Table XIII. Experimental Results for 2,2,4,10,12,12-Hexamethyl-7-(3,4,5-trimethylhexyl)tridecane, $C_{28}H_{58}$(M.W., 394.7)

Temp., ° C.	State	Vapor Press., Torr.
35.0	Liquid	1.50×10^{-5}
45.0	Liquid	5.16×10^{-5}
60.0	Liquid	2.32×10^{-4}
70.0	Liquid	6.37×10^{-4}
80.0	Liquid	1.90×10^{-3}
90.0	Liquid	5.46×10^{-3}
110.0	Liquid	2.91×10^{-2}
120.0	Liquid	5.56×10^{-2}

$A = -5147$; $B = 11.869 \pm 0.108$

The experimental results for each hydrocarbon were a good fit to the equation:

$$\log_{10} P = \frac{A}{T} + B$$

where P is the vapor pressure (torr.), T is the temperature (° K.) and A and B are constants, specific for each hydrocarbon.

The values of A and B for each hydrocarbon were calculated by the method of least squares. The experimental vapor pressures obtained for each hydrocarbon together with the values of the two constants (with a confidence limit at the 95% level) are given in Tables I-XIII.

Vapor pressures reported here are in good agreement with values for higher temperatures published by API Project 4 (*1*). This is illustrated for one hydrocarbon in Figure 1.

ACKNOWLEDGMENT

The author wishes to acknowledge the loan of hydrocarbons from Research Project 42 by the American Petroleum Institute.

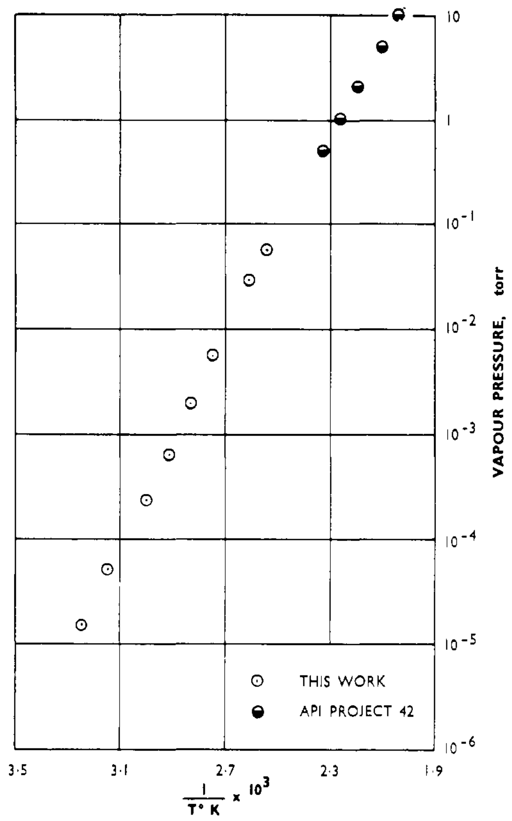

Figure 1. Vapor pressure of 2,2,4,10,12,12-hexamethyl-7-(3,5,5-trimethylhexyl)tridecane

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A Method for Determining the Solubility of Gases in Relatively Nonvolatile Liquids

Solubility of Methane in *n*-Decane

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FREQUENTLY, industrial operations require knowledge of the solubility of a permanent gas in an essentially nonvolatile liquid. A knowledge of the phase behavior of binary systems consisting of components of widely differing boiling points is essential in the chromatographic study of vapor-liquid equilibria (*2*, *7*). An experimental technique for obtaining such information has been developed and applied to the methane-*n*-decane binary system.

EXPERIMENTAL APPARATUS

A schematic diagram of the equipment used in this study is presented in Figure 1.

The equilibrium vessel was made of nonmagnetic 304 stainless steel 18¼ inches in length, 1.213 inches outside diameter, and 0.750 inch inside diameter. The lower end was closed and the upper end sealed to high pressure by means of an O-ring design (*2*). A ⅝-inch diameter ball bearing was placed within the vessel and used to equilibrate the mixture by raising and lowering a strong horseshoe magnet fitted directly around the cylinder body.

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Experimental values of the solubility of methane in *n*-decane have been obtained from measurements of pressure, temperature, and volume only. Data have been taken for 40°, 20°, 0°, and −20° F. over the pressure range 200–1000 p.s.i.a. From the observation that the vapor phase is essentially all methane, K-values for methane have been computed for the methane–*n*-decane system. The results are consistent with the work of other investigators at higher temperatures.

The volume of a brass cylinder 7⅞ inches in length with an outside diameter of 1⅞ inches closed at one end was determined by filling the vessel with distilled water and weighing it on a large analytical balance. The known volume was used to determine the volume of the irregular system *V*. Both valve *A* and valve *E* were special angle valves which were inserted directly into vessels V_0 and *V*. This allowed the volume of the valve up to the stem in the closed position to be included in V_0 determination. The use of such a valve in the equilibrium cell diminished the volume available to trap *n*-decane upon injection to about 0.1 cc. To avoid even this amount of trapping the *n*-decane was introduced at a pressure 500–1200 p.s.i. above the system pressure so that essentially none of the injected liquid would remain in the small dead portion of the valve as depicted elsewhere (*2*).

The *n*-decane was metered into the cell at a pressure of 1500 p.s.i.a. from a high pressure mercury pump calibrated to 0.01 cc. Sub-ambient temperatures in the bath were maintained by the use of refrigeration coils from a ⅓ HP Freon 12 refrigeration unit. A controlled electric emersion heater was then used to counteract the cooling system and thus, achieve temperature stability.

The pressure measuring apparatus was similar to that described by Canfield (*1*), except that pressure was transmitted directly from the gas to the gauge oil through a mercury column rather than through the use of a differential pressure indicator. It may be seen from Figure 2 that the system pressure *P* may be calculated from P_G, the observed piston gauge pressure, P_B, the barometric pressure, and the indicated hydraulic heads by the following equation:

$$P = P_G + P_B + (h_L - h_R)\,\rho_{Hg}\frac{g}{g_c} + (h_G - h_L)\,\rho_0\frac{g}{g_c} \tag{1}$$

MATERIALS USED

The methane gas used in this study was donated by the Tennessee Gas Transmission Co. and Associated Oil and Gas Co. The dried gas was analyzed by mass spectrography and found to contain 99.7 mole per cent methane, 0.2 mole per cent nitrogen and 0.1 mole per cent others, primarily ethane. The *n*-decane was research grade material obtained from Phillips Petroleum Co. with a steel purity of 99.35 mole per cent.

THEORY

The binary system methane–*n*-decane at low temperatures is characterized by the widely differing volatilities of the two components which makes possible the assumption that the vapor phase is essentially all methane over a wide range of conditions. Under the experimental conditions reported herein, NGAA (5) estimates the K-value of decane to be less than 0.0003. This corresponds approximately to a vapor mole fraction of the same magnitude. Hence, a knowledge of the solubility of methane in *n*-decane in the liquid phase makes possible the accurate calculation of the methane K-value from the simple relation:

$$K_1 = y_1/x_1 = 1.0/x_1 \tag{2}$$

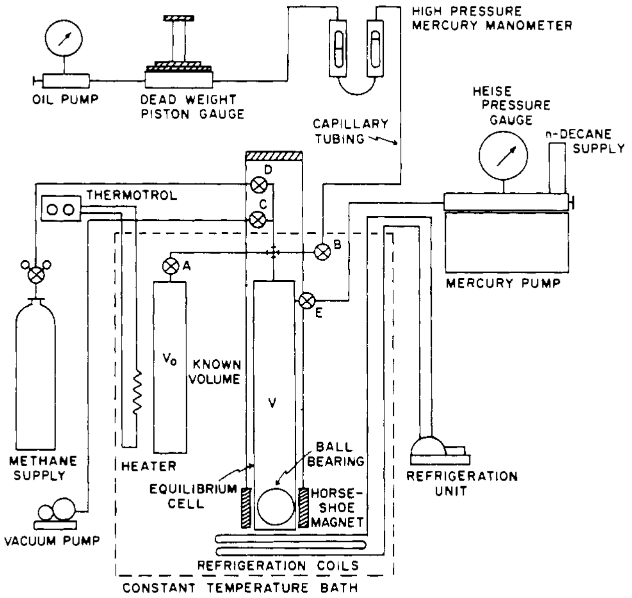

Figure 1. Schematic diagram of solubility apparatus

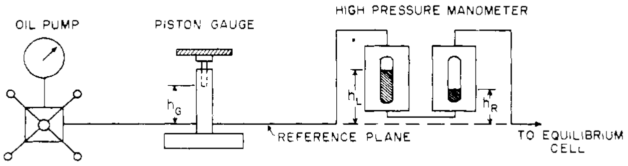

Figure 2. Schematic diagram of pressure measuring apparatus for solubility measurements

To determine x_1, the mole fraction of methane in the liquid phase, a known amount of *n*-decane is metered into a cell containing a known quantity of pure methane. After stirring, an equilibrium is reached between the vapor phase and the liquid phase and the amount of methane remaining in the vapor phase is calculated. The difference in the methane present as vapor before and after the introduction of *n*-decane to the cell represents the amount of methane dissolved in the *n*-decane liquid.

A schematic diagram of the solubility apparatus is shown in Figure 1. Reference will be made to the diagram in the following derivation. After the entire system has been evacuated the known volume V_0 is filled to a desired pressure with methane and valves *A* and *B* are closed. The total moles of methane in V_0 and the tubing transmitting the pressure to the manometer may be expressed as:

$$n_0 = \frac{P_0 V_0}{Z_0 RT} + \frac{V_{D_0} P_0}{Z_{D_0} RT_a} \tag{3}$$

where the subscript *D* refers to the dead volume from valve *B* to the top of the mercury level in the right side of the high pressure manometer. This volume can be expressed as:

$$V_D = C_D + h_R^{\circ} C_M \tag{4}$$

with C_D the volume of the capillary tubing from valve B to the manometer, h_r°, the height of the vapor space in the right leg, and C_m the volume per unit length of the right leg of the manometer. The gas in V_D is essentially at room temperature T_a.

After re-evacuation of the equilibrium cell valves D and C are closed and valves A and B are opened allowing the methane to expand into the cell. If V represents the volume of the cell plus the tubing between the four valves A, B, C, and D, the following expression may be written for the moles of methane present:

$$n_F = n_0 = \frac{P_F(V_0 + V)}{Z_F RT} + \frac{V_{D_F} P_F}{Z_{D_F} RT_a} \tag{5}$$

where the subscript F refers to the final values of P, Z, V_D, Z_D, after expansion. Equating 3 and 5, and solving for V gives:

$$V = V_0\left[\frac{P_0 Z_F}{P_F Z_0} - 1\right] + \left(\frac{T}{T_a}\right)\left[\frac{P_0 Z_F}{P_F Z_D} V_D - \frac{Z_F}{Z_{F_D}} V_{D_F}\right] \tag{6}$$

Using Equation 6 a precise determination of V may be made. Valve A is then closed and a known quantity of n-decane metered into the equilibrium cell at a constant pressure P above that of the system P_i. After equilibrium has been established the final pressure P_F is measured and the moles of methane dissolved, N_A given by:

$$N_A = N_i - N_F = \left[\frac{P_i V}{Z_i RT} + \frac{P_i V_{D_i}}{Z_{D_i} RT_a}\right] - \left[\frac{P_F V_F}{Z_F RT} + \frac{P_F V_{D_F}}{Z_{D_F} RT_a}\right] \tag{7}$$

which may be rearranged as:

$$N_A = \frac{1}{RT}\left[\frac{P_i V}{Z_i} - \frac{P_F V_F}{Z_F}\right] + \frac{1}{RT_a}\left[\frac{P_i V_{D_i}}{Z_{D_i}} - \frac{P_F V_{D_F}}{Z_{D_F}}\right] \tag{8}$$

where V_F is simply V less the liquid volume,

$$V_F = V - (v_{10} n_{10} + v_1 N_A) \tag{9}$$

and v_{10} and v_1 represent the partial molal volumes of n-decane and dissolved methane respectively. The mole fraction of methane in the liquid is then:

$$x_1 = \frac{N_A}{N_A + n_{10}} \tag{10}$$

where n_{10}, the moles of n-decane introduced is given by:

$$n_{10} = \frac{(V_{10}\rho_{10})_{PT_a}}{142.34} \tag{11}$$

with V_{10} and ρ_{10} the n-decane volume and density at pump pressure P and room temperature T_a.

Equation 8 provides a simple expression relating the basic parameter N_A to easily obtainable P-V-T data.

DISCUSSION

From the solubility experiments K-values for methane in the methane-n-decane system were calculated for the temperatures 40°, 20°, 0° and −20° F., and for pressures ranging from 200 p.s.i.a. to 1000 p.s.i.a. K-values for methane at lower pressures were obtained from a plot of mole fraction methane in the liquid as a function of pressure, making use of the fact that the mole fraction of methane is zero at the vapor pressure of n-decane.

The errors involved in calculating a K-value for methane from experimental solubility data arise from the following sources: measurement of pressure, measurement of temperature, determination of volumes involved, and estimation of compressibility factors. In order to evaluate the magnitude of the errors produced from each of these sources Equations 2 and 10 are rewritten in the following form:

$$K_1 = 1 + \frac{n_{10}}{N_A} \tag{12}$$

Total differentiation of Equation 12 gives:

$$dK_1 = \frac{dn_{10}}{N_A} + \frac{n_{10}}{N_A^2}\, dN_A \tag{13}$$

Assuming the errors to be small, the differentials may be replaced by delta expressions where $\Delta x = x_{\text{true}} - x_{\text{exptl}}$. Thus:

$$\Delta K_1 = \frac{1}{N_A}\Delta n_{10} + \frac{n_{10}}{N_A^2}\Delta N_A = \frac{n_{10}}{N_A}\left[\frac{\Delta n_{10}}{n_{10}} + \frac{\Delta N_A}{N_A}\right]$$

$$= (K_1 - 1)\left[\frac{\Delta n_{10}}{n_{10}} + \frac{\Delta N_A}{N_A}\right] \tag{14}$$

To evaluate ΔN_A, Equation 8 may be totally differentiated and the differentials replaced by delta quantities to give:

$$\begin{aligned}\Delta N_A = {} & \frac{P_i V}{Z_i RT}\left[\frac{\Delta V}{V} + \frac{\Delta P_i}{P_i} + \frac{\Delta Z_i}{Z_i}\right] + \frac{P_F V_F}{Z_F RT}\left[\frac{\Delta V_F}{V_F} + \frac{\Delta P_F}{P_F} + \frac{\Delta Z_F}{Z_F}\right] \\ & + \left[\frac{P_i V}{Z_i} - \frac{P_F V_F}{Z_F}\right]\left[\frac{\Delta T}{T}\right] + \frac{P_i V_{D_i}}{Z_{D_i} RT_r}\left[\frac{\Delta V_{D_i}}{V_{D_i}} + \frac{\Delta P_i}{P_i} + \frac{\Delta Z_{D_i}}{Z_{D_i}}\right] \\ & + \frac{P_F V_F}{Z_{D_F} RT_R}\left[\frac{\Delta V_{D_F}}{V_{D_F}} + \frac{\Delta P_F}{P_F} + \frac{\Delta Z_{D_F}}{Z_{D_F}}\right] + \left[\frac{P_i V_{D_i}}{Z_{D_i}} - \frac{P_F V_{D_F}}{Z_{D_F}}\right]\left[\frac{\Delta T_R}{T_{\mathrm{R}}}\right]\end{aligned} \tag{15}$$

Note that the signs of all delta quantities have been so chosen as to predict the maximum possible error in N_A from estimated probable errors in the measured and estimated quantities entering into the calculation.

ΔV_F is given by differentiation of Equation 9:

$$\Delta V_F = \Delta V + v_{10} n_{10}\left[\frac{\Delta n_{10}}{n_{10}} + \frac{\Delta v_{10}}{v_{10}}\right] + v_1 n_1\left[\frac{\Delta n_1}{n_1} + \frac{\Delta v_1}{v_1}\right] \tag{16}$$

and Δn_{10} by differentiation of Equation 11.

$$\Delta n_{10} = n_{10}\left[\frac{\Delta \rho_{10}}{\rho_{10}} + \frac{\Delta V_{10}}{V_{10}}\right] \tag{17}$$

Estimated errors are:

(1) The estimated error in measured pressure is:

$$\Delta P = \pm\ (10^{-4}P + 10^{-4})\ \text{atm.} \tag{18}$$

with the first term being governed by the accuracy of the weight calibration and the second arising from errors in the barometric pressure.

(2) Temperature control was maintained to ±0.1° F. so that $\Delta T = \pm 0.056°$ K.

(3) Table I lists the results of several determinations of the known volume V_0 and several of the system volume V. The average per cent deviation from the mean value of V_0 is less than 0.02 per cent while that for V is 0.08 per cent. These values will be used as the probable error in V_0 and V, respectively.

Table I. Determination of Known Volume, V_o, and System Volume, V, in Solubility Experiments

Determination No.	V_o,[a] cc.	V,[b] cc.
1	238.468	125.36
2	238.441	125.56
3	238.354	125.47
4	238.389	125.33
	Av. 238.413 ± 0.042	Av. 125.43 ± 0.085

[a] Determined by volume of water required to fill the vessel, measured gravimetrically. [b] Determined by expansion from V_0.

Table II. K-values and Liquid Phase Compositions for Methane in the Methane–*n*-Decane Binary System from Solubility Experiments

Press. P.S.I.A.	x_{CH_4}	K_{CH_4}	Press. P.S.I.A.	x_{CH_4}	K_{CH_4}
	T = 40° F.			T = 20° F.	
251.5	0.0947	10.55	227.2	0.0920	10.87
328.6	0.1243	8.04	311.1	0.1246	8.03
410.0	0.1498	6.67	499.3	0.1928	5.19
546.8	0.1923	5.20	671.2	0.2433	4.11
757.0	0.2525	3.96	969.8	0.3185	3.14
925.7	0.2901	3.45			
	T = 0° F.			T = −20° F.	
227.0	0.0982	10.18	232.0	0.1103	9.07
319.4	0.1356	7.37	307.4	0.1453	6.88
434.1	0.1783	5.61	462.4	0.2061	4.85
604.6	0.2402	4.16	641.1	0.2640	3.79
916.5	0.3248	3.08	1000.7	0.3641	2.75

(4) The methane compressibility factors used in this study are those reported by Mueller and coworkers (*4*). They gave a maximum error of 0.13 per cent so a probable error of 0.05 per cent will be assumed, recognizing that, in general, the actual error is much less than the maximum.

(5) The volume of *n*-decane metered into the equilibrium cell is measured with an accuracy of ±0.005 cc.

(6) Densities or partial molal volumes for methane and *n*-decane are extrapolated from the data of Sage and Lacey (*6*). They report an accuracy of 0.2 per cent, so an assumption of 0.5 per cent accuracy in the extrapolated values seems reasonable.

Using the probable errors stated above and Equations 14 through 17, the following maximum errors have been calculated for low, medium, and high pressures at the lowest and highest temperatures investigated.

T = −20° F.		T = 40° F.	
Pressure P.S.I.A.	$(\Delta K_1/K_1)_{Max.}$	Pressure P.S.I.A.	$(\Delta K_1/K_1)_{Max.}$
225.0	0.052	173.5	±0.041
641.1	0.050	546.8	±0.049
1000.7	0.045	925.7	±0.046

It is seen that the maximum error is about 5 per cent with very little difference between the two temperatures. However, the probable error is generally much less than the maximum error. In this case the probable error is thought to be about 1½ per cent.

The primary contributors to the maximum error in the methane K-values as determined by the solubility experiments proved to be the volumes involved and the compressibility factors. Although these quantities were known to an accuracy of one-tenth of one per cent or less the error analysis indicates that the slighest errors in these quantities may be magnified in the calculation of K.

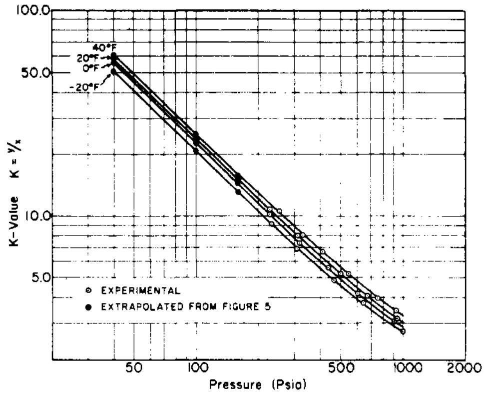

Figure 3. K-values for methane in the methane–*n*-decane system

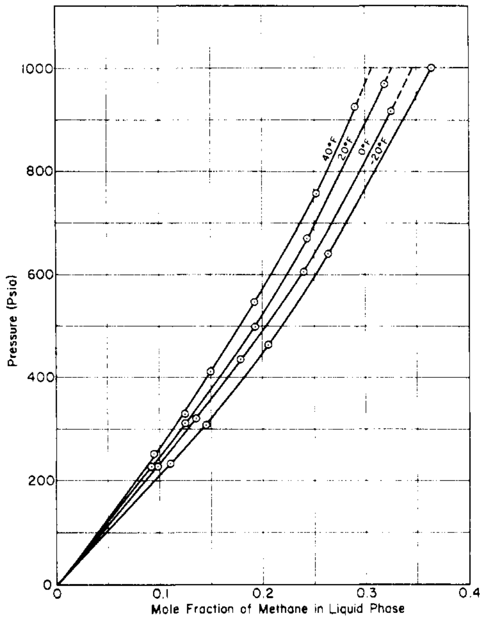

Figure 4. Solubility of methane in *n*-decane: pressure *vs.* mole fraction of methane in the liquid phase

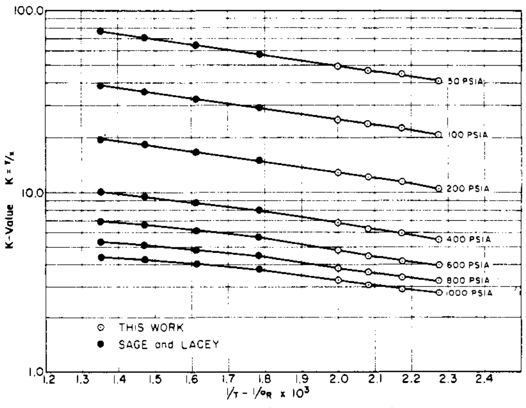

Figure 5. Consistency of K-values for methane in the methane–*n*-decane system obtained by the solubility technique with those obtained by Sage and Lacey (*6*) at higher temperatures

The results of the experimental solubility data are tabulated in Table II. In Figure 3 the methane K-values are presented. Figure 4 shows the extrapolation of the solubility data to the vapor pressure of *n*-decane. A temperature crossplot of the K-values for methane obtained from the solubility data in this work along with those obtained by Sage and Lacey (*6*) at higher temperatures is presented in Figure 5. The agreement of results from the experiments outlined herein with those of more complex static equilibrium studies is quite favorable.

ADVANTAGE OF THE SOLUBILITY TECHNIQUE

The validity of the volumetric, static experiments described herein for determining the solubility of a highly volatile material in another which is quite nonvolatile is established by the consistency of the results with those of other investigators. The technique has the distinct advantage of furnishing vapor-liquid equilibria information from *P-V-T* measurements, with no need for sampling or analysis of either phase when the assumption that the vapor contains essentially none of the nonvolatile components is valid.

ACKNOWLEDGMENT

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NOMENCLATURE

C_D = volume of capillary tubing from equilibrium system to the high pressure mercury manometer.
C_M = volume per unit length of the right leg of the high pressure manometer.
g = local acceleration of gravity.
g_c = standard acceleration of gravity.
h_G = height of the base of the piston above the reference plane.
h_L = height of left leg of high pressure mercury manometer above reference plane.
h_R = height of right leg of high pressure mercury manometer above reference plane.
n_{10} = moles of *n*-decane admitted to equilibrium cell.
N_A = moles of methane dissolved in or absorbed by *n*-decane.
N_i = moles of methane in cell before admission of *n*-decane.
N_F = moles of methane in vapor phase after admission of *n*-decane.
P = system pressure as measured with dead weight piston gauge.
P_0 = initial pressure in known volume before expansion into equilibrium cell to determine cell volume.
P_i = initial pressure in equilibrium cell before admission of *n*-decane to the cell.
P_F = final pressure in equilibrium cell after expansion from known volume or after admission of *n*-decane.
P_G = uncorrected pressure indicated by weights placed on dead weight piston gauge.
P_B = barometric pressure in piston gauge pressure measurement
T = system temperature (absolute)
T_a = ambient temperature (absolute)
v_i = molal volume of component i
V = volume of equilibrium system
V_{10} = total volume of *n*-decane admitted to the equilibrium cell
V_F = gas volume of equilibrium system after admission of *n*-decane
V_0 = calibrated known volume used
V_D = dead volume of capillary tubing and manometer used to transmit pressure from equilibrium system to piston gauges
V_{D_0} = value of V_D before expansion from V_0 into V
V_{D_i} = initial value of V_D before admission of *n*-decane into V
V_{D_F} = value of V_D corresponding to V_F
x_1 = mole fraction methane in the liquid phase at equilibrium
Z_0 = compressibility factor corresponding to P_0, T
Z_i = compressibility factor corresponding to P_i, T
Z_F = compressibility factor corresponding to P_F, T
Z_{D_0} = compressibility factor corresponding to P_0, T_a
Z_{D_i} = compressibility factor corresponding to P_i, T_a
Z_{D_F} = compressibility factor corresponding to P_F, T_a
ρ_{10} = density of *n*-decane
ρ_0 = density of piston gauge oil
ρ_{Hg} = density of mercury

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Vapor-Liquid Equilibrium Coefficients Determined by Gas-Liquid Partition Chromatography

The Systems Methane–Propane–*n*-Decane and Methane–Propane–*n*-Heptane

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THE VALIDITY of using gas-liquid partition chromatography (GLPC) to determine vapor-liquid equilibrium data has been established by a number of workers. Porter, Deal, and Stross (*15*), and Anderson and Napier (*1*) found agreement between partition coefficients determined by GLPC near atmospheric pressures and those obtained by classical static methods. Stalkup and Kobayashi (*20*) reported agreement between K-values or vapor-liquid equilibrium coefficients determined chromatographically at pressures up to 2000 p.s.i.a. and those reported by the

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