in developing the charts. In addition, uncertainties in interpolation on the Kellogg charts were eliminated by providing continuous interpolation for the effects of all variables.

Distribution coefficients from the P.T.C. charts were compared with experimental *K*'s from the author's investigation and with the literature data listed in Table 3 except for data on the methane-ethylene-ethane system. No binary data were included in the comparisons because data used in developing the Kellogg correlation were calculated for binary systems by the Benedict equation, and it was desired to test applicability of the P.T.C. charts to complex mixtures.

Table 4 shows the results of the comparison. Comparisons with the author's data are shown separately from comparisons with data of other investigators. Number of comparisons, distribution of deviations, algebraic average deviation, and absolute average deviation are shown for hydrocarbons methane through *n*-pentane. The algebraic average deviation is the algebraic sum of the deviations divided by the number of deviations, and the absolute average deviation is the arithmetic sum of the deviations divided by the number of deviations. In comparisons with the author's data, *K* values for hydrocarbons not present in experimental mixtures were read by interpolation on the smoothing curves for the experimental *K*'s. No interpolated data are included in the comparisons with data from other investigations.

TABLE 4

COMPARISON OF OBSERVED *K*'S WITH *K*'S FROM P.T.C. CHARTS

<i>Author's data*</i>		Number of deviations			Deviation summary	
Component	Number of comparisons	Minus	0	Plus	Alg. avg., %	Abs. avg., %
Methane	29	15	2	12	-0.7	2.6
Ethane	33	18	1	14	-0.2	4.1
Propane	29	15	0	14	-1.6	4.0
<i>i</i> -butane	29	12	3	14	+2.3	5.5
<i>n</i> -butane	29	13	4	12	0	4.8
<i>i</i> -pentane	14	4	2	8	+2.5	6.9
<i>n</i> -pentane	14	1	2	11	+13.8	18.0
All components	177	78	14	85	+1.3	5.5
<i>Data listed in Table 3</i>						
Methane	65	29	6	30	+1.6	5.2
Ethylene	14	9	1	4	-1.7	2.1
Ethane	13	1	0	12	+4.0	5.6
Propane	33	20	0	13	-0.7	4.4
<i>i</i> -butane	17	3	0	14	+4.9	6.9
<i>n</i> -butane	11	5	0	6	+4.4	12.0
<i>n</i> -pentane	43	21	3	19	-1.4	8.3
All components	196	88	10	98	+0.9	6.1

*Includes data derived by interpolation on log *K_e* vs. boiling-point curves.

Deviation, % = 100 (chart *K* - observed *K*)/observed *K*.

Agreement of the correlation with observed distribution coefficients is generally satisfactory, and summarized deviations from the two sets of data are about the same. Most of the author's data were taken at low temperatures and moderate pressures; whereas the data from the other investigations tend to be for higher temperatures and higher pressures. Relatively poor agreement is shown for *n*-pentane vs. the author's experimental investigation. The number of comparisons, however, is low, and the deviations are probably due, in part, to uncertainties in analysis of vapor phases having low concentrations of *n*-pentane or heavier hydrocarbons. A greater number of comparisons could be made with other data on *n*-pentane, and agreement would be satisfactory, as shown in the table. Absolute accuracy of the experimental data is difficult to define, as outlined in the discussion of the author's data above. Some of the deviations summarized in Table 4 probably result from uncertainties in experimental measurements.

The comparisons in Table 4 show the value of the parameter molal average boiling point in correlating the effects of phase composition on distribution coefficients. In an *n*-component phase, the fugacity coefficient of each component is a function of pressure, temperature, and *n*-1 composition variables. Some of the deviations shown undoubtedly result from failure of b_L and b_V to correlate completely the effects of composition in complex mixtures. The body of experimental data currently available is probably not sufficiently accurate or large to evaluate the absolute accuracy of the molal average boiling point as

a correlating parameter because of the difficulty in separating the effects of temperature and pressure.

Generalized Correlation. The generalized correlation is inherently less accurate than the P.T.C. charts because the effects of phase composition are not correlated. Distribution coefficients read from the nomographs are average values which can be read in a minimum of time from a single setting of a straight edge. The correlation is consistent with the P.T.C. charts in representing the effects of temperature and pressure and is accurate enough for preliminary estimates of b_L , b_V , and liquid-vapor mole ratios for calculations with the P.T.C. charts.

A summarized comparison of experimental *K*'s with those read from the nomographs is shown in Table 5. The comparison is based on the same experimental data as the comparison for *K*'s from the P.T.C. charts shown in Table 4, except that data for 1000 lb.sq.in.abs. are outside the range of the charts and were not included. Average deviations are larger for the nomographs than for the P.T.C. charts, but the algebraic summations show that *K*'s from nomographs are about evenly split between plus and minus deviations.

Comparisons with Other Methods

As noted above, the Benedict equation of state is the most accurate method available for calculating light-hydrocarbon distribution coefficients. In Table 6 fugacity functions derived from the P.T.C. charts by use of Equations (3) and (4) are compared with fugacity functions calculated directly from the

TABLE 5
COMPARISON OF OBSERVED *K*'S WITH *K*'S FROM GENERALIZED CORRELATION

Author's data*	Number of comparisons	Number of deviations			Deviation summary	
		Minus	0	Plus	Alg. avg., %	Abs. avg., %
Methane	29	19	0	10	-4.0	10.2
Ethane	33	9	1	23	+2.2	5.8
Propane	29	17	2	10	-4.7	8.3
<i>i</i> -butane	29	12	1	16	+0.2	6.5
<i>n</i> -butane	29	18	1	10	-5.0	9.0
<i>i</i> -pentane	14	7	1	6	-4.5	12.2
<i>n</i> -pentane	14	5	1	8	+2.7	14.3
All components	177	87	7	83	-1.9	8.7
Data listed in Table 3						
Methane	32	8	1	23	+15.3	17.0
Ethylene	6	0	0	6	+17.6	17.6
Ethane	5	1	0	4	+1.2	5.4
Propane	22	10	0	12	-0.8	10.0
<i>i</i> -butane	6	6	0	0	-10.5	10.5
<i>n</i> -butane	1	1	0	0	-8.6	8.6
<i>n</i> -pentane	21	19	0	2	-19.4	20.4
All components	93	45	1	47	+1.1	15.0

*Includes data derived by interpolation on log K_e vs. boiling-point curves.

Deviation, % = 100 (correlation *K* - observed *K*)/observed *K*.

TABLE 6

COMPARISON OF FUGACITY FUNCTIONS CALCULATED
FROM BENEDICT EQUATION (6) WITH VALUES FROM P.T.C. CHARTS

Temperature, 100 °F.

Vapor phase

System*	Pressure, lb./sq. in. abs.	b_V , °F.	Methane				Propane				<i>n</i> -pentane			
			<i>B</i>	1/ <i>B</i>	<i>f</i> / <i>py</i>	Dev., %	<i>B</i>	1/ <i>B</i>	<i>f</i> / <i>py</i>	Dev., %	<i>B</i>	1/ <i>B</i>	<i>f</i> / <i>py</i>	Dev., %
C_1 - nC_6	88.8	-240	1.009	0.991	0.9917	-0.1	1.055	0.947	0.9469	-	1.095	0.913	0.9081	+0.4
C_1 - nC_4	217.9	-180	1.000	1.000	0.9976	+0.3	1.22	0.819	0.8290	-1.2	1.46	0.685	0.6928	-1.2
C_1 - C_3	498.6	-120	0.894	1.118	1.177	-4.9	1.72	0.581	0.5547	+4.7	3.08	0.324	0.2661	+21.8
C_1 - C_2	783.7	-180	1.000	1.000	0.9808	+2.0	2.02	0.495	0.5052	-1.0	4.00	0.250	0.2746	+3.6
											Alg. avg.			+2.0
											Abs. avg.			3.4

Liquid phase

System*	Pressure, lb./sq. in. abs.	b_L , °F.	Methane				Propane				<i>n</i> -pentane			
			<i>A</i>	<i>A_p</i>	<i>f</i> / <i>x</i>	Dev., %	<i>A</i>	<i>A_p</i>	<i>f</i> / <i>x</i>	Dev., %	<i>A</i>	<i>A_p</i>	<i>f</i> / <i>x</i>	Dev., %
C_3 - nC_4	104.9	0	23.6	2475	2467	+0.3	1.41	148.0	152.5	-2.9	0.143	15.01	15.84	-5.3
C_2 - C_3	282	-60	8.1	2284	2184	+4.5	0.540	152.2	158.0	-3.7	0.068	19.17	18.60	+3.0
C_2 - C_3	528	-90	4.05	2140	2049	+4.3	0.300	158.4	171.6	-7.7	0.048	25.4	22.69	+11.8
C_1 - nC_5	876.5	0	3.25	2845	2790.7	+1.9	0.215	188.2	186.1	+1.1	0.0235	20.6	19.96	+3.2
											Alg. avg.			+0.9
											Abs. avg.			4.1

*Functions were calculated for binary mixtures of normal paraffins.

Deviation, % = 100 (*f*/*py* - 1/*B*) / *f*/*py* or 100 (*f*/*x* - *A_p*) / *f*/*x*.

Benedict equation (6). The values of *f*/*x* and *f*/*py* were read from tables of the functions which were calculated to provide basic data for the Kellogg correlation. Fugacity functions are compared for methane, propane, and *n*-pentane in both vapor and liquid phases. Average deviation of values derived from the P.T.C. charts from the calculated values is 3.4% for fugacity functions in the vapor phase and 4.1% for fugacity functions in the liquid phase. These deviations are about equal in magnitude to the deviations from smooth curves on plots of the functions vs. pressure (6).

Comparisons were made between experimental data and *K*'s from the P.T.C. charts, the Kellogg charts, the generalized correlation, the Scheibel and Jenny nomograph (34), and Standard Oil Company (Indiana) charts published by the Natural Gasoline Supply Men's Association (15), referred to below as S.O.I. charts. The S.O.I. charts are based on fugacity values compiled by Lewis and coworkers (23). The author's data on multicomponent mixtures, data on ternary and multicomponent systems listed in Table 3, and data on binary systems listed in Table 7 were used to make the comparison.

These data represent a large portion of the reported investigations on vapor-liquid equilibrium in

light-hydrocarbon systems. Comparisons with the author's data are limited to hydrocarbons present in the mixtures investigated. For other investigations, a random sampling of the reported experimental data was made to cover the range of experimental conditions. The comparisons with binary and ternary systems include many determinations near the critical points of the experimental mixtures. The same experimental data were used for all comparisons, except that for the pressure-temperature correlations part of

TABLE 7

EXPERIMENTAL DATA ON BINARY SYSTEMS
USED IN MAKING COMPARISONS WITH CORRELATIONS

System	Literature cited	Temperature, °F.	Pressure, lb./sq. in. abs.
Ethane, <i>n</i> -butane	21	0 - 225	100 - 500
Ethane, <i>n</i> -heptane	16	275 - 467	200 - 800
Methane, isobutane	26	100 - 220	200 - 600
Methane, <i>n</i> -butane	32	70 - 220	60 - 800
Methane, <i>n</i> -pentane	39	100 - 220	200 - 800
Methane, propane	29	70 - 160	200 - 800
<i>n</i> -pentane, <i>n</i> -heptane	11	285 - 447	147 - 445
Propane, isobutylene	33	125 - 260	200 - 620

the data either are outside the range of conditions represented or are for components not included in the correlations. Summaries of the comparisons are shown in Table 8. The first part of the table lists

comparisons by component for the author's data and binary and ternary data from the literature. The second part of the table shows summaries by component for all systems and an over-all summary for

TABLE 8
AVERAGE DEVIATIONS OF FIVE CORRELATIONS FROM EXPERIMENTAL DATA*

Systems	P.T.C.			Kellogg (22)			Generalized			Scheibel & Jenny (34)			S.O.I. (15)		
	No. of points	Alg. avg., %	Abs. avg., %	No. of points	Alg. avg., %	Abs. avg., %	No. of points	Alg. avg., %	Abs. avg., %	No. of points	Alg. avg., %	Abs. avg., %	No. of points	Alg. avg., %	Abs. avg., %
Methane															
Author	26	-1.8	3.5	26	-5.4	6.6	26	-3.2	10.8	18	+10.1	25.3	26	+2.6	25.4
Ternary†	17	+3.0	4.7	17	+2.6	5.8	7	+18.2	23.6	7	+30.6	31.0	7	+40.6	41.0
Binary	23	+5.4	7.9	23	-1.1	7.1	23	+35.4	38.8	23	+41.1	41.1	23	+51.6	51.6
Ethylene															
Ternary	4	-1.1	1.6	4	-3.9	4.9	2	+23.7	23.7	2	+19.0	19.0			
Ethane															
Author	29	-0.4	4.2	29	-1.0	7.9	29	+3.2	6.7	21	+6.8	10.1	29	+6.3	8.2
Ternary	5	+3.8	8.0	5	+0.3	5.3	2	-3.1	7.5	2	-0.1	7.4	2	-8.1	8.1
Binary	9	-2.3	5.3	8	-3.0	5.1	9	+16.0	18.2	8	+25.7	26.4	8	+17.2	18.7
Propane															
Author	29	-5.1	7.6	29	-6.5	9.0	29	-5.1	9.9	21	+6.8	10.3	29	-0.9	11.6
Ternary	9	+2.5	8.1	9	+5.4	7.7	4	+7.5	9.8	4	+19.9	19.9	4	+10.5	14.2
Binary	12	-5.4	6.4	12	-4.2	7.0	12	+2.4	9.7	12	+7.1	13.4	12	-1.2	7.2
Isobutane															
Author	6	+9.3	9.3	6	+10.9	11.4	6	+3.3	7.0	4	+8.6	11.1	6	+6.4	8.5
Ternary	4	-1.2	4.9	4	+6.2	6.8	2	-11.5	11.5	2	+0.7	1.2	2	+9.0	9.0
Binary	6	+2.9	3.3	6	-2.4	2.4	6	-6.2	7.7	6	+5.1	7.6	6	+9.5	9.5
Isobutylene															
Binary	6	-1.2	4.8	6	+2.7	6.5									
n-butane															
Author	19	-1.1	5.5	19	0	6.2	19	-4.0	8.5	17	+8.0	9.2	19	+7.6	10.5
Ternary	4	+7.8	11.8	4	+13.8	15.8	1	-3.0	3.0	1	+22.8	22.8	1	+40.0	40.0
Binary	12	-3.6	4.1	12	0	3.6	12	-12.2	13.0	12	+1.5	9.3	12	+7.5	12.7
n-pentane															
Author	7	+11.4	19.7	7	+11.7	24.4	7	+2.3	21.6	7	+4.1	17.0	7	+16.9	26.2
Ternary	11	-2.4	8.8	11	-5.1	10.2	5	-13.7	15.8	5	-2.2	9.8	5	+25.1	30.2
Binary	11	+1.5	3.6	11	+0.8	5.0	11	-5.3	6.2	11	+14.3	16.8	11	+0.1	5.8
n-heptane															
Binary	9	+2.7	11.8	9	+1.8	10.7	9	-35.2	35.2	9	-10.9	12.4	9	-3.9	15.7
All systems															
Methane	66	+1.9	5.3	66	-1.8	6.6	56	+15.3	23.9	48	+28.0	33.8	56	+27.4	38.2
Ethylene	4	-1.1	1.6	4	-3.9	4.9	2	+23.7	23.7	2	+19.0	19.0			
Ethane	43	-0.3	4.9	42	-1.2	7.1	40	+5.8	9.1	31	+11.2	14.2	39	+7.8	10.4
Propane	50	-3.8	7.4	50	-3.8	8.3	45	-2.0	9.8	37	+8.4	12.4	45	+0.1	10.2
Isobutane	16	+4.3	6.0	16	+4.8	6.8	14	-2.9	7.9	12	+5.5	7.7	14	+8.1	9.0
Isobutylene	6	-1.2	4.8	6	+2.7	6.5									
n-butane	35	-0.9	5.7	35	+1.6	6.4	32	-7.0	10.0	30	+5.9	9.7	32	+8.6	12.3
n-pentane	29	+2.4	9.5	29	+1.2	11.7	23	-4.8	16.4	23	+7.6	15.3	23	+11.6	17.3
n-heptane	9	+2.7	11.8	9	+1.8	10.7	9	-35.2	35.2	9	-10.9	12.4	9	-3.9	15.7
All hydrocarbons															
	258	+0.2	6.4	257	-0.7	7.7	221	+1.6	15.0	192	+12.3	17.8	218	+11.2	18.8

*Author's data, ternary and multicomponent data listed in Table 4, and binary data listed in Table 7.

†Summaries on ternary data include three runs on five-component systems.

Deviation, % = 100 (correlation - observed) / observed.

each correlation. The number of points, algebraic average deviation, and absolute average deviation are shown for each summary.

The comparisons listed in Table 8 show that the P.T.C. correlation is in better agreement with experimental data than any other correlation for which comparisons were made. The average absolute deviation for all comparisons is 6.4% for the P.T.C. charts, 7.7% for the Kellogg charts, 15.0% for the generalized correlation, 17.8% for the Scheibel and Jenny nomograph, and 18.8% for the S.O.I. charts. The algebraic summations are also of interest because they show to what extent the deviations from experimental data are evenly distributed in sign and magnitude. The algebraic average deviation is +0.2% for the P.T.C. charts, -0.7% for the Kellogg charts, +1.6% for the generalized correlation, +12.3% for the Scheibel and Jenny nomograph, and +11.2% for the S.O.I. charts. The P.T.C. charts show better agreement than the Kellogg correlation because some adjustments were made in constructing the charts, and interpolation is more accurate. Deviations of the three pressure-temperature correlations are much greater than those for the P.T.C. charts and the Kellogg charts because composition is not treated as a variable.

The generalized correlation shows better agreement with experimental data than does either of the other two pressure-temperature correlations. Average absolute deviations are smaller, and the average algebraic deviations show that K 's from the generalized correlation represent a good average of experimental values.

Calculation Methods

Calculation procedures which combine use of the two correlations of distribution coefficients presented above lead to accurate solutions which can be obtained from minimum expenditure of time. Both the P.T.C. charts and the generalized correlation have disadvantages as sources of distribution coefficients for vapor-liquid equilibrium calculations. Distribution coefficients from the P.T.C. charts are accurate, but use of the correlation is slow because phase compositions must be established by trial and error to estimate the effects of composition. Calculations with K 's from the generalized correlation can be made in a minimum of time, but the K values are comparatively inaccurate. The effects of the respective disadvantages of the two correlations are largely eliminated if the generalized correlation is used in pre-

TABLE 9
CALCULATION OF BUBBLE-POINT TEMPERATURE

Pressure: 500 lb./sq. in. abs.

Preliminary: K 's from generalized correlation

Component	x_i	Assumed temp., °F.			200		300		260	
		b_i , °F.	$x_i b_i$	K_i	$y_i = K_i x_i$	K_i	$y_i = K_i x_i$	K_i	$y_i = K_i x_i$	$y_i b_i$
C ₂	0.013	-127.5	-1.7	2.52	0.033	3.80	0.049	3.28	0.043	-6.3
C ₃	0.362	-43.7	-15.8	1.17	0.423	2.02	0.730	1.65	0.597	-26.1
n-C ₄	0.373	+31.1	+11.6	0.505	0.188	1.00	0.373	0.77	0.286	+8.9
n-C ₅	0.146	+96.8	+14.1	0.225	0.033	0.53	0.078	0.383	0.056	+5.4
n-C ₇	0.106	+209.2	+22.2	0.056	0.006	0.173	0.018	0.112	0.012	+2.5
	1.000		$b_L = +30.4$		0.683		1.248		0.994	-15.6

Final: K 's from P.T.C. charts

Assumed temp., °F.		260					275					282				
$b_V = \sum y_i b_i / \sum y_i$, °F.		-15.7					-1.3					+1.7				
Component	A_i	B_i	$K_i = A_i/B_i$	$y_i = K_i x_i$	$y_i b_i$	A_i	B_i	$K_i = A_i/B_i$	$y_i = K_i x_i$	$y_i b_i$	A_i	B_i	$K_i = A_i/B_i$	$y_i = K_i x_i$	$y_i b_i$	
C ₂	2.30	0.98	2.25	0.029	-3.7	2.34	0.95	2.22	0.029	-3.7	2.38	0.95	2.26	0.029	-3.7	
C ₃	1.05	1.24	1.30	0.470	-20.5	1.12	1.18	1.32	0.478	-20.9	1.16	1.18	1.37	0.496	-21.7	
n-C ₄	0.525	1.58	0.83	0.310	+9.6	0.60	1.53	0.918	0.342	+10.6	0.607	1.52	0.923	0.344	+10.7	
n-C ₅	0.295	1.97	0.581	0.085	+8.2	0.337	1.93	0.650	0.095	+9.2	0.359	1.89	0.678	0.099	+9.6	
n-C ₇	0.081	3.08	0.250	0.025	+5.2	0.098	3.0	0.294	0.031	+6.5	0.105	2.93	0.307	0.032	+6.7	
				0.919	-1.2				0.975	+1.7				1.000	+1.6	

liminary calculations to estimate values of unknown variables and the P.T.C. charts are used for final calculations. This approach is valid for all calculations of light-hydrocarbon behavior to which distribution coefficients can be applied. Calculations of dew points, bubble points, and equilibrium flash vaporizations are discussed below as typical examples.

For calculation of dew points or bubble points, the composition of one phase and either temperature or pressure are known. The unknown temperature or pressure, and composition of the other phase are calculated by successive approximations.

Table 9 shows the calculation of bubble-point temperature of a liquid at a pressure of 500 lb./sq.-

in.abs. In Part 1 of the table, K 's from the generalized correlation are used to calculate the approximate temperature and vapor-phase composition. The calculated temperature and vapor composition and the given liquid composition are used to read K 's from the P.T.C. charts in the first trial of the final calculation (Part 2 of the table). The calculated bubble point was 282°F., compared with the preliminary estimate of 260°F., and b_V for the bubble-point vapor was 1.6°F., compared with the preliminary estimate of -15.6°F. Three trials in the preliminary calculation were completed in less time than that necessary for one trial of the final calculation.

The calculation illustrated in Table 9 is typical of all dew- and bubble-point calculations. The same

TABLE 10
CALCULATION OF EQUILIBRIUM FLASH SEPARATION

Pressure: 500 lb./sq. in. abs. Temperature: 90°F.

Preliminary: K 's from generalized correlation

Component	b_i , °F.	n_i , moles	Assumed:		$L/V=0.1$		$L/V=0.3$		$v_i b_i$	l_i	$l_i b_i$
			K_i	$n_i K_i$	$L/V+K_i$	v_i	$L/V+K_i$	v_i			
C ₁	-258.9	372	5.25	1955	5.35	366	5.55	352	-91350	20	-5170
C ₂	-127.5	360	1.31	473	1.41	335	1.61	294	-37500	66	-8440
C ₃	-43.7	142	0.455	65	0.555	117	0.755	86	-3760	56	-2448
i-C ₄	+10.9	22	0.220	4.8	0.320	15	0.520	9	+98	13	+142
n-C ₄	+31.1	58	0.155	8.5	0.255	33	0.455	19	+591	39	+1216
n-C ₆	+155.7	46	0.022	1.0	0.122	8	0.322	3	+467	43	+6700
		1000				874		763	-131454	237	-8000
			Calculated:		$L/V=0.144$		$L/V=0.311$		$b_V=-172$		$b_L=-34$

Final: K 's from P.T.C. charts

Assumed:		$L/V=0.31$		$b_L=-34$		$b_V=-172$				$L/V=0.32$		$b_L=-40$		$b_V=-170$		
Component	A_i	B_i	$K_i=A_i B_i$	$L/VK+1$	v_i	$v_i b_i$	l_i	$l_i b_i$	A_i	B_i	$K_i=A_i B_i$	$L/VK+1$	v_i	$v_i b_i$	l_i	$l_i b_i$
C ₁	4.95	0.995	4.91	1.063	350	-90600	22	-5690	4.95	0.990	4.90	1.065	349	-90500	23	-5950
C ₂	1.00	1.30	1.30	1.238	291	-37100	69	-8810	0.99	1.31	1.30	1.246	289	-36850	71	-9060
C ₃	0.290	1.61	0.467	1.663	85	-3710	57	-2490	0.290	1.62	0.470	1.681	84	-3670	58	-2535
i-C ₄	0.133	2.10	0.279	2.111	10	+109	12	+131	0.134	2.11	0.283	2.131	10	+109	12	+131
n-C ₄	0.088	2.02	0.178	2.742	21	+654	37	+1153	0.088	2.03	0.179	2.788	21	+654	37	+1153
n-C ₆	0.0107	3.40	0.0364	9.52	5	+779	41	+6390	0.0108	3.45	0.0372	9.61	5	+779	41	+6390
					762	-129868	238	-9316					758	-129478	242	-9871
Calculated:		$L/V=0.312$		$b_L=-39.1$		$b_V=-170.4$				$L/V=0.319$		$b_L=-40.8$		$b_V=-170.8$		

$$v_i = \frac{n_i K_i}{L/V+K_i} = \frac{n_i}{L/VK_i+1}; \quad b_L = \sum l_i b_i / \sum l_i; \quad b_V = \sum v_i b_i / \sum v_i$$

procedure, modified to suit the particular problem, applies to calculation of bubble-point pressure at known temperature, dew-point temperature at known pressure, and dew-point pressure at known temperature.

The known quantities for calculation of equilibrium flash vaporizations are composition of feed, temperature, and pressure. The unknown quantities, liquid-vapor mole ratio (L/V) and compositions of the equilibrium phases, are calculated by successive approximation. Preliminary calculation with K 's from the generalized correlation are made to estimate L/V , b_L , and b_V for the first trial of final calculations with the P.T.C. charts.

Table 10 shows the calculation of the equilibrium flash vaporization of a given feed at 90°F. and 500 lb./sq.in.abs. Part 1 of the table is a preliminary calculation made with generalized correlation K 's. The preliminary calculation was not carried to complete agreement between assumed and calculated L/V because K 's from the P.T.C. charts might shift the ratio in either direction. Part 2 of the table is the final calculation. For the first trial with K 's from the P.T.C. charts, b_L and b_V were calculated from preliminary estimates of phase compositions, and assumed L/V was 0.31. Agreement between calculated and assumed L/V , b_L , and b_V for the second trial with P.T.C. charts and the small change in phase compositions from the previous trial indicates that the calculation is complete. Final values of $L/V = 0.319$, $b_L = -40.8^\circ\text{F.}$, and $b_V = -170.8^\circ\text{F.}$, compared with values from the preliminary calculation of $L/V = 0.311$, $b_L = -34^\circ\text{F.}$, and $b_V = -172^\circ\text{F.}$, show the value of the preliminary calculation.

Summary and Recommendations

Two correlations of distribution coefficients were developed for use in calculation of vapor-liquid equilibrium relations of light hydrocarbons. The pressure-temperature-composition (P.T.C.) correlation provides a convenient, yet accurate, means for predicting K values for light hydrocarbons. Distribution coefficients are obtained from the P.T.C. charts as a product of fugacity factors for the vapor and liquid phases, shown as functions of temperature, pressure, and molal average boiling point of phase on two charts for each hydrocarbon. The generalized correlation is believed to be an improvement over previously available pressure-temperature correlations. Both correlations were developed from the Kellogg charts presented by Benedict, Webb, Rubin, and Friend (6, 7).

Experimental data were obtained on complex mixtures of light hydrocarbons at temperatures from -60° to 300°F. and at pressures from 96 to 797 lb./sq.in.abs. The greater number of experimental determinations were made at temperatures between -100°

and 100°F. , because of the scarcity of experimental data in that temperature range. Varying the composition of experimental mixtures resulted in information on the effects of composition at constant temperature and pressure. The author's experimental data and experimental data available in the literature were used in making minor adjustments to the P.T.C. charts as initially drawn and in checking the accuracy of both correlations.

The two correlations were compared with previous methods for predicting K to obtain a quantitative estimate of comparative accuracy. Average deviations of fugacity functions derived from the P.T.C. charts from fugacity functions calculated from the Benedict equation of state were 3.4% for the vapor phase and 4.1% for the liquid phase. A wide sampling of experimental data on binary, ternary, and complex systems was used as the basis for a comparison of distribution-coefficient deviations for the two correlations with deviations for three correlations previously available. Absolute average deviations from experimental data are P.T.C. charts, 6.4%; Kellogg charts, 7.7%; generalized correlation, 15.0%; Scheibel and Jenny nomograph, 17.8%, and S.O.I. charts, 18.8%. Algebraic average deviations are P.T.C. charts, +0.2%; Kellogg charts, -0.7%; generalized correlation, +1.6%; Scheibel and Jenny nomograph, +12.3%; and S.O.I. charts, +11.2%. The P.T.C. and Kellogg charts show better agreement because the effects of phase composition are included; whereas in the other three correlations, K is shown as a function of temperature and pressure only.

Practical calculation methods were outlined that combine use of the two correlations to obtain accurate solutions of phase-equilibrium problems from reasonable expenditure of calculation time. Preliminary calculations are made with K 's from the generalized correlation to estimate values of unknown variables, and final calculations are made with K 's from P.T.C. charts to obtain more accurate solutions.

A discussion of the range of applicability and accuracy of the P.T.C. charts is, in effect, an evaluation of the suggested system of calculation methods because the final accuracy of the results depends on the accuracy of the P.T.C. charts. The P.T.C. charts are recommended for calculations on systems containing paraffin and olefin hydrocarbons in the boiling point range from methane through decane. It is probable that no additional error would be introduced by the presence of paraffins or olefins heavier than decane, but comparative evaluations have not been made.

Distribution coefficients for paraffins or olefins not included in the presentation can be estimated by plotting $\log K$ for other hydrocarbons in the same boiling-point range, at the same conditions of temperature, pressure, b_L , and b_V , vs. boiling point.

Distribution coefficients read by interpolation on the smooth curve through the points will be of the same order of accuracy as $\log K$ read from the charts.

Certain limitations to the Kellogg charts (7) apply equally to the P.T.C. charts. The charts may be used for systems containing nonhydrocarbon components having no polarity, such as nitrogen and carbon dioxide, but should not be used when more than 30% of a polar compound is present in either phase. The charts are less reliable for systems containing aromatics and naphthenes; however, Solomon (36) has proposed a method for correcting K 's from the Kellogg charts for nonparaffinicity which may be applicable to the P.T.C. charts. Chart values are less reliable near the critical point because the composition parameter, molal average boiling point, does not adequately correlate the effects of composition in the critical region. Good results will usually be obtained except when the pressure is within 50 lb./sq.in. of the critical pressure of the system.

Notation

- A = fugacity function for liquid phase
- B = fugacity function for vapor phase
- b_i = normal boiling point, °F.
- b_L = molal average boiling point of liquid, °F.
- b_V = molal average boiling point of vapor, °F.
- f = fugacity, lb./sq.in.abs.
- K = distribution coefficient
- L = moles of liquid
- l = moles of component in liquid
- n = moles of component in feed
- p = pressure, lb./sq.in.abs.
- t = temperature, °F.
- V = moles of vapor
- v = moles of component in vapor
- x = mole fraction in liquid
- y = mole fraction in vapor

Subscripts

- e = experimental
- i = i th component
- s = smoothed

Superscripts

- L = liquid
- V = vapor

Literature Cited

1. Benedict, M., E. Solomon, and L. C. Rubin, *Ind. Eng. Chem.*, **37**, 55 (1945).
2. Benedict, M., G. B. Webb, and L. C. Rubin, *J. Chem. Phys.*, **8**, 334 (1940).
3. *Ibid.*, **10**, 747 (1942).
4. Benedict, M., G. B. Webb, and L. C. Rubin, *Chem. Eng. Progress*, **47**, 419 (1951).
5. *Ibid.*, **47**, 449 (1951).
6. Benedict, M., G. B. Webb, L. C. Rubin, and L. Friend, *Chem. Eng. Progress*, **47**, 571 (1951).
7. *Ibid.*, **47**, 609 (1951).
8. Billman, G. W., B. H. Sage, and W. N. Lacey, *Am. Inst. Mining Met. Engrs., Tech. Pub. No. 2232* (1947).
9. Brown, G. G., and M. Souders, *Refiner Natural Gasoline Mfr.*, **11**, 376 (1932).
10. Carter, R. T., B. H. Sage, and W. N. Lacey, *Am. Inst. Mining Met. Engrs., Tech. Pub. No. 1250* (1940).
11. Cummings, L. W. T., F. W. Stones, and M. A. Volante, *Ind. Eng. Chem.*, **25**, 728 (1933).
12. Dourson, R. H., B. H. Sage, and W. N. Lacey, *Am. Inst. Mining Met. Engrs., Tech. Pub. No. 1490* (1942).
13. Edmister, W. C., *Petroleum Refiner*, **28**, No. 5, 149 (1949).
14. *Ibid.*, **28**, No. 9, 95 (1949).
15. "Engineering Data Book," Natural Gasoline Supply Men's Association (1951).
16. Gamson, B. W., and K. M. Watson, *Natl. Petroleum News*, **36**, No. 36, R 623 (1944).
17. Guter, M., D. M. Newitt, and M. Ruhemann, *Proc. Roy. Soc. (London)*, **A176**, 140 (1940).
18. Hadden, S. T., *Chem. Eng. Progress*, **44**, 135 (1948).
19. Hanson, G. H., and G. G. Brown, *Ind. Eng. Chem.*, **37**, 821 (1945).
20. Katz, D. L., and K. H. Hachmuth, *Ind. Eng. Chem.*, **29**, 1072 (1937).
21. Kay, W. B., *Ind. Eng. Chem.*, **32**, 353 (1940).
22. Kellogg Equilibrium Charts, *Chem. Eng. Progress*, **46**, 20 (1950).
23. Lewis, W. K., *Ind. Eng. Chem.*, **28**, 257 (1936).
24. Miller, C. O., and R. C. Barley, *Ind. Eng. Chem.*, **36**, 1018 (1944).
25. Nederbrgt, G. W., *Applied Scientific Research*, **A1**, 237 (1948).
26. Olds, R. H., B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **34**, 1008 (1942).
27. Prengle, H. W., L. R. Greenhaus, and R. York, *Chem. Eng. Progress*, **44**, 863 (1948).
28. Reamer, H. H., J. M. Fiskin, and B. H. Sage, *Ind. Eng. Chem.*, **41**, 2871 (1949).
29. Reamer, H. H., B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **42**, 534 (1950).
30. *Ibid.*, **43**, 1436 (1951).
31. Roland, C. H., D. E. Smith, and H. H. Kaveler, *Oil Gas J.*, **39**, No. 46, 128 (1941).
32. Sage, B. H., B. L. Hicks, and W. N. Lacey, *Ind. Eng. Chem.*, **32**, 1085 (1940).
33. Scheeline, H. W., and E. R. Gilliland, *Ind. Eng. Chem.*, **31**, 1050 (1939).
34. Scheibel, E. G., and F. J. Jenny, *Ind. Eng. Chem.*, **37**, 80 (1945).
35. Smith, K. A., and K. M. Watson, *Chem. Eng. Progress*, **45**, 494 (1949).
36. Solomon, E., *Chem. Eng. Progress Symposium Series*, No. 3, **48**, 91 (1952).
37. Souders, M., Jr., C. W. Selheimer, and G. G. Brown, *Ind. Eng. Chem.*, **24**, 517 (1932).
38. Stutzman, L. F., and G. M. Brown, *Chem. Eng. Progress*, **45**, 139 (1949).
39. Taylor, H. S., G. W. Wald, B. H. Sage, and W. N. Lacey, *Oil Gas J.*, **38**, No. 10, 46 (1939).
40. Taylor, T. R., and A. S. Parker, Thesis, Mass. Inst. Technol. (1935).
41. Webber, C. E., *Am. Inst. Mining Met. Engrs., Tech. Pub. No. 1252* (1940).
42. White, R. R., and G. G. Brown, *Ind. Eng. Chem.*, **34**, 1162 (1942).
43. Winn, F. W., *Chem. Eng. Progress Symposium Series*, No. 2, **48**, 121 (1952).

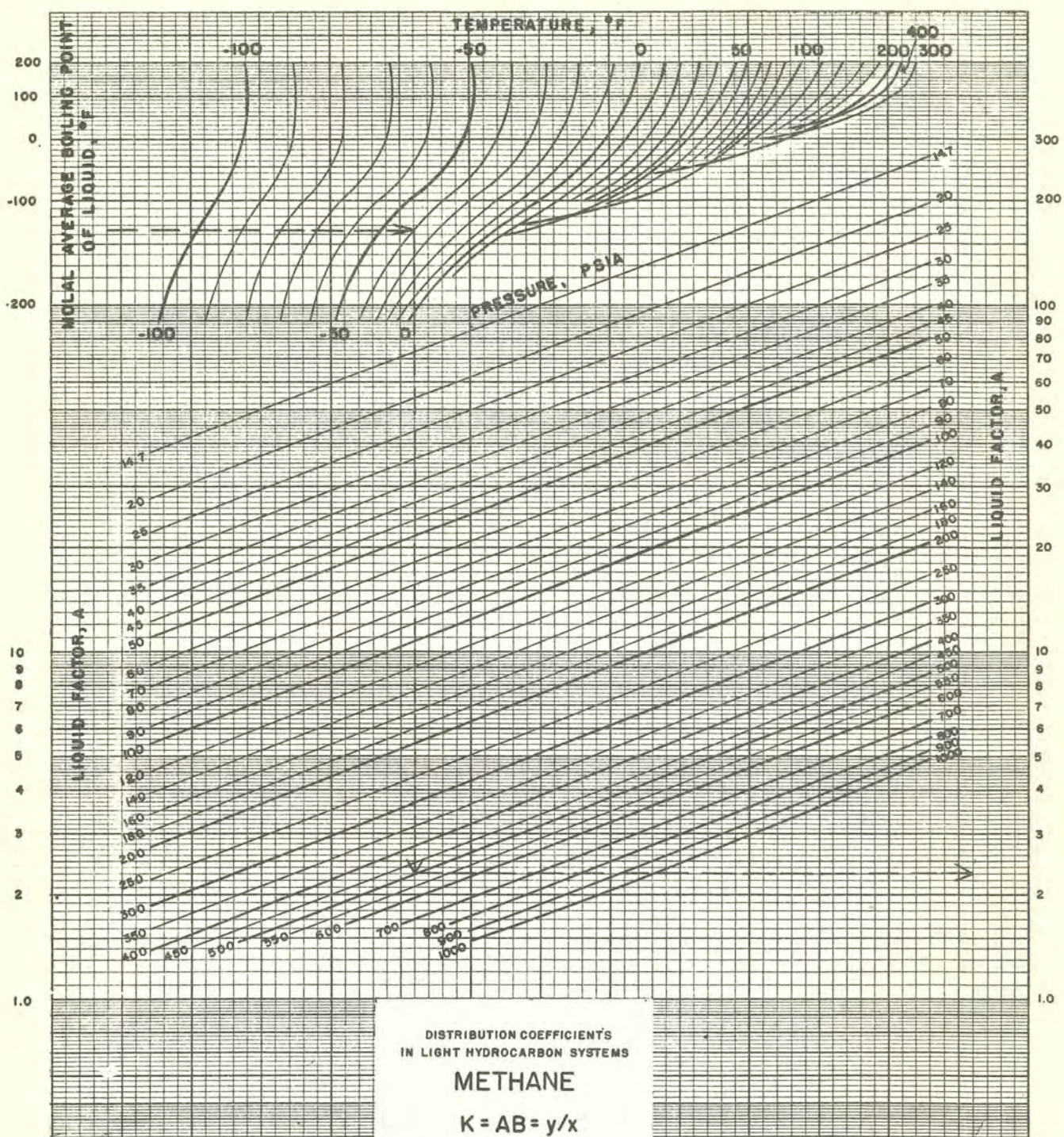


Fig. 7. Liquid factor for methane.

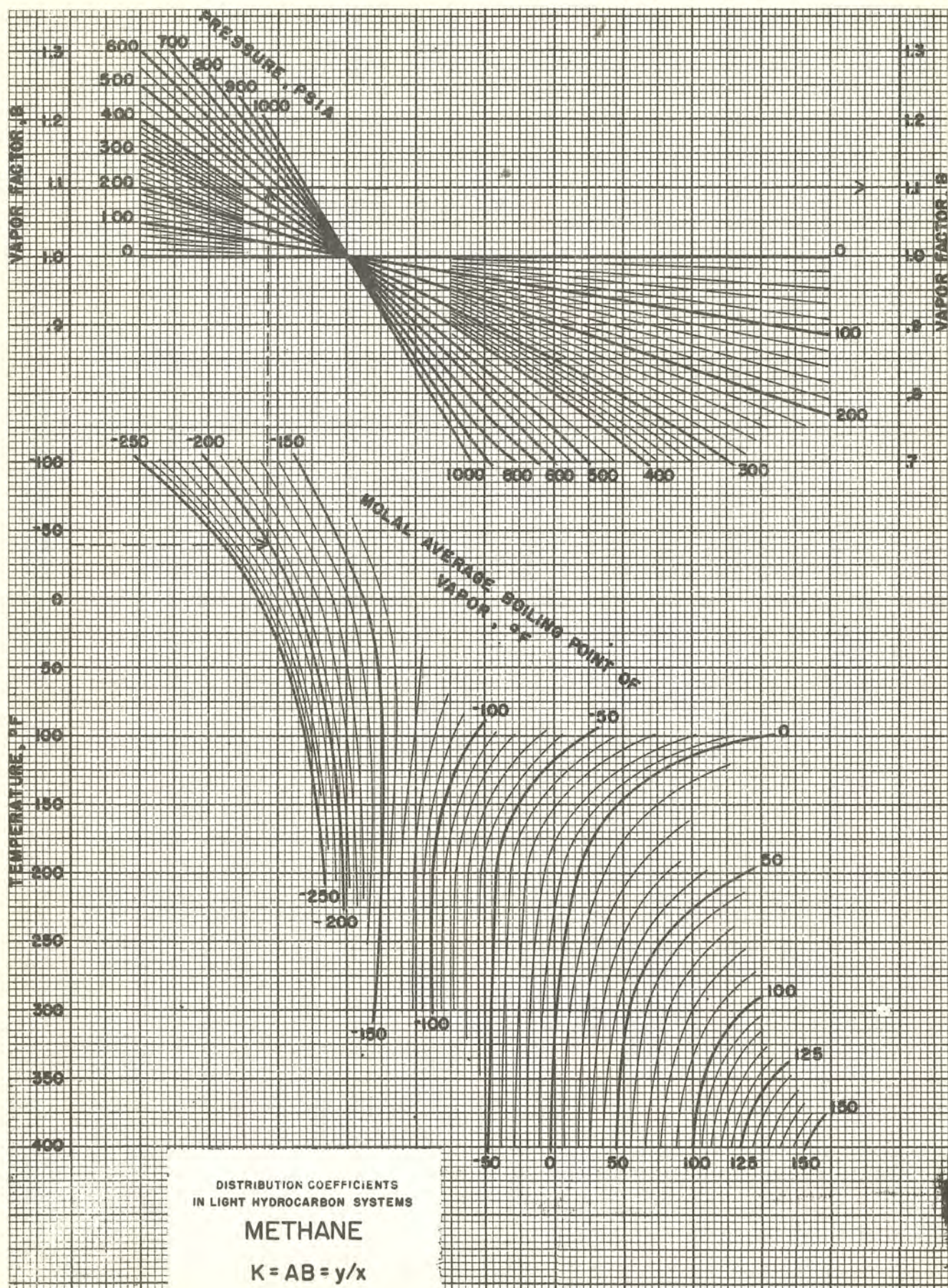


Fig. 8. Vapor factor for methane.

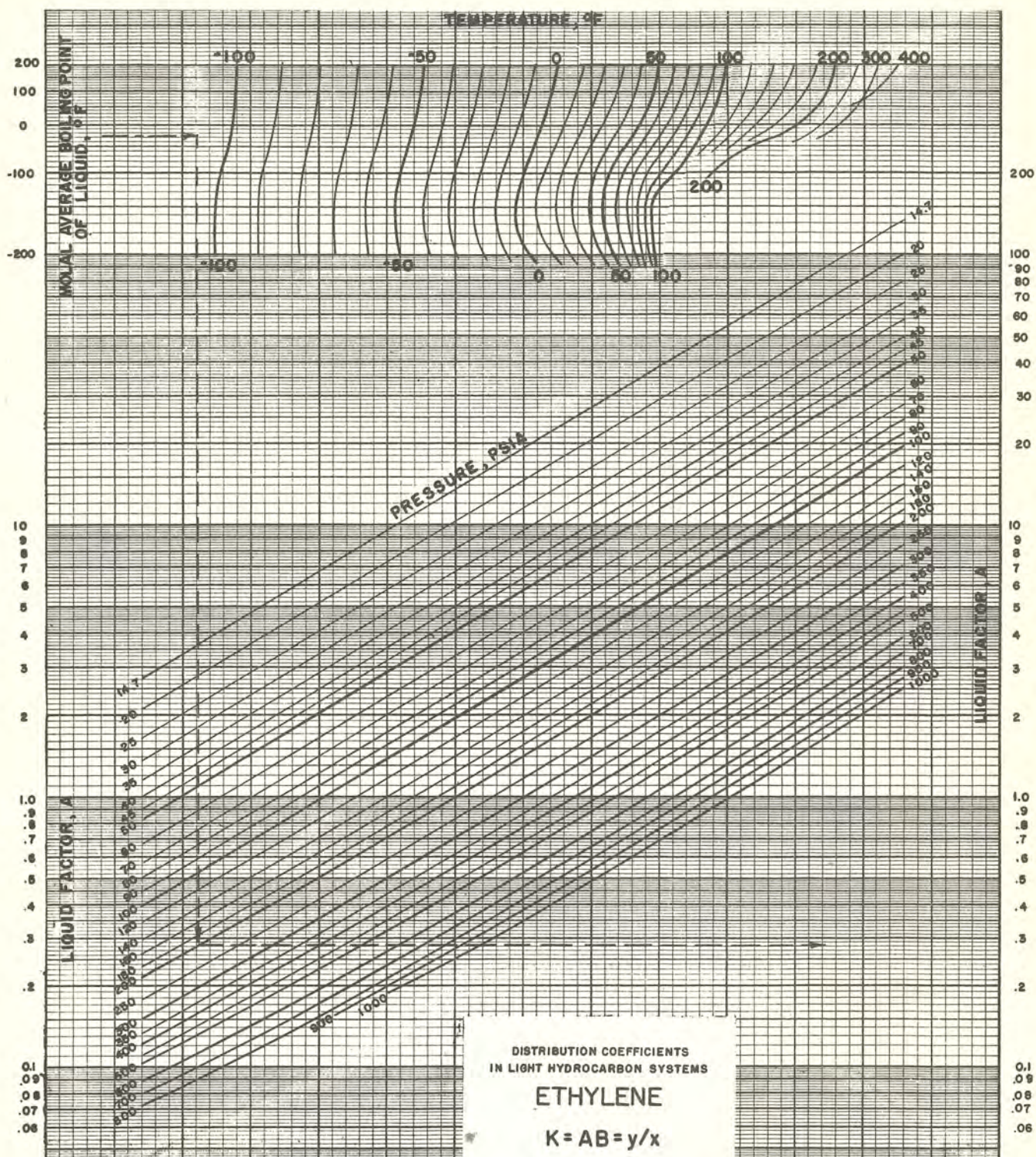


Fig. 9. Liquid factor for ethylene.

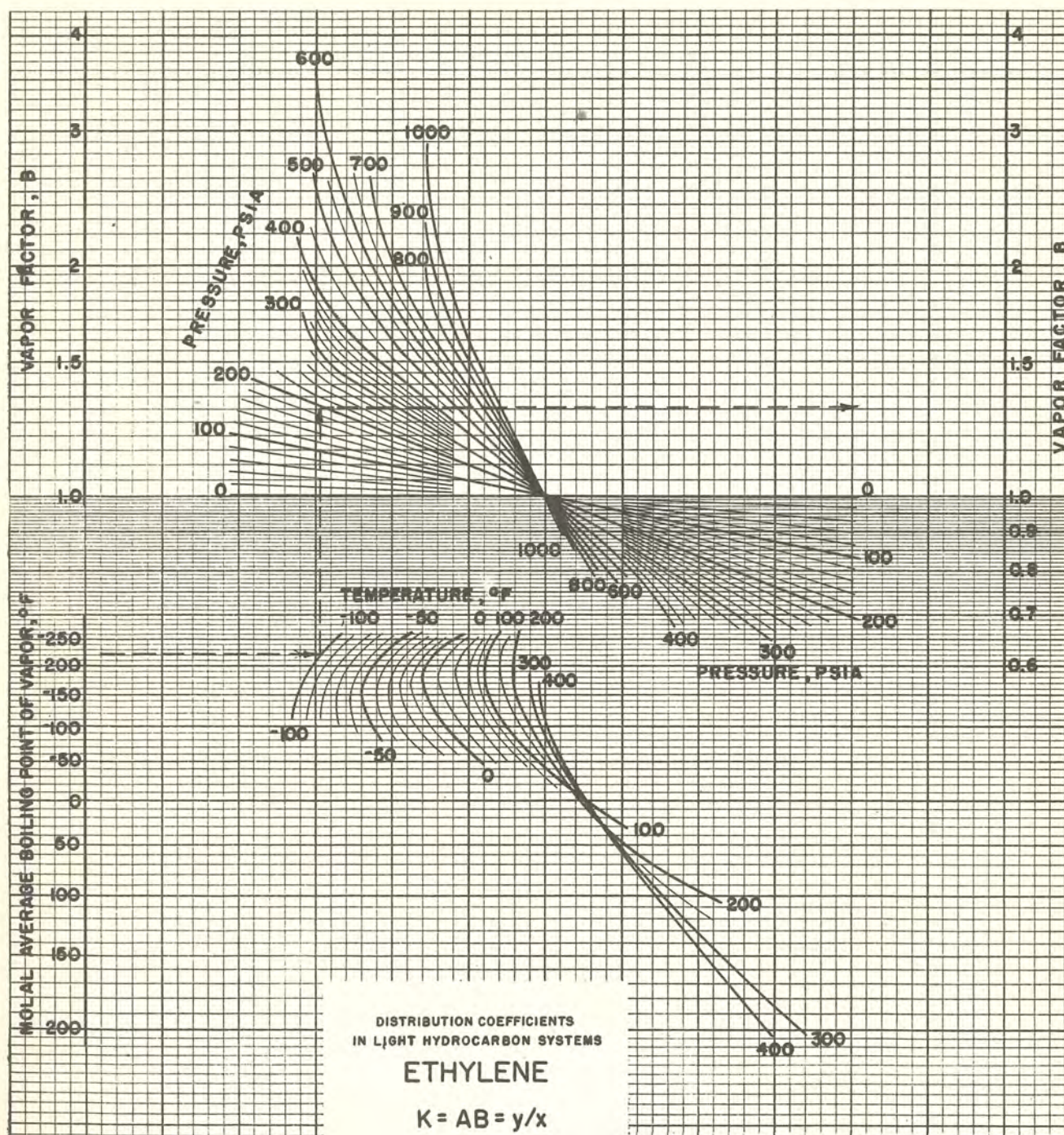


Fig. 10. Vapor factor for ethylene.

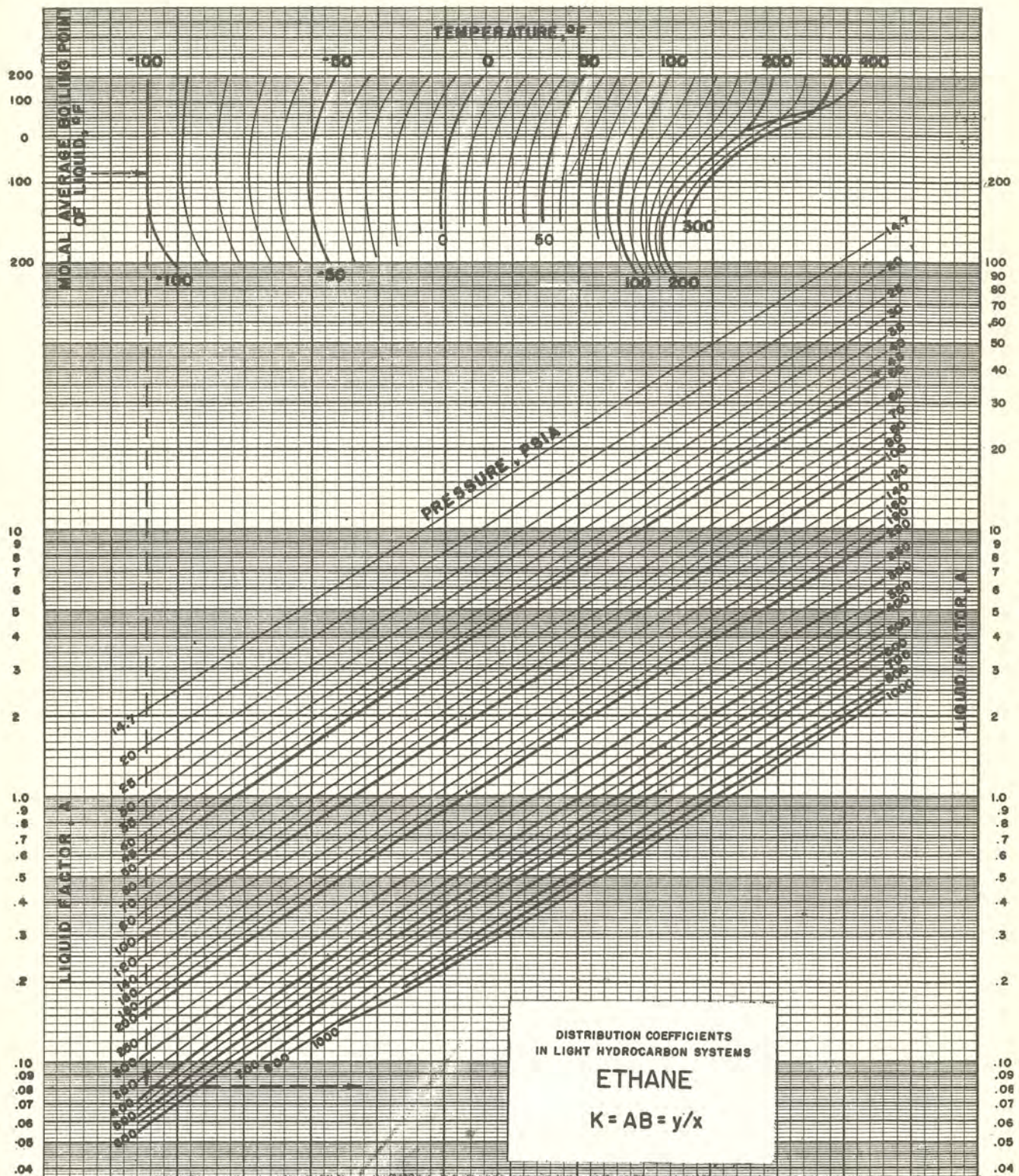


Fig. 11. Liquid factor for ethane.

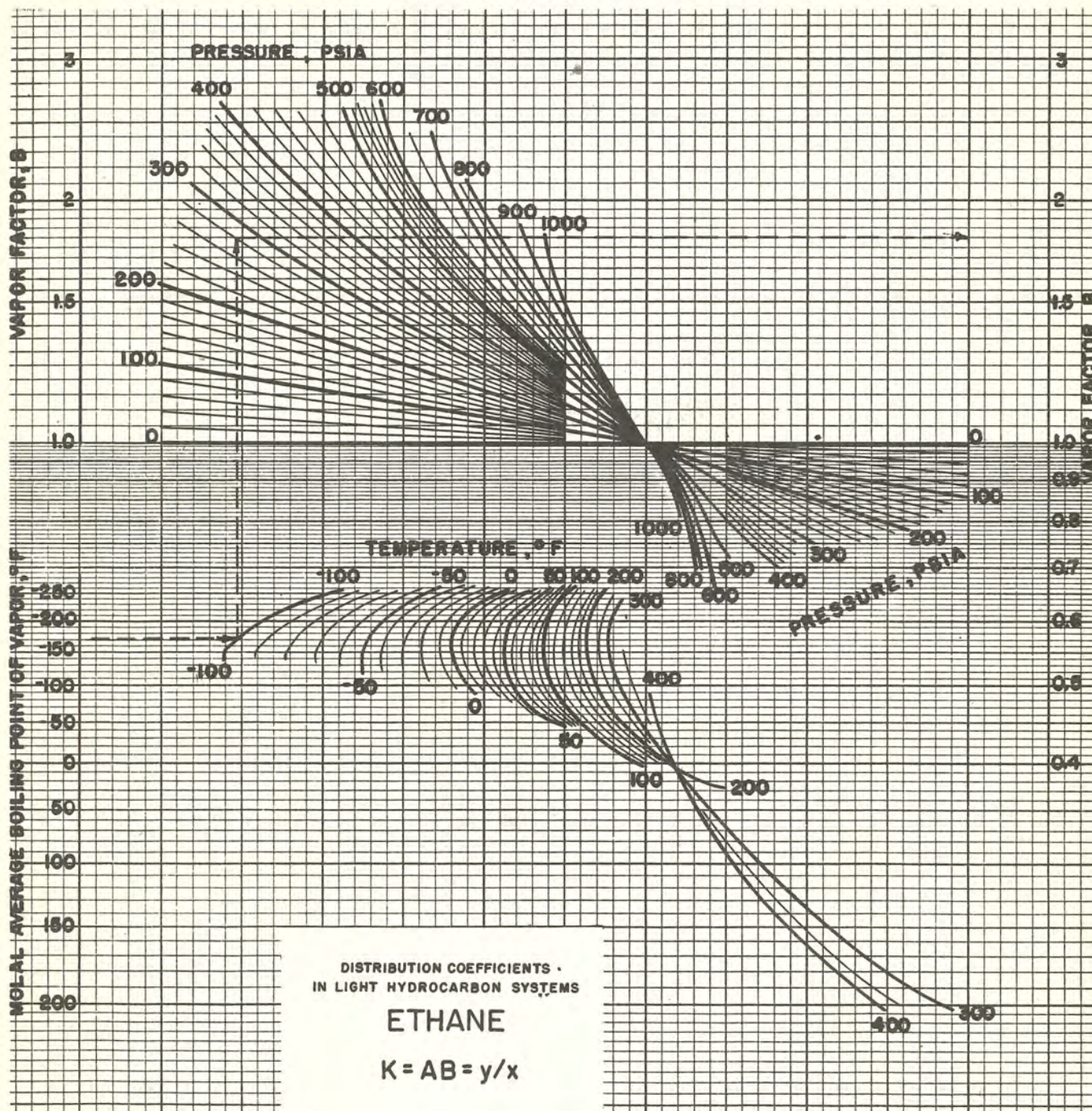


Fig. 12. Vapor factor for ethane.

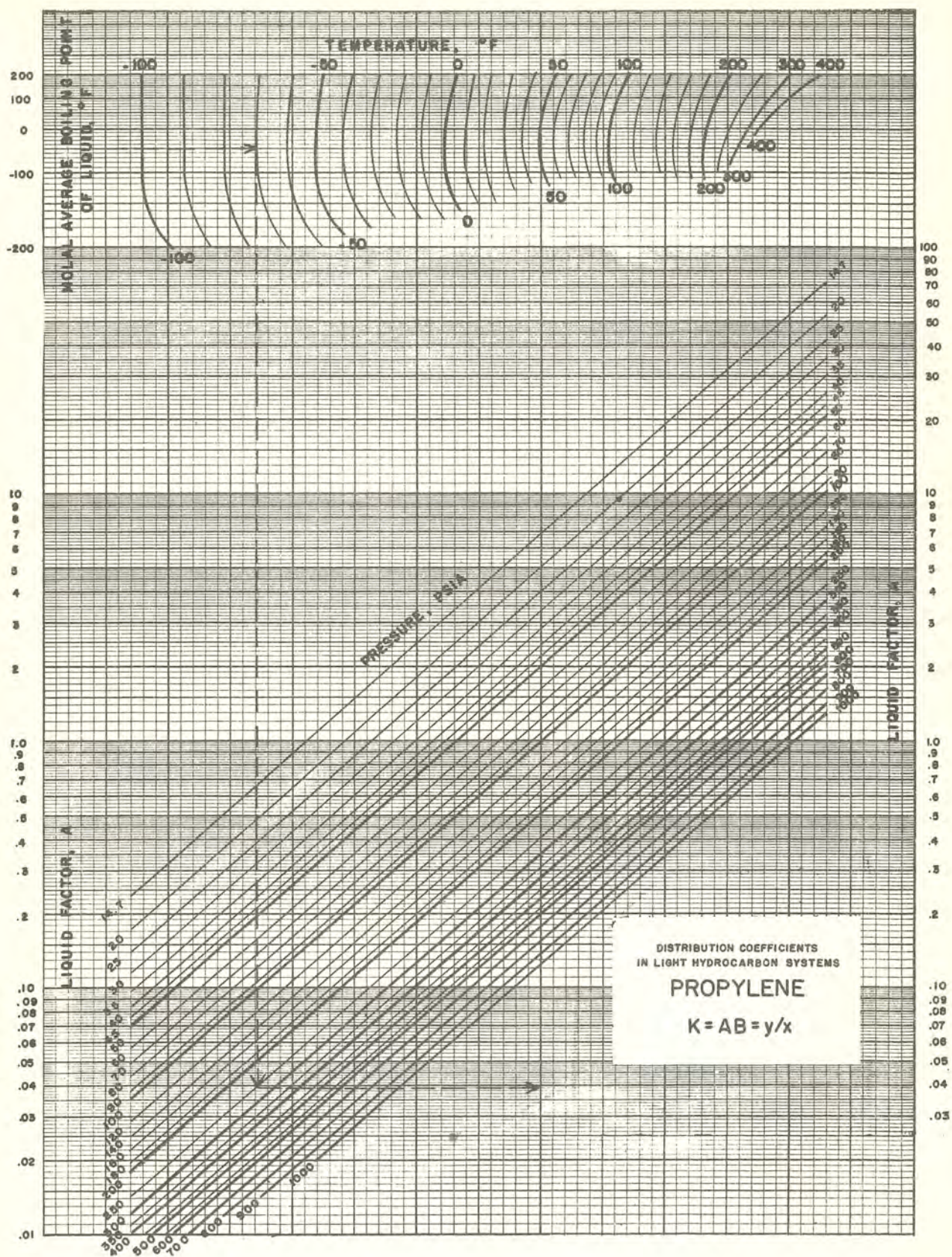


Fig. 13. Liquid factor for propylene.

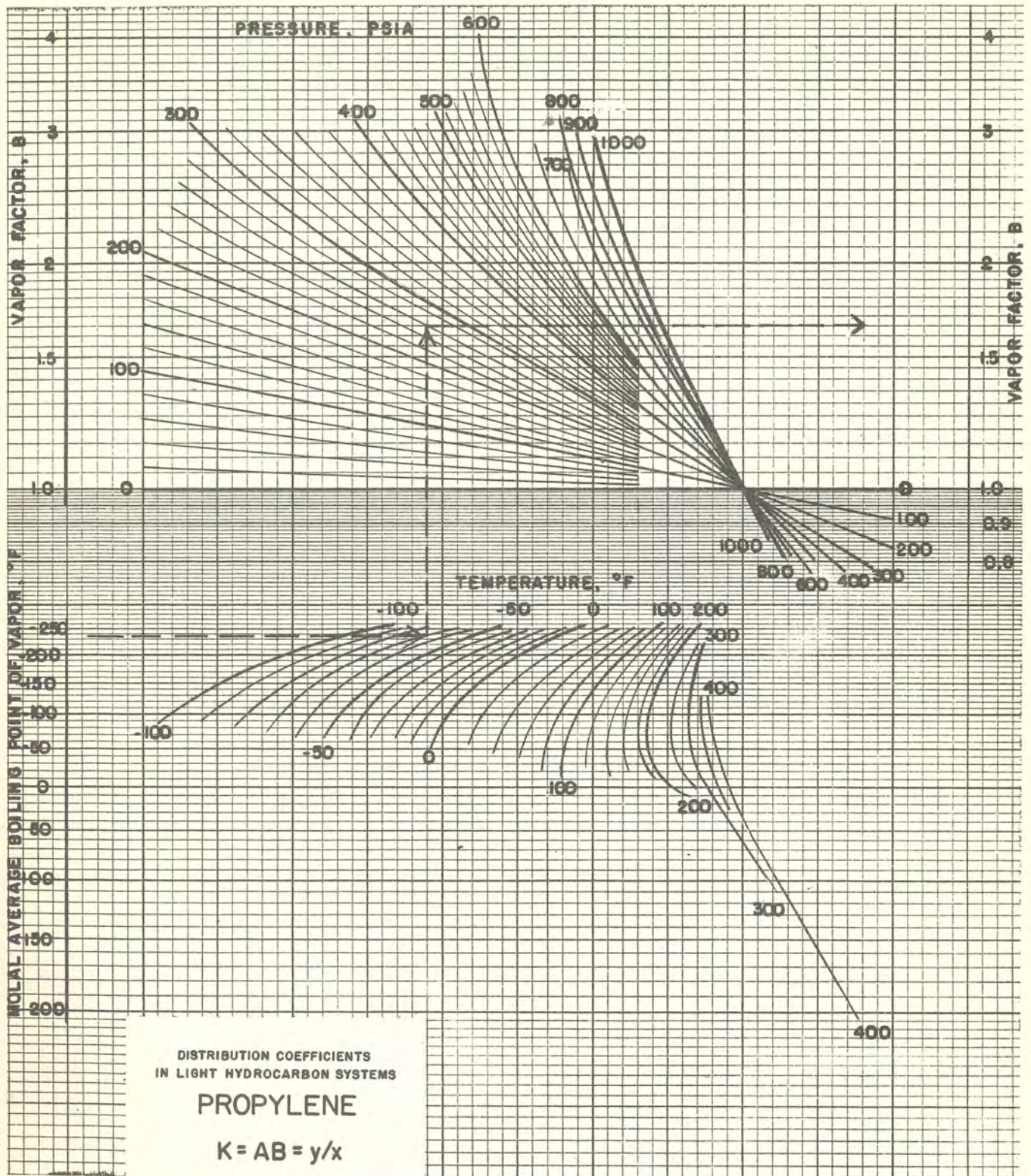


Fig. 14. Vapor factor for propylene.

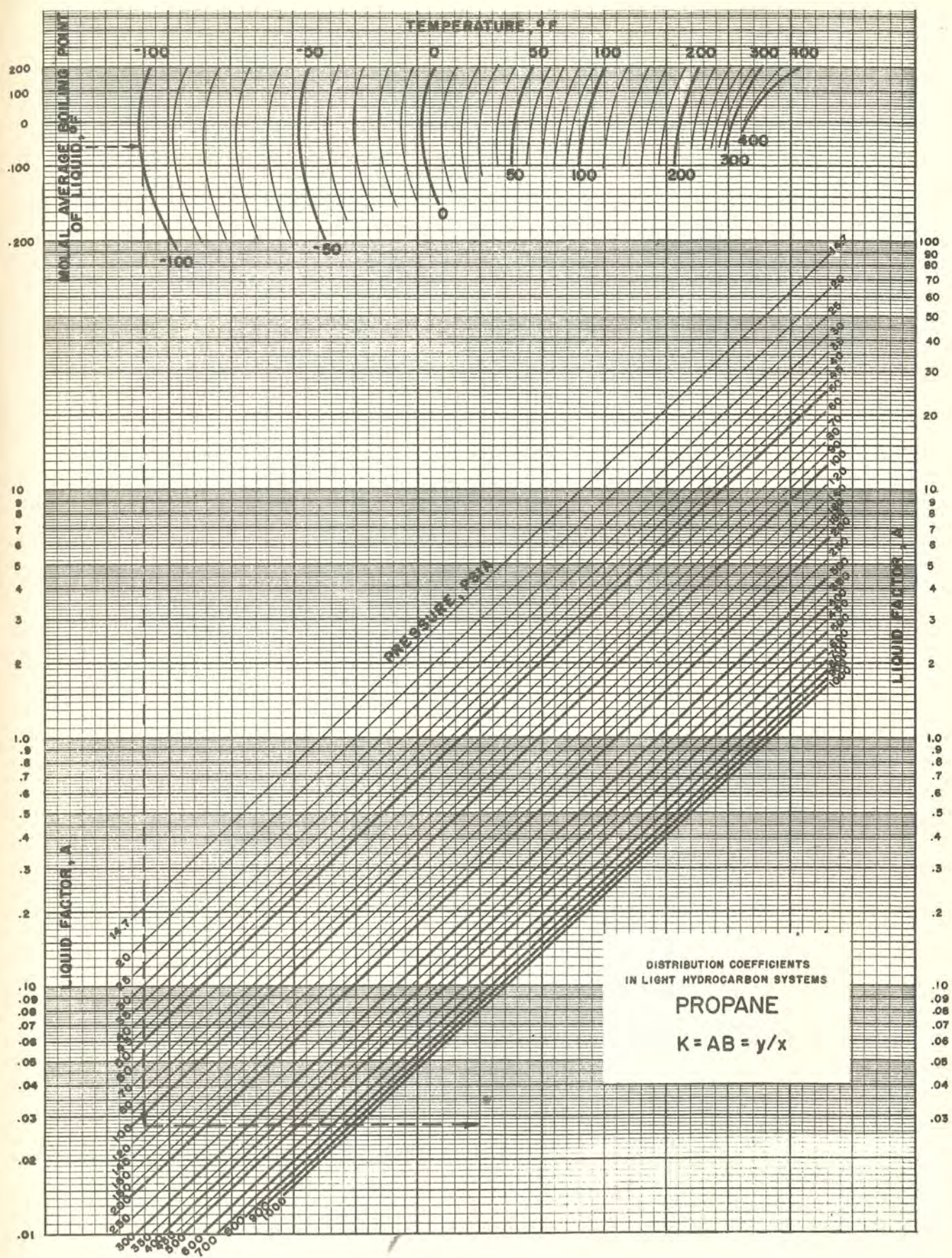


Fig. 15. Liquid factor for propane.

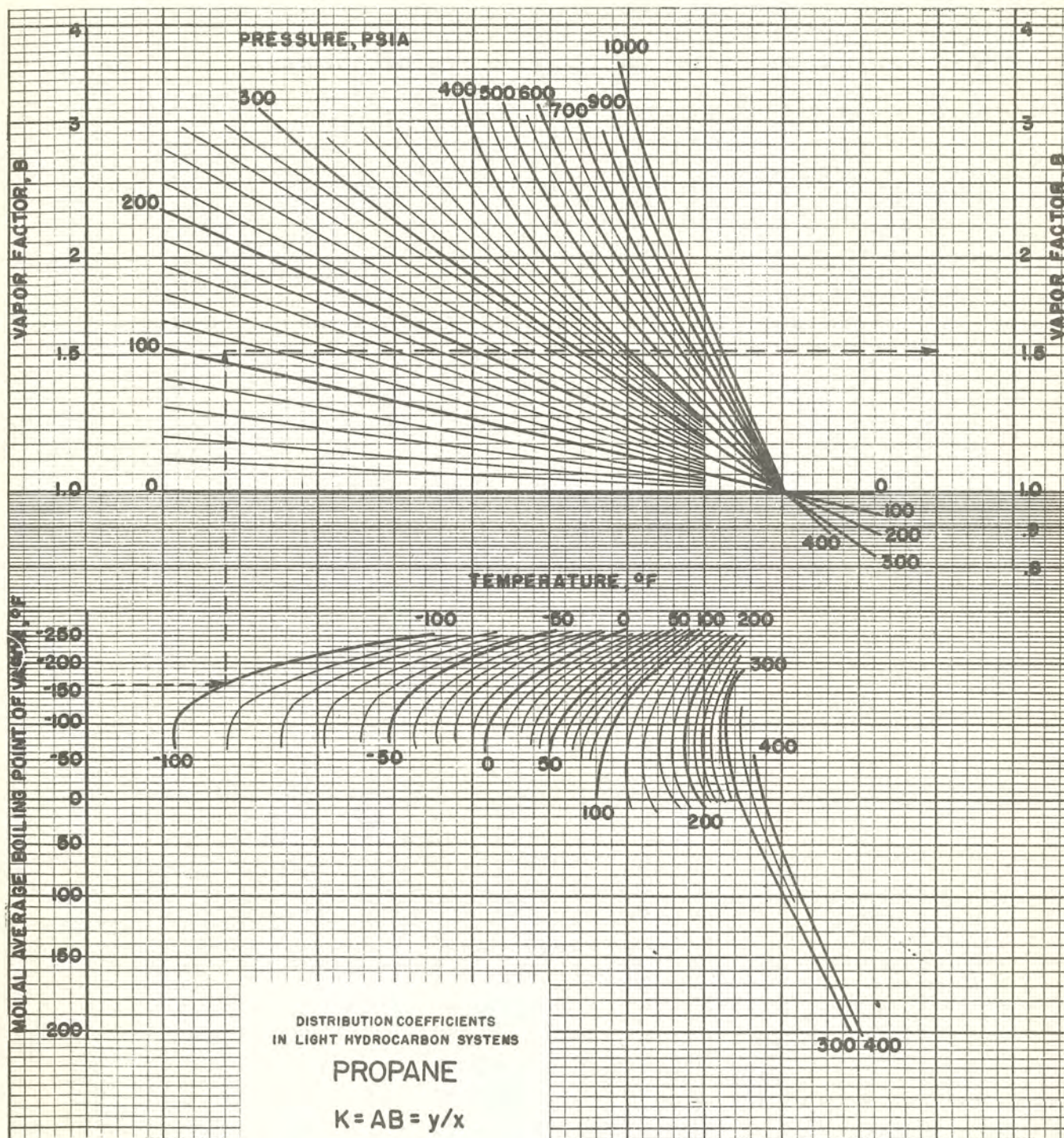


Fig. 16. Vapor factor for propane.

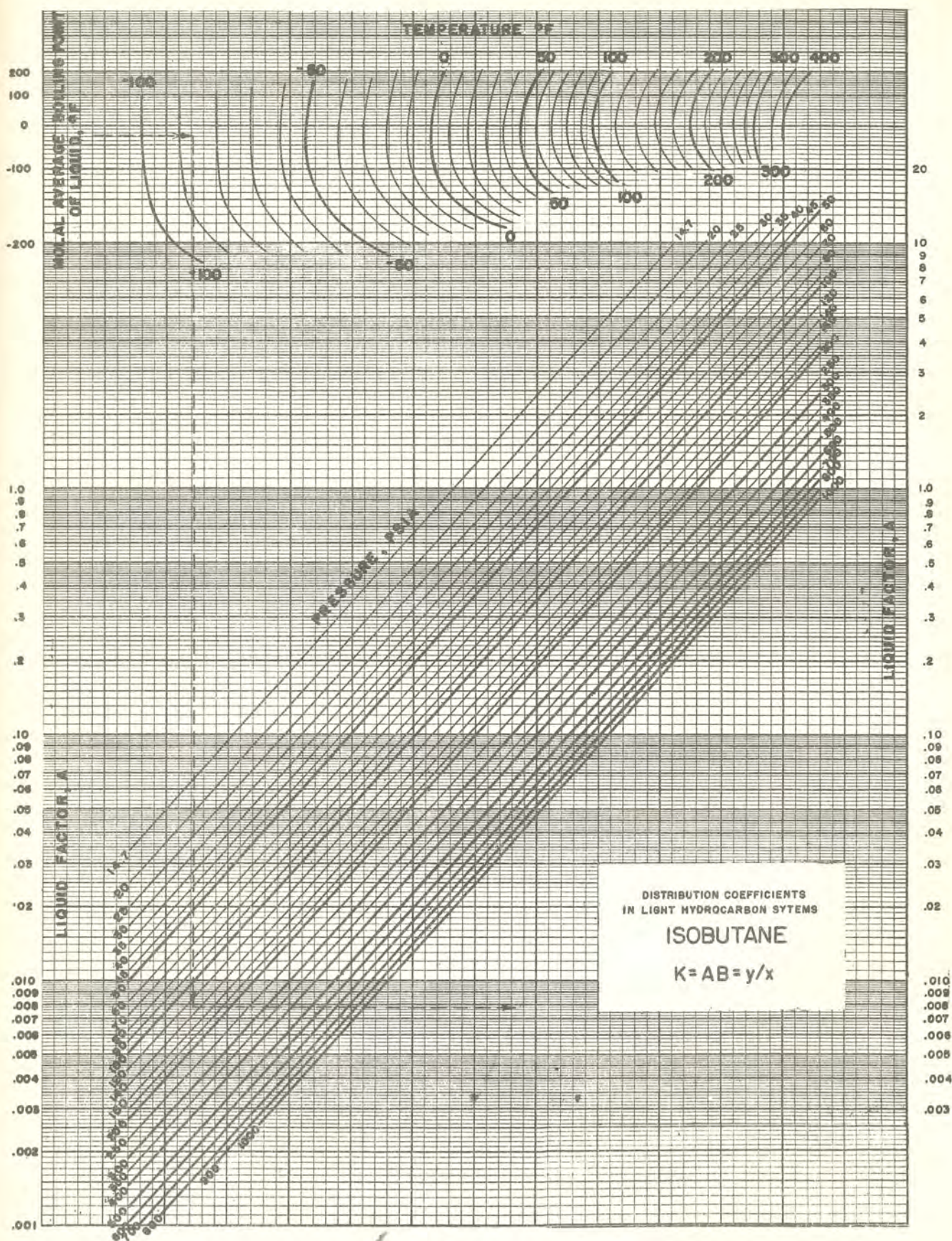


Fig. 17. Liquid factor for Isobutane.

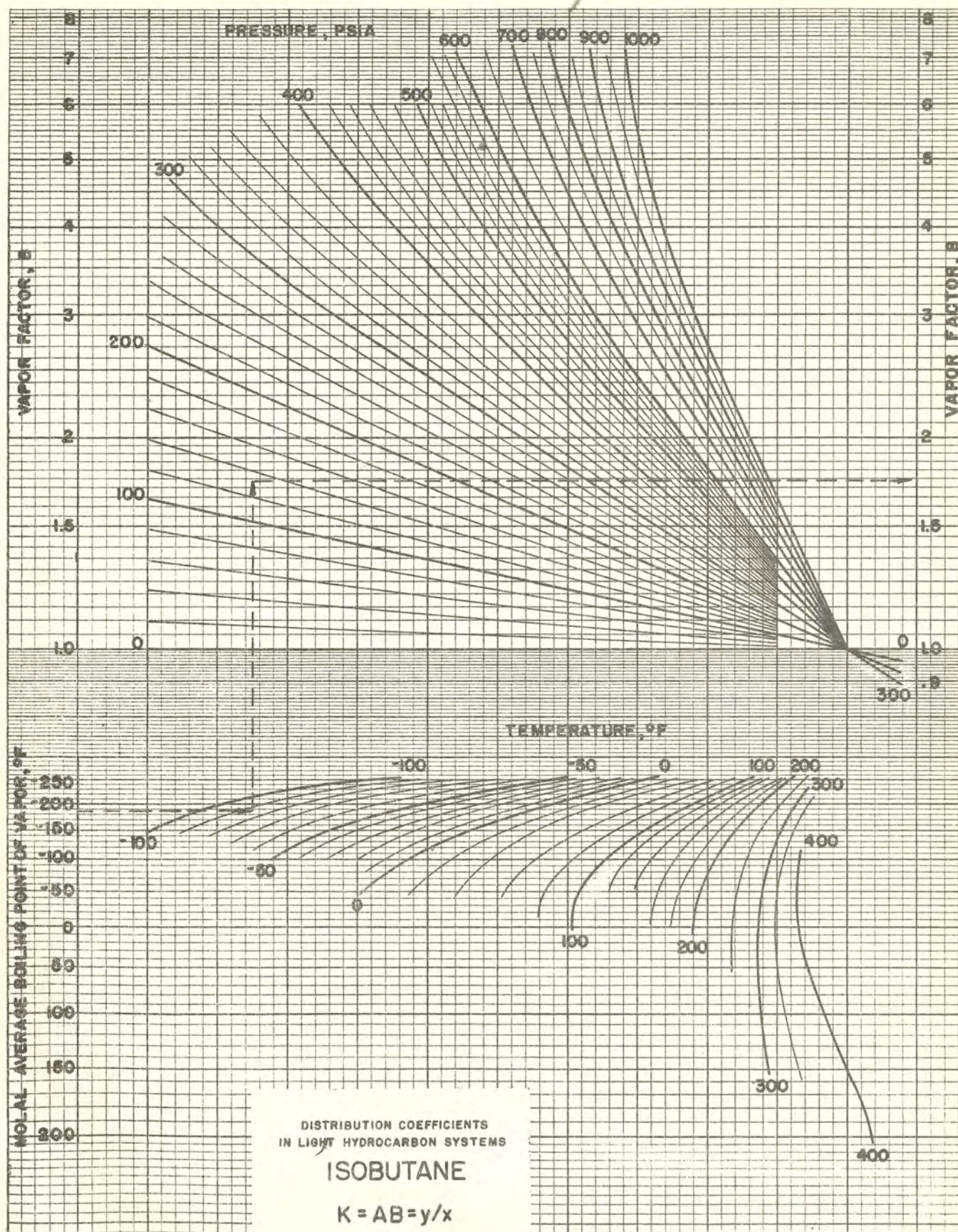


Fig. 18. Vapor factor for isobutane

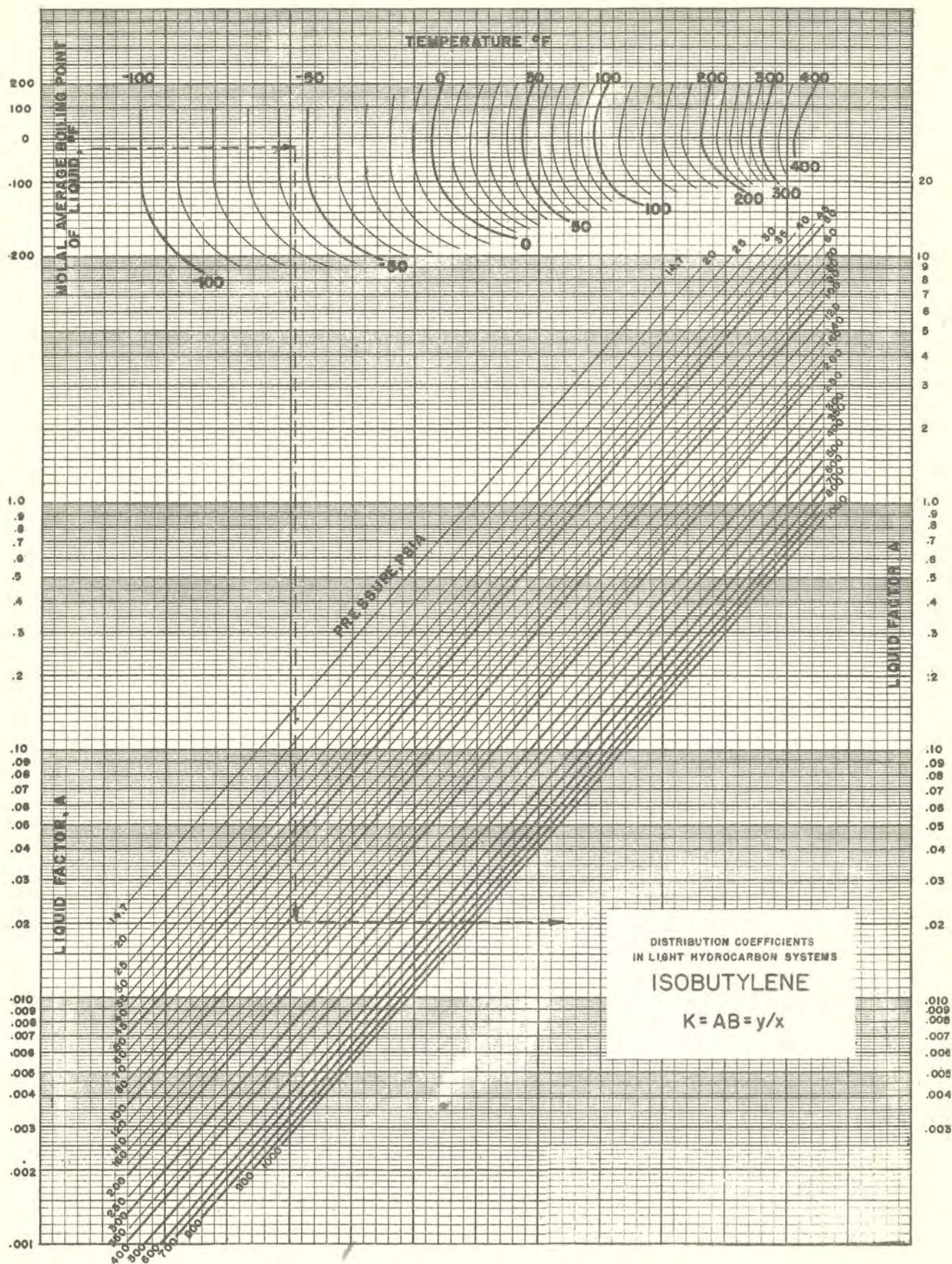


Fig. 19. Liquid factor for isobutylene.

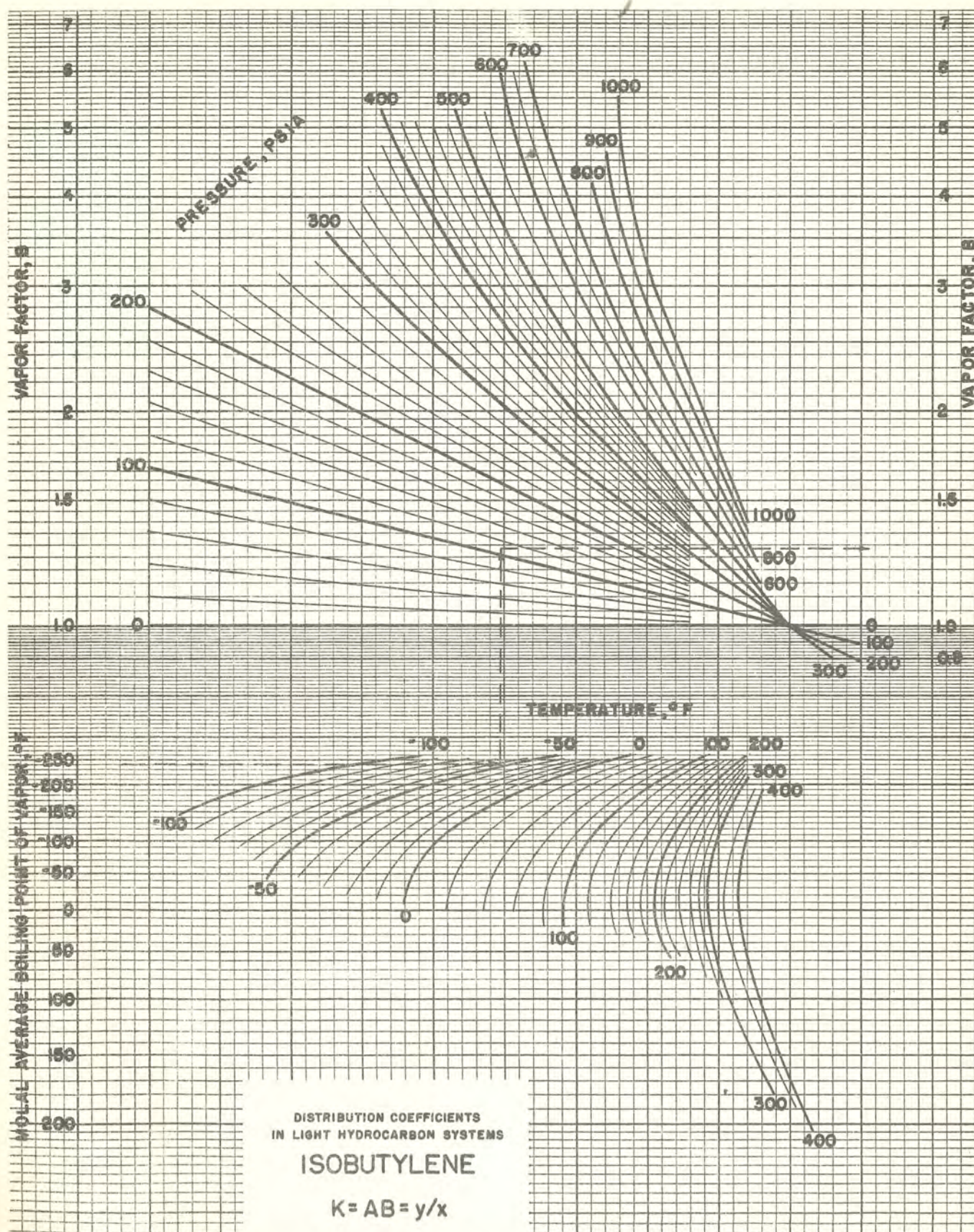


Fig. 20. Vapor factor for isobutylene.

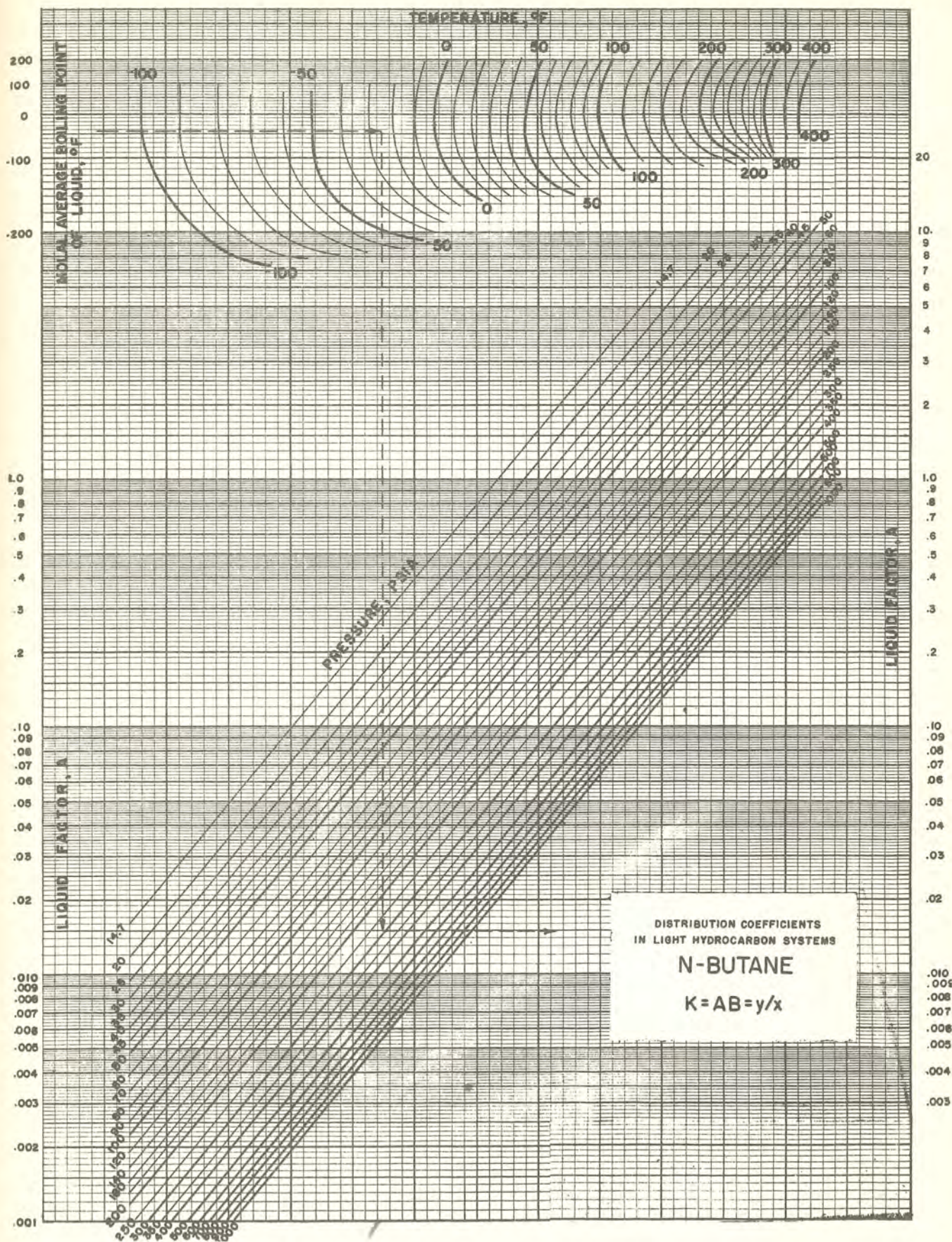
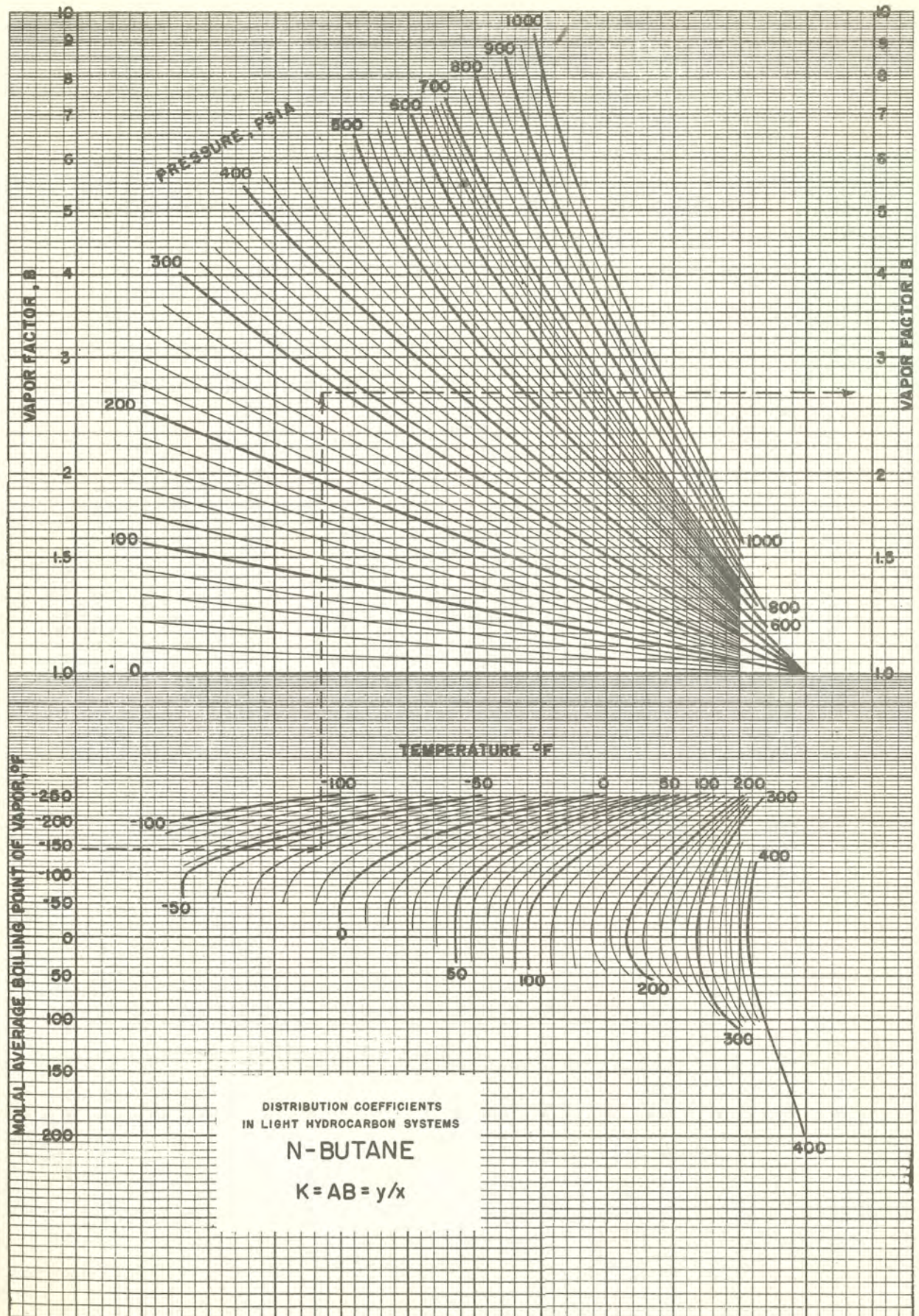


Fig. 21. Liquid factor for n-butane.

Fig. 22. Vapor factor for *n*-butane.

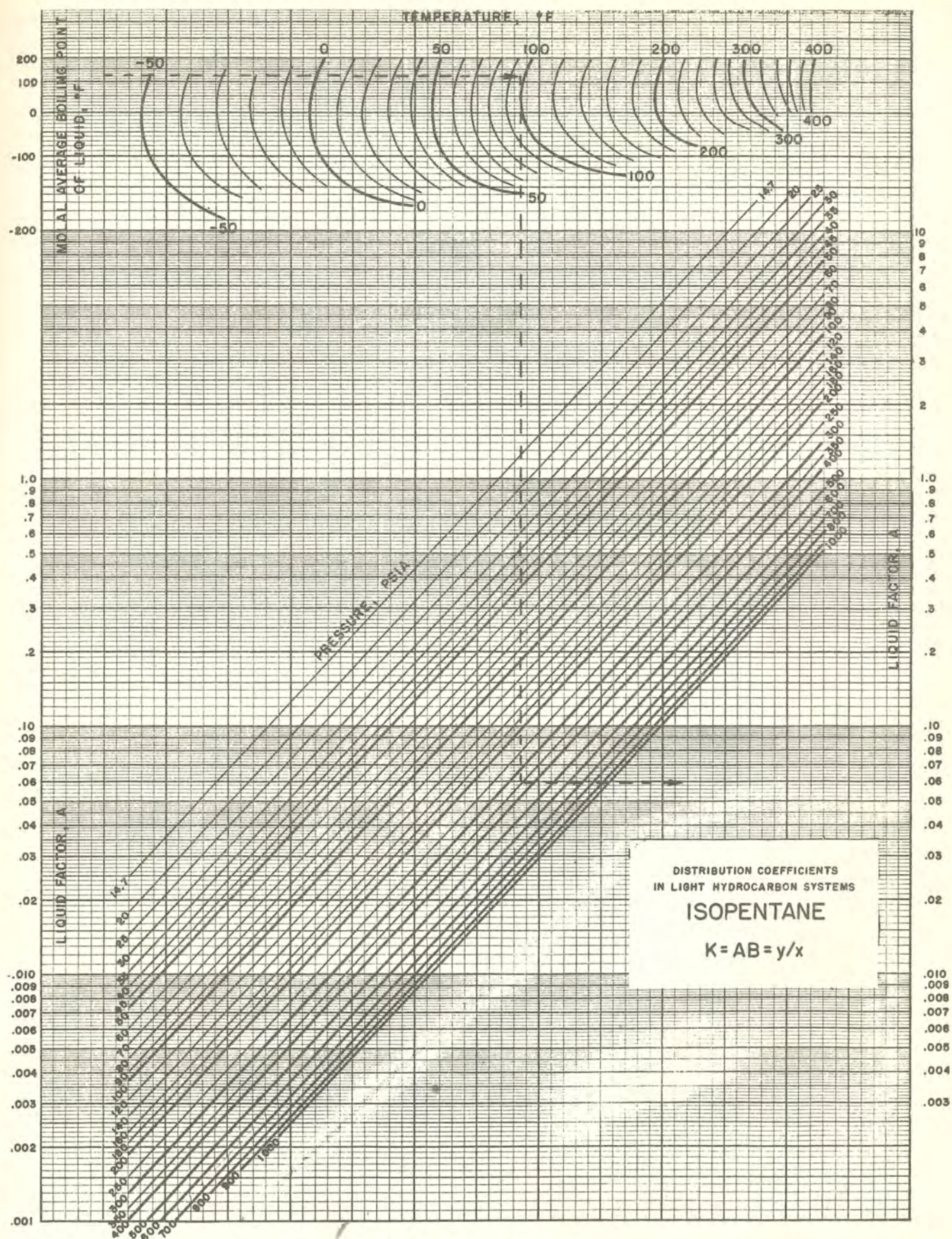


Fig. 23. Liquid factor for isopentane.

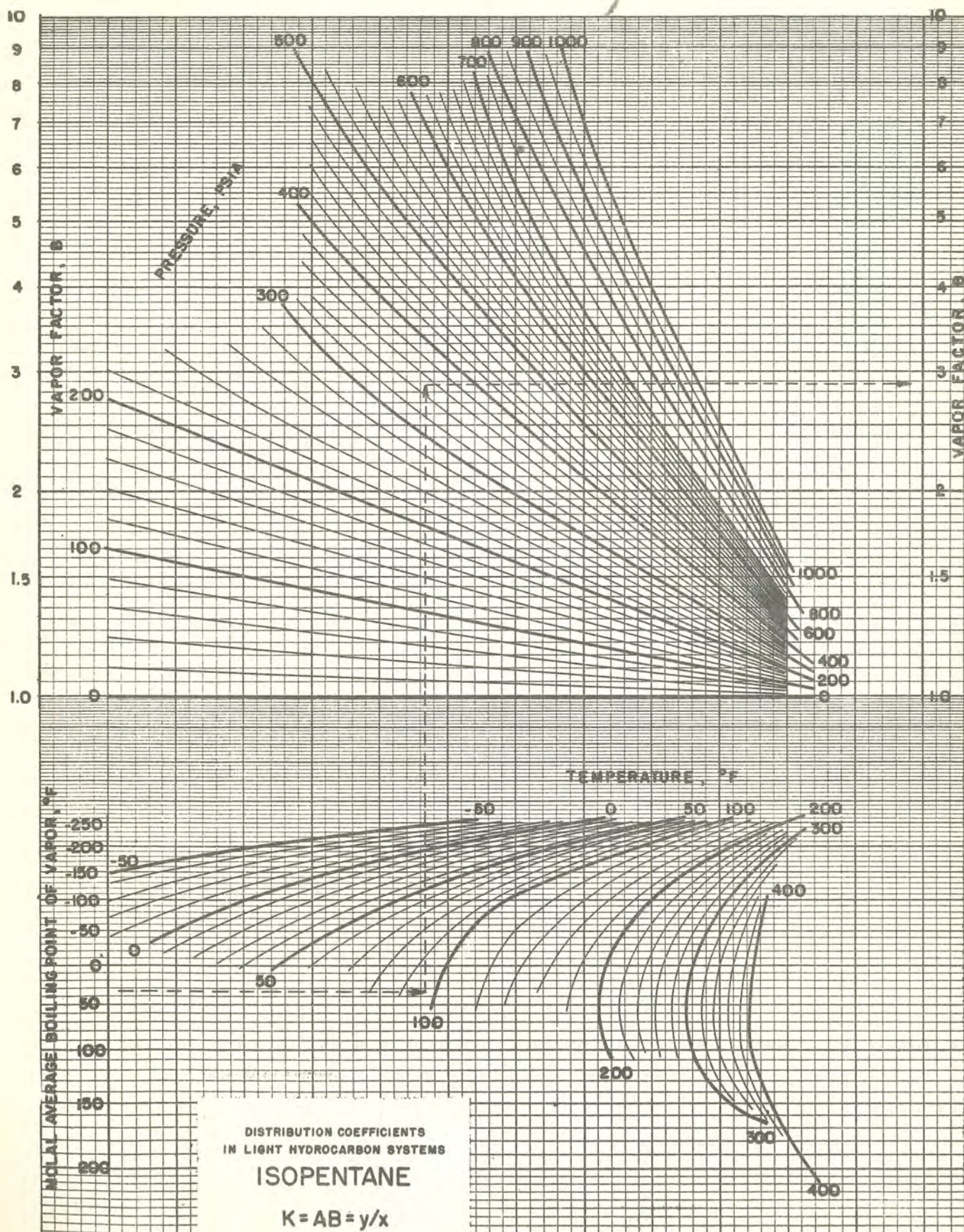


Fig. 24. Vapor factor for isopentane.

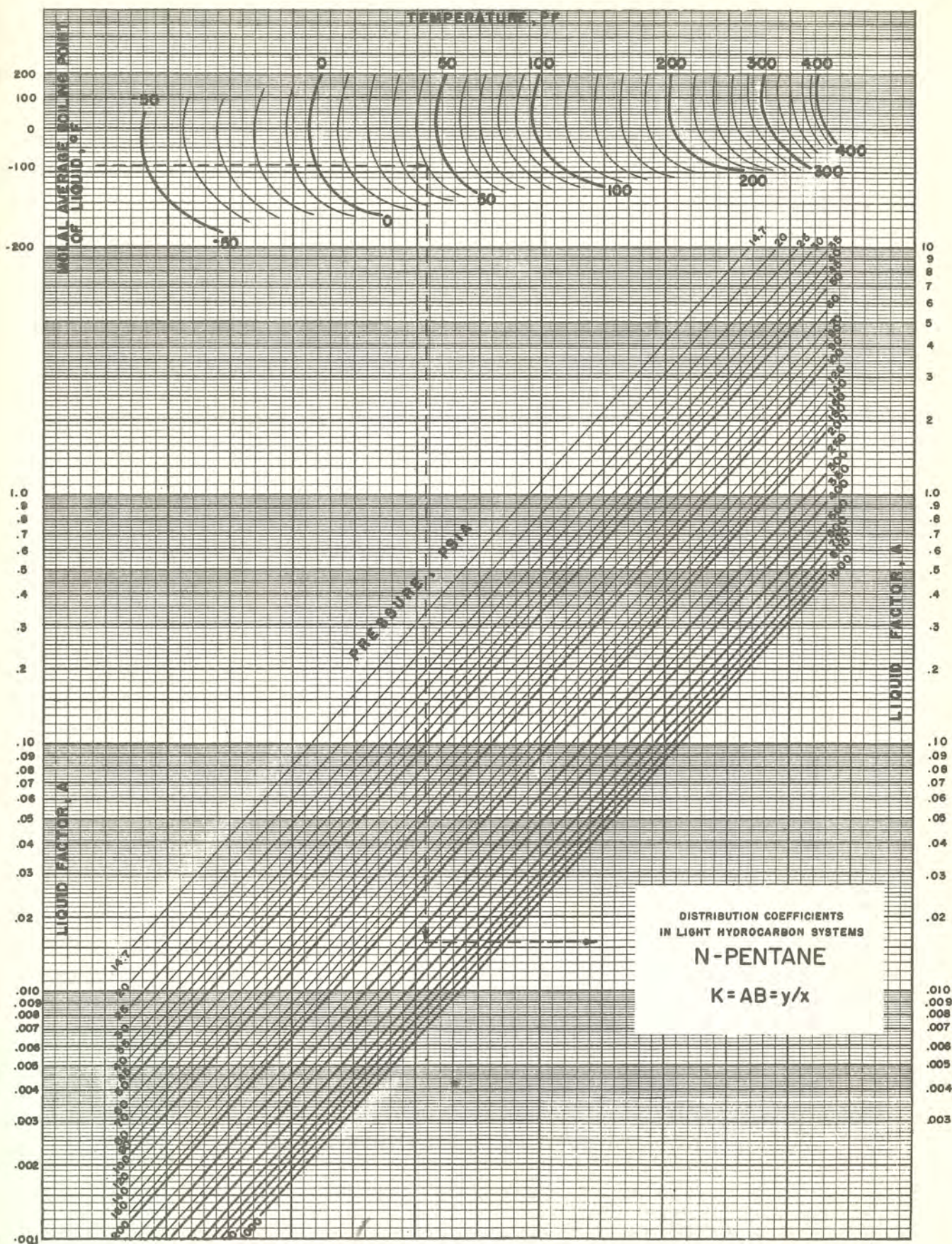


Fig. 25. Liquid factor for n-pentane

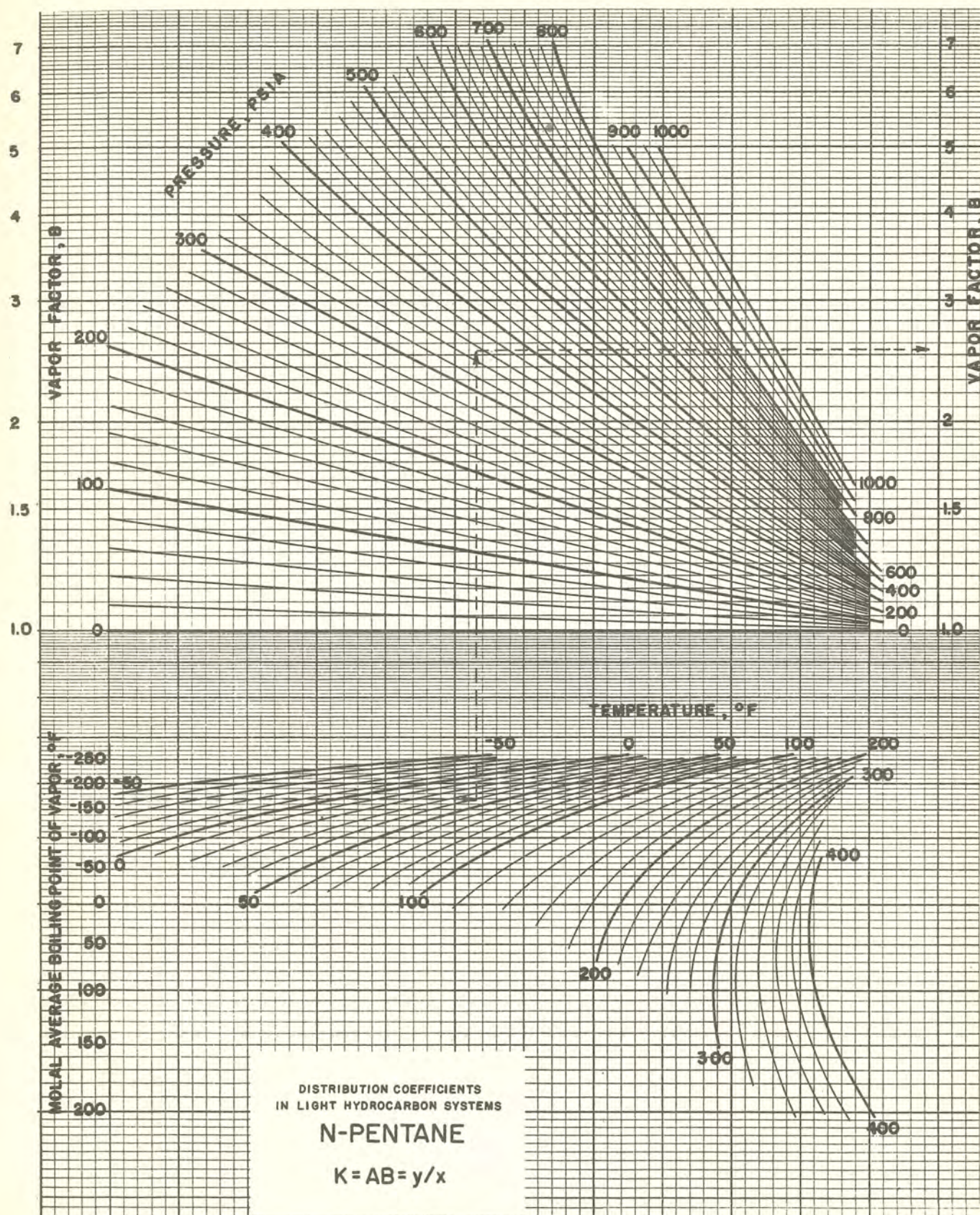


Fig. 26. Vapor factor for n-pentane.

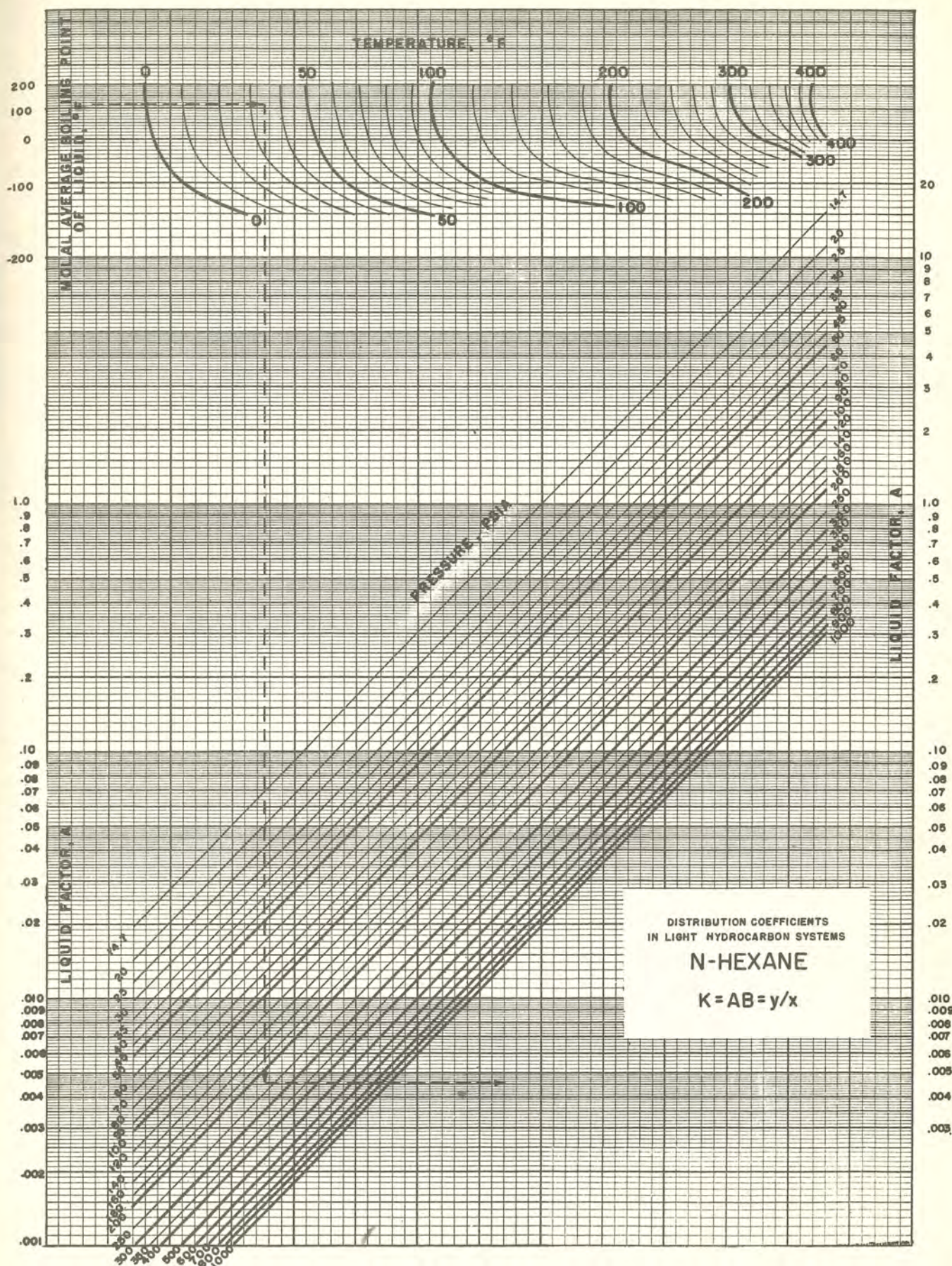


Fig. 27. Liquid factor for *n*-hexane.

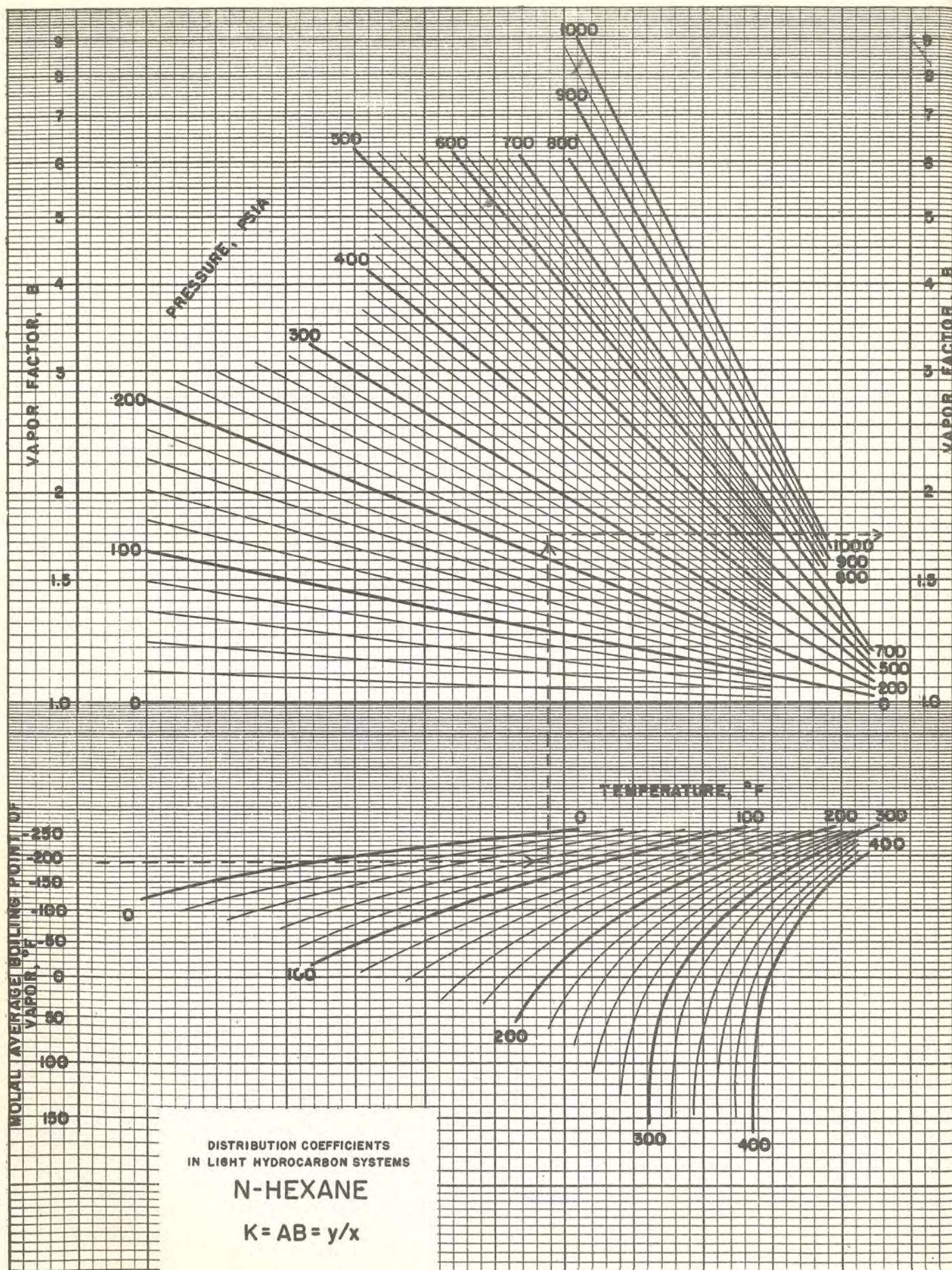


Fig. 28. Vapor factor for n-hexane

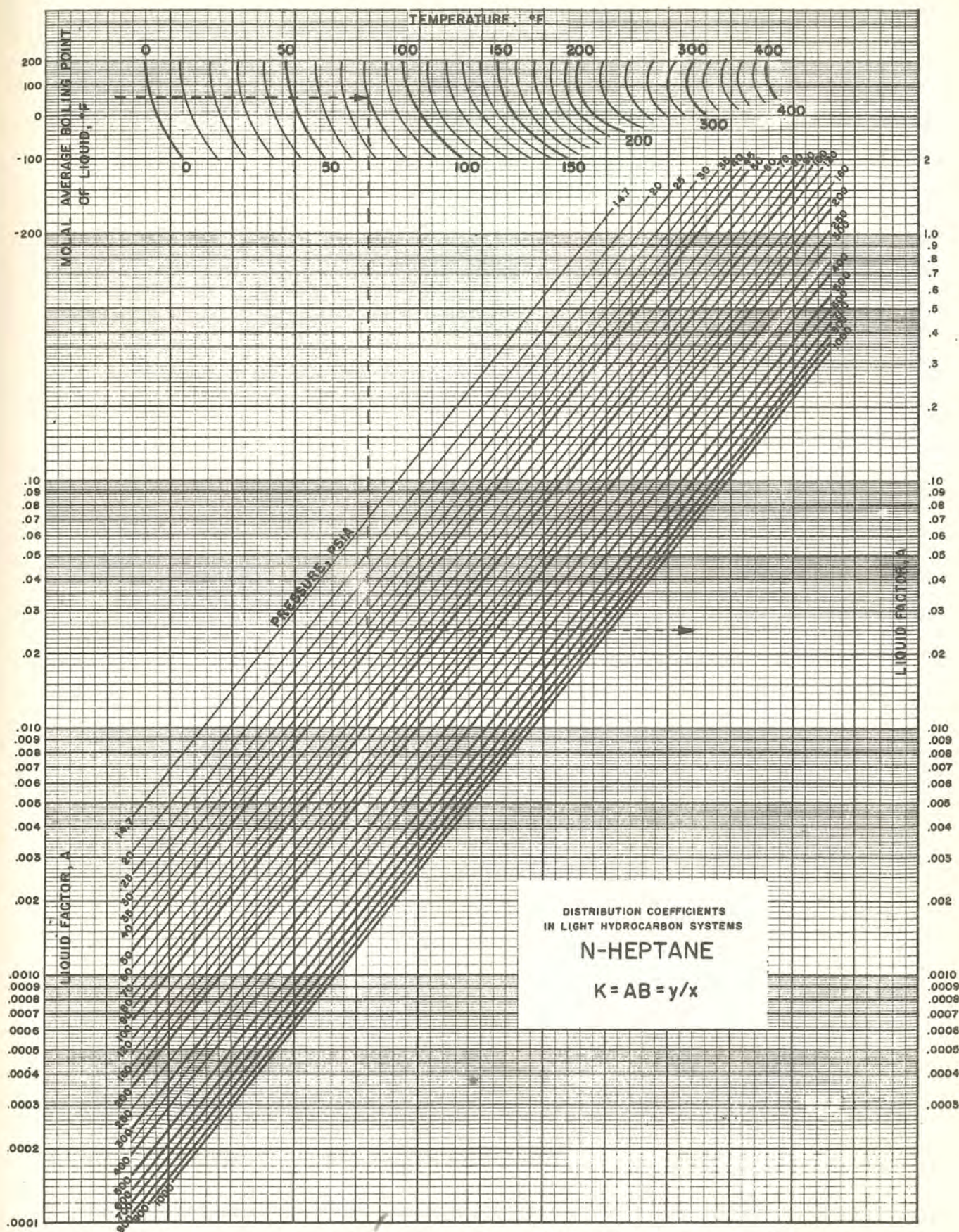


Fig. 29. Liquid factor for *n*-heptane.

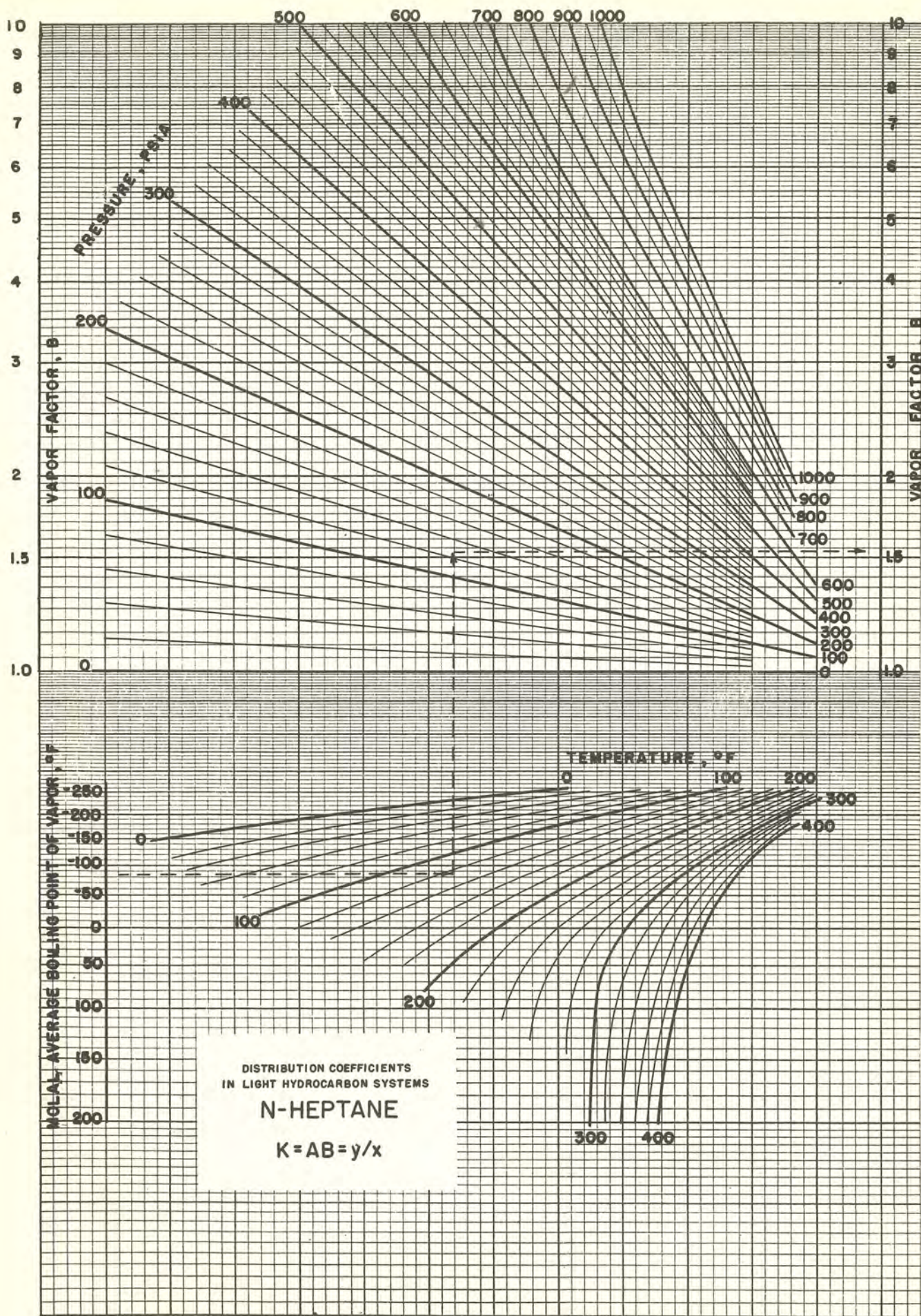
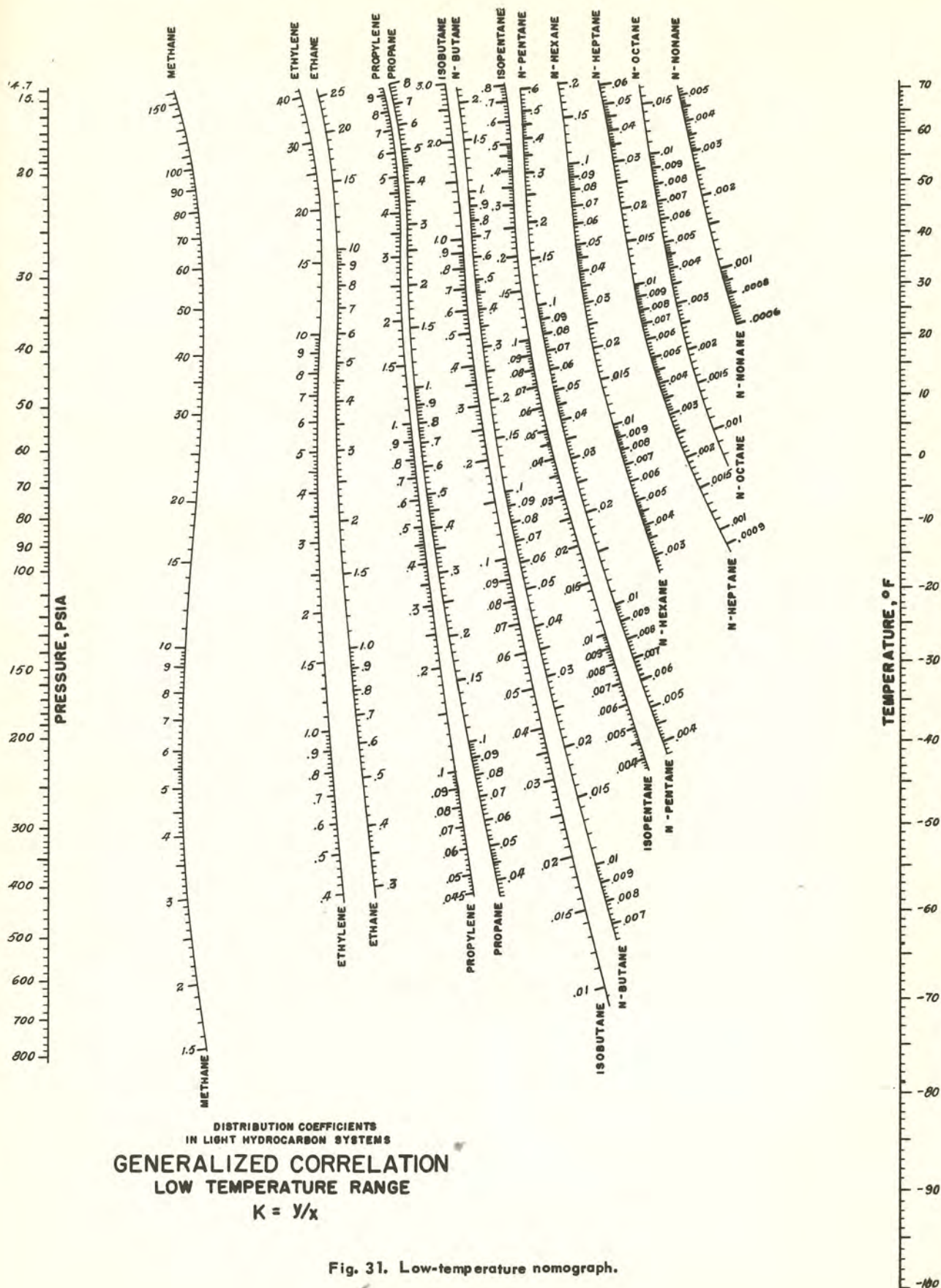


Fig. 30. Vapor factor for *n*-heptane.



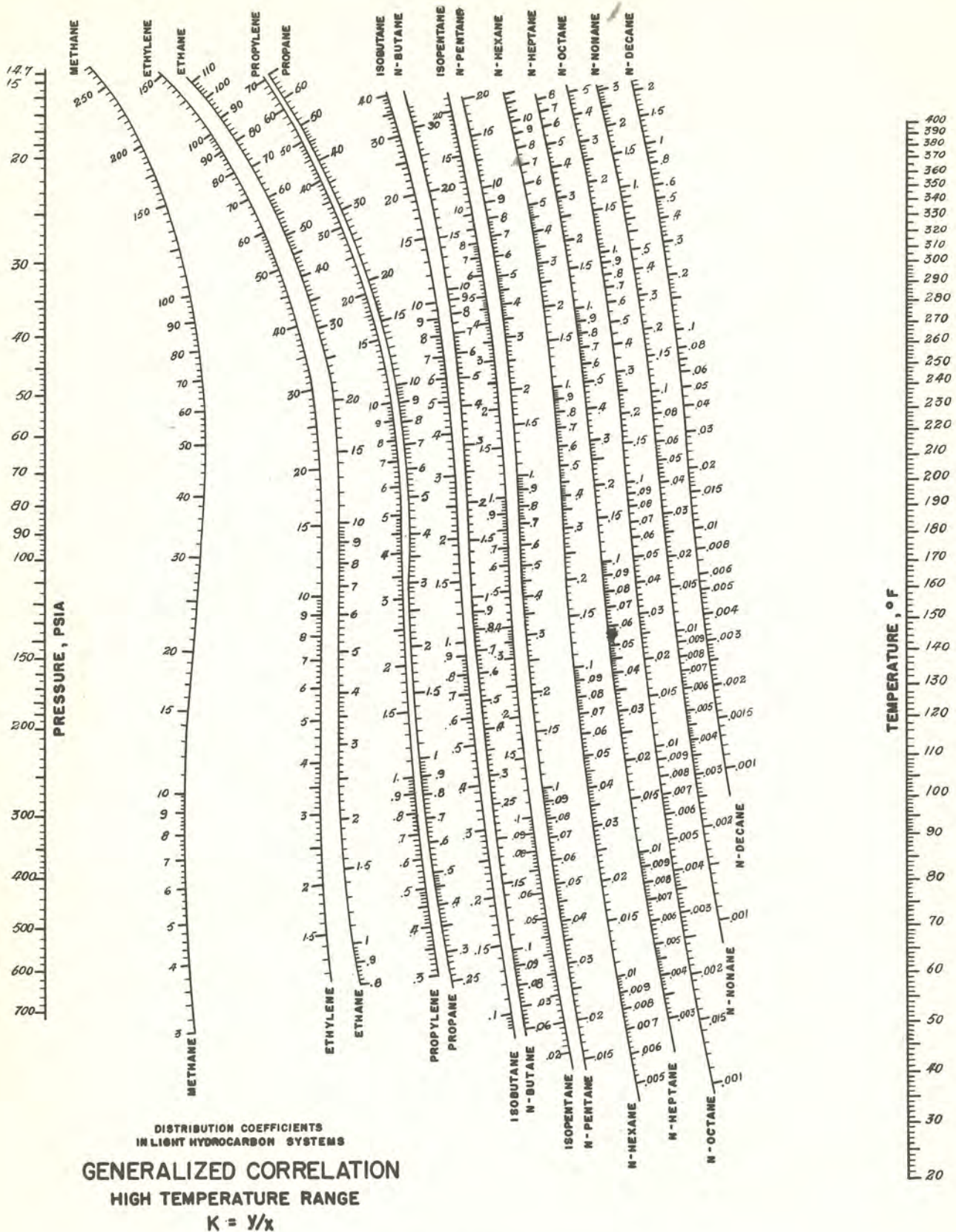
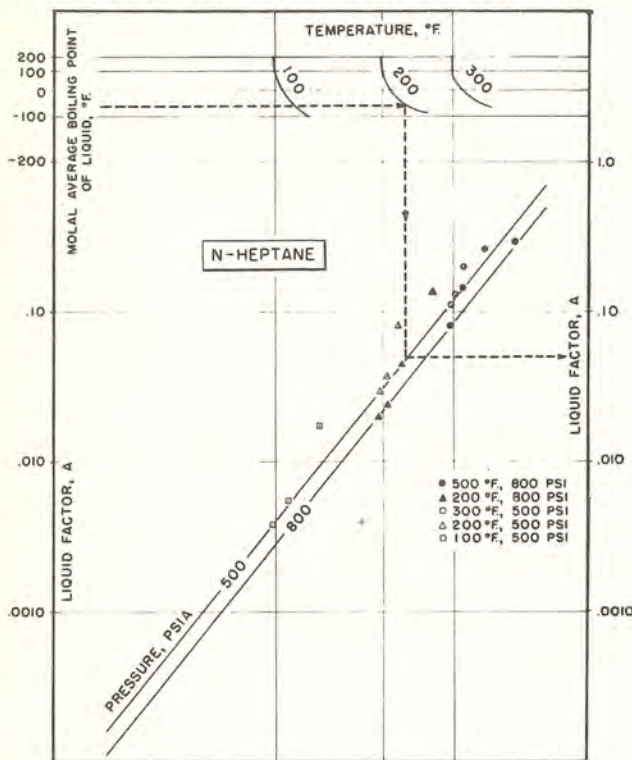


Fig. 32. High-temperature nomograph.

Discussion

Leo Friend (The M. W. Kellogg Co., New York, N.Y.): I should like to give a word of caution in the use of these charts and in assuming that they will give exactly the same answer as the Kellogg charts. As an example, I have taken the conditions for methane at 1,000 lb., a liquid molal average boiling point at 0°F., and a vapor molal average boiling point of -200°F. and compared the values — the ratio of the K values obtained by DePriester's charts to those obtained from the Kellogg charts at temperatures of -50°, 0°, +50°, +100°, +200°, and +300°F. The ratios, under these temperatures and conditions, are as follows: 1.13, 1.15, 1.09, 0.982, 1.18 and 1.58. The deviation therefore is considerable and does not truly represent the figures obtained from the Kellogg charts. I have prepared a chart to show this comparison for heptane also. This heptane chart was abstracted



from DePriester's chart by tracing the significant lines, and I have made a comparison for heptane at 500 and 800 lb. Now, following the solid points for 800 lb., as temperature increases, one will see that the deviations vary considerably from the 800-lb. line, both at 200° and 500°F. The same is true at 500 lb. However, at low temperatures, which are more generally met, the agreement is good. So, in

summary, DePriester's charts do not give exactly the same results as the Kellogg charts in all regions.

C. L. DePriester: The P.T.C. charts do not show exactly the same values of the fugacity functions as the Kellogg charts for all hydrocarbons at all conditions represented. However, agreement is quite close in most instances, and the P.T.C. charts agree with experimental data with the same order of accuracy as the Kellogg charts. Some discrepancies between the two presentations result from smoothing of Kellogg chart values to construct the P.T.C. charts and adjustment of P.T.C. charts to give better agreement with experimental data. For most conditions represented, the methods used to develop the P.T.C. charts resulted in apparently valid smoothing and eliminated minor internal inconsistencies in the original presentation. After the charts were drawn, they were checked with experimental data, and adjustments were made in location of temperature lines on the liquid factor charts for methane and ethane to obtain better agreement with data on ternary and multicomponent systems.

Other discrepancies between the two presentations exist at relatively high pressures for some temperature and composition ranges because of approach to states that cannot be accurately represented on the P.T.C. charts. Wherever possible, doubtful regions were checked with experimental data, and the range of variables was limited to give a chart accuracy within limits represented by the deviation summaries.

The deviation data show little change with temperature, pressure, or composition, and the summaries presented are representative of all ranges of conditions that were checked.

E. Clarence Oden (Cities Service Refining Corporation, Lake Charles, La.): With all the catalytic work which goes on and the unsaturated compounds available, why is it we hardly ever have any theoretical studies of the unsaturated compounds present?

W. C. Edmister (California Research Corporation, Richmond, Calif.): This paper was presented by a laboratory engaged in petroleum production activities — surface processing — and I don't believe their interest lies in the olefinic hydrocarbons, but I think the work quoted, Benedict, Webb, Rubin, and Friend (6, 7), does include the olefin hydrocarbons. I think the point well taken, however. We do need to branch out and not concentrate on these paraffins too much. There is much more which could be done for the olefinic and even the aromatic hydrocarbon systems.

(Presented at Cleveland meeting of A. I. Ch. E.)