Of these the last may eventually prove to be most important.

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NOTATION

A_s = cross-sectional area of empty reactor, sq.cm.
a = packed bed surface area per unit of volume, cm.$^{-1}$
C = concentration, moles/liter
D = molecular diffusivity, sq.cm./sec.
f = fractional acid conversion, dimensionless
k = first-order reaction velocity constant
L = bed height
n = number of spheres
M_1 = mass flux rate for a single reacting sphere, moles/sq.cm-sec.
N_{Re} = Reynolds number based on average particle diameter and superficial velocity, dimensionless
N_T = molar concentration of surface active sites
R_o = over-all rate of reaction, moles/liter sec.
s = interfacial condition
t = time
t_f = time-of-flight (difference between the observed time for the start of concentration fall off at the exit of the bed and the inlet to the bed)
U_s = linear velocity based on free cross section, cm./sec.

Greek Letters

δ = boundary-layer thickness, cm.
ϵ = fraction voids in beds
ω = dimensionless time ratio, t_e/t_f
λ = constant
θ = time

Subscripts

f = bulk fluid condition
e = exit condition
i = inlet condition
m = mean value across the bed

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Heterogeneous Phase and Volumetric Behavior of the Methane *n*-Heptane System at Low Temperatures

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The phase behavior of the methane-*n*-heptane system was determined at temperatures from —200° to 340°F. at pressures up to 1,500 lb./sq. in. abs. The system was found to have a miscibility gap in the liquid-vapor region. The compositions of phases along the three phase (L_1—L_2—V) locus indicate that the L_1 phase is approximately 0.64 mole fraction methane and that the L_2 and V phases are substantially pure methane phases. The quadruple point (L_1—L_2—S_1—V) was found at a temperature of —154.4°F. and a pressure of 339 lb./sq. in. abs. A singular point (type *k*) at which the L_2 phase is in critical identity with the vapor phase was found at —114.6°F. and at a pressure of 694 lb./sq. in. abs.

The fugacity of methane at constant temperature as a function of the composition of dissolved methane was found to be linear in the low-temperature range. The plot of Henry's law constant expressed as fugacity mole fraction methane ratio vs. reciprocal absolute temperature was linear in the temperature range from —130° to approximately 100°F. These data indicate that the solution thermodynamics of methane-*n*-heptane is particularly simple in the low-temperature range.

Volumetric and phase behavior of binary hydrocarbon systems have continued to occupy a position of theoretical and practical importance. The low-temperature region frequently enables the separation of components which are difficult if not impossible to separate at high temperatures. The present study was undertaken in view of the scarcity of low-temperature phase and volumetric data on binary hydrocarbon systems.

Mixtures of methane and *n*-heptane have been studied by Boomer (*1*, *2*) who studied mixtures which contained small amounts of nitrogen at pressures up to 3,000 lb./sq. in. abs. and temperatures from 70° to 160°F. An excellent study of mixtures of methane and *n*-heptane was made by Reamer (*14*) who covered the temperature range from 40° to 460°F. at pressures up to 10,000 lb./sq. in. abs. The Reamer data were compared with the data of the present study, and excellent agreement was obtained.

The volumetric behavior of the pure components has been extensively

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Additional data has been deposited as document 6753 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

studied. Methane has been studied by several groups of investigators (*5, 9, 10*) and was summarized by Olds (*13*). Matthews and Hurd (*10*) have evaluated the thermodynamic properties from the pressure-volume temperature data previously mentioned (*5, 9, 10*).

The properties of *n*-heptane have been established by several studies (*1, 12, 15*). There is a small difference in the density of liquid *n*-heptane at elevated temperatures as reported by Beattie (*1, 15*) and by Nichols (*12*). The present study presents values which agree with those of Beattie.

APPARATUS

The equipment of the type employed in this investigation has been described in detail (*6*). Pressures were determined by 16-in. dial tube gauges which were compared during each experimental determination to a dead weight piston gauge. It is believed that the pressures of the samples were determined with a probable error of 0.1% or 1 lb./sq. in. abs., whichever is the larger measure of uncertainty.

The volume of gas metered to the equilibrium cell was measured with a calibrated mercury pump which displaced the gas from a stainless steel bomb. The gas volumes displaced were known with a probable error of ± 0.006 cc. or 0.06%, whichever is the larger measure of uncertainty. The Pyrex glass equilibrium cells employed in the study were calibrated with a 10-ml. macro burrette. The volumes are believed to be known to ± 0.01 cc. or 0.1%, whichever is the larger measure of uncertainty.

The line volume from the variable level mercury bomb to the equilibrium cell was calibrated with methane gas. The bourdon tubes were filled with mercury and calibrated for increase in volume as a function of pressure. These calibrations are believed correct to ± 0.01 cc. or 1.0%, whichever is the larger measure of uncertainty.

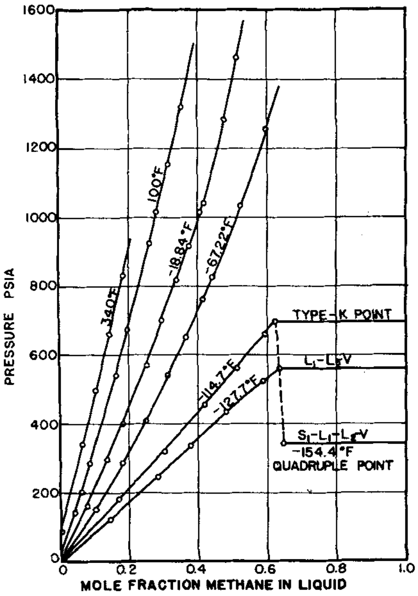

Fig. 1. Experimental isotherms.

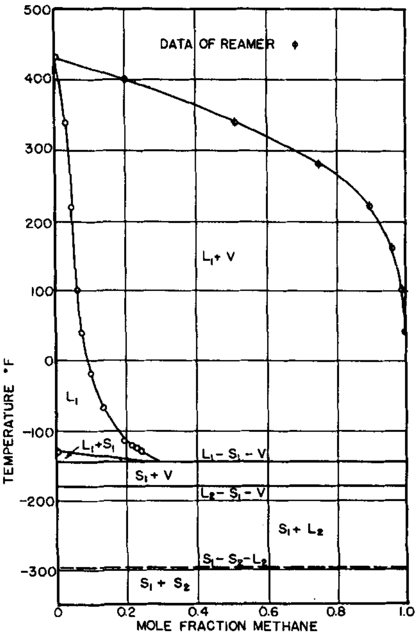

Fig. 2. Temperature composition, 200 lb./sq. in. abs.

The temperature of the sample was taken as that of a vigorously agitated bath in which the equilibrium cell was immersed. The bath was confined in a cylindrical dewar flask. The temperatures were determined with a platinum resistance thermometer which had been calibrated against primary and secondary standard fixed points. It is believed that the calibration is within ± 0.04°F. of the International Platinum Scale of temperature.

EXPERIMENTAL PROCEDURE

Saturated liquid compositions and molar volumes were obtained with Pyrex glass equilibrium cells of 5 and 12 ml. capacity. The 12-ml. cell produced better accuracy, particularly at the lower pressures, but could not be used at pressures much higher than 1,000 lb./sq. in. abs. without danger of glass failure. The 5-ml. Pyrex cells were used at pressures up to 1,500 lb./sq. in. abs. In making a measurement of bubble-point composition and volume the cell was charged with liquid *n*-heptane to a level which left a nominal amount of volume above the liquid. The cell was put under a vacuum equal to the vapor pressure of the *n*-heptane to remove air and was maintained in the constant-temperature bath. Gaseous methane was then added to the cell in incremental quantities from the variable level mercury bomb. The bomb was maintained at constant temperature and pressure so that the volume of the gas displaced by the mercury could be translated into mass units. The rate of methane absorption into the liquid phase was greatly facilitated by agitating the liquid-gas mixture by a magnetically actuated stainless steel ball which was inside the cell. The pressure of the cell was raised by approximately 150 lb./sq. in. abs. increments by each addition of methane gas. At each equilibrium point the pressure and liquid level of the material in the cell was noted. The concentration of methane in the liquid state and the molar volume of the liquid state could be calculated at each equilibrium point from the pressure, temperature, and volumetric data taken. The initial liquid level of *n*-heptane was chosen so that the cell was completely filled with liquid at the highest pressure. At this point rigorous liquid concentrations could be calculated directly because the vapor-state volume was negligible. At the lower pressures the vapor-state volume was not negligible, and corrections had to be applied for the amount of *n*-heptane in the vapor state. These corrections were important only at temperatures above 160°F. The information needed for the corrections were obtained from the dew-point studies.

The dew-point cells were similar to the cells employed in the bubble point studies but had a short bottom section made of 2.5-ml. I.D. capillary tubing. The capillary section was very carefully marked and calibrated for small amounts liquid. In obtaining measurements of dew-point composition and molar volume the dew-point cell was injected with a small amount of *n*-heptane. The cell was flushed several times with gaseous methane to remove air and was maintained at constant temperature while methane was added in incremental amounts from the variable level mercury bomb. Equilibrium at any pressure was attained by stirring the mixture with a small magnetically actuated ball. At equilibrium the liquid volume, total cell volume, and total amount of methane added to the cell were used to calculate the concentration of *n*-heptane in the gas phase. The molar liquid concentrations and volumes necessary for the calculation were obtained from the bubble-point studies. The interdependent nature of the method

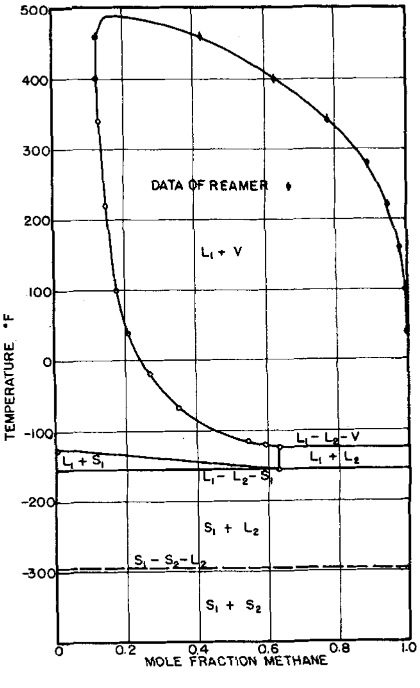

Fig. 3. Temperature composition, 600 lb./sq. in. abs.

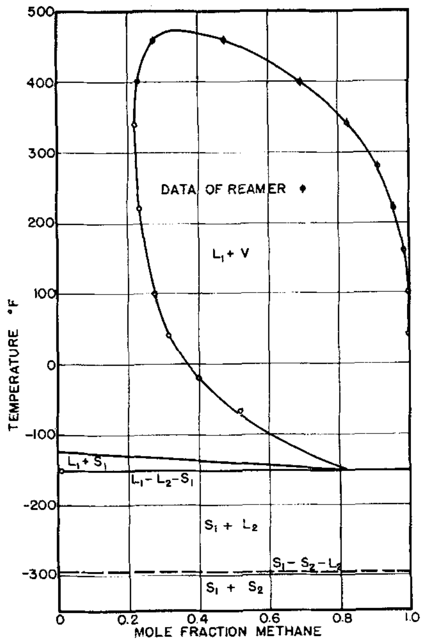

Fig. 4. Temperature composition, 1,000 lb./sq. in. abs.

of calculating dew points and bubble points did not affect the accuracy of the results. The final calculations were made completely rigorous by residual correction techniques.

Solid-liquid, solid-liquid-vapor, and liquid-liquid-vapor phase equilibria points were determined with the bubble-point cells. Several different techniques were employed for this part of the study. One technique entailed maintaining the cell at constant temperature and noting the pressure at which a new phase appeared. This technique was employed in finding the L_2 phase when the cell already contained liquid and vapor. However once the three phases $L_1 - L_2 - V$ coexisted in the cell, there was only one deg. of thermodynamic freedom and the quadruple point and the type *k* singular point were obtained easily by changing only the temperature.

Solid-liquid-vapor phase points were easily obtained by cooling the cell which contained a constant mass sample of liquid and vapor until the solid phase appeared. By alternately heating and cooling the cell the phase transition point was determined to approximately 0.2°F. A series of such points were obtained at different pressures by this technique.

MATERIALS

The methane and *n*-heptane were pure grade materials and had 99% minimum purity. The impurities in the methane were reported to be ethane, nitrogen, and carbon dioxide. The methane was passed through a silica gel drying tube at 1,500 lb./sq. in. abs. pressure. The gas was then passed at 1,500 lb./sq. in. abs. into a steel bomb containing activated charcoal. The bomb was maintained at —40°F. in a bath of dry ice and acetone. An isotherm determined on the effluent gas at —123.1°F. indicated that the quality of the vapor was increased from 0.1 to 0.90 by a pressure increase of 5 lb./sq. in. abs. The molecular weight of the gas by gas density measurement was 16.13. It is believed that the purity of the methane used is at least 99.5 mole %.

The *n*-heptane was deaerated before each experimental run and used without further purification.

EXPERIMENTAL RESULTS

Representative experimental saturated liquid isotherms are presented in Figure 1. Each experimental isotherm was determined in two different sized equilibrium bubble-point cells. The average deviation of each pair of experimental runs was ± 0.0015 mole fraction and ± 3 lb./sq. in. abs. At temperatures above —114.7°F. these isotherms are typical of those of methane in light hydrocarbon solvents. At lower temperatures the phase behavior is unique in binary paraffin mixtures because of the existence of two liquid phases. The type *k* singular point is shown at —114.7°F. and at 694 lb./sq. in. abs. At this point L_2 phase (a liquid phase having the properties of pure liquid methane) is in critical identity with the vapor phase in the presence of saturated L_1 phase. Between —114.7° and —154.4°F. and between the indicated pressures three saturated phases exist. The $L_1 - L_2 - V$ line is the binary system analogue of the vapor-pressure curve of a pure component. The liquid phase L_1 contains approximately 63 mole % methane at —114.7°F. The composition of L_1 phase increases to 64.7 mole % methane at —154.4°F. The L_2 and V phases are substantially pure methane at all temperatures on the $L_1 - L_2 - V$ line. The evidence for a substantially pure methane V phase is direct. Dew-point data at low temperatures showed that all vapor phases at temperatures below 0°F. contained less than 0.001 mole fraction *n*-heptane at all pressures higher than 100 lb./sq. in. abs. Several different aspects of the data along the $L_1 - L_2 - V$ line constituted indirect evidence for a substantially pure methane L_2 phase. First, at all temperatures which support the existence of the L_2 phase the equilibrium pressures were reasonably close to the vapor pressures of pure methane. Second, the molar volumes of the L_2 phase were within ± 0.003 cu. ft./lb. mole of the molar volumes of pure liquid methane at the same temperatures. Third, as pure methane was added to the equilibrium cell containing the $L_1 - L_2 - V$ phases the L_2 phase was definitely condensed from the V phase which is known to contain much less than 0.001 mole fraction *n*-heptane. The L_1 phase did not change in volume, while the entire vapor phase was converted to L_2 phase. The pressure was only raised a few pounds per square inch absolute by the complete condensation of V phase which no doubt was evidence that a very small amount of nitrogen was present. At —154.4°F. and 339 lb./sq. in abs. exists the quadruple point ($L_1 - L_2 - S_1 - V$), a unique state at which the four indicated phases are in equilibrium. The S_1 phase is regarded to be pure solid *n*-heptane, as the likelihood of a solid solution existing in this system is extremely remote.

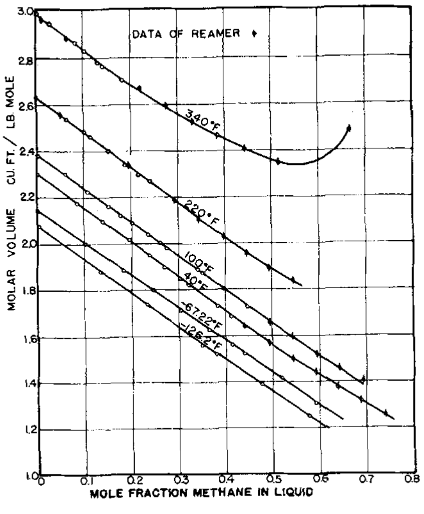

Fig. 5. Saturated liquid molar volumes.

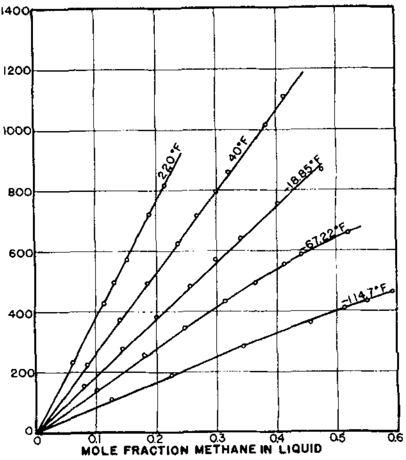

Fig. 6. Fugacity of methane in *n*-heptane.

Figures 2, 3, and 4 present temperature—composition diagrams at three different pressures. Figure 2 shows that the liquid-vapor region is intersected by a solid-vapor region. This behavior is similar to that observed in the methane-carbon dioxide and methane-hydrogen sulfide systems (*4*, *7*). The dew points indicated are those of Reamer (*14*).

Figure 3 shows that a small region of two liquid phases exists as a miscibility gap intersecting the vapor-liquid region. Figure 4 shows phase behavior similar to that displayed in Figure 2. The dashed line $S_1 - S_2 - L_2$ in Figures 2, 3, and 4 has not been

TABLE 1. SATURATED LIQUID COMPOSITION AT LOW TEMPERATURES
(Composition in mole fraction methane)

Pressure, lb./sq. in. abs.	Temperature 40	20	0	—20	—40	—60	—80	—100	—110	—120	—130
100	0.036	0.040	0.044	0.049	0.055	0.063	0.072	0.084	0.091	0.100	0.132
200	0.072	0.081	0.089	0.098	0.110	0.124	0.140	0.163	0.181	0.206	0.250
300	0.108	0.119	0.131	0.144	0.159	0.179	0.203	0.240	0.267	0.306	0.350
400	0.141	0.156	0.171	0.187	0.207	0.232	0.262	0.310	0.351	0.403	0.459
500	0.174	0.192	0.209	0.228	0.249	0.279	0.323	0.387	0.435	0.498	0.578
600	0.204	0.223	0.244	0.266	0.294	0.329	0.375	0.460	0.520	0.582	(0.635)*
700	0.235	0.257	0.278	0.302	0.330	0.370	0.433	0.530			
800	0.264	0.288	0.312	0.336	0.366	0.410	0.476	0.565			
900	0.291	0.315	0.340	0.370	0.406	0.450	0.515				
1,000	0.318	0.342	0.369	0.402	0.443	0.492	0.552				
1,100	0.346	0.370	0.398	0.431	0.473	0.524	0.584				
1,200	0.372	0.394	0.422	0.457	0.502	0.556					
1,300	0.395	0.416	0.444	0.480	0.527	0.585					
1,400	0.416	0.438	0.466	0.504	0.554	0.610					
1,500	0.440	0.462	0.489	0.527	0.578	0.640					

* Two liquid phases.

experimentally determined but is indicated at a temperature equal to the triple point of pure methane. When one considers the over-all behavior of this system, the temperature indicated should be within 2°F. of the correct temperature.

Figure 5 presents the saturated liquid molar volumes of the system as a function of temperature and composition. Data of Reamer (*14*) are included at the, four higher temperatures, where Reamer's study covered a more extensive pressure and composition range. A comparison of the liquid molar volumes of this study with those of Reamer (*14*) were made at temperatures of 40°, 100°, 220°, and 340°F. The average deviation of all the points compared was ± 0.003 cu. ft./lb. mole.

At temperatures higher than 300°F. Beattie (*1*) has presented slightly lower values for the density of pure *n*-heptane than those reported by Reamer (*14*). This study agrees well with the values reported by Beattie (*1*). The molar liquid volumes are believed to be correct to within 0.3% over the entire range of temperature investigated.

Table 1 presents the smoothed compositions of the saturated liquid phase L_1 in the low-temperature range. The average deviation of the saturated liquid compositions of Reamer (*14*) is +0.004 mole fraction. Reamer's liquid compositional values were all higher than those of this study. The data of Boomer (*2, 3*) for methane-*n*-heptane and nitrogen indicated liquid compositions which were all lower than those of this study. The average deviation of Boomer's data corrected for the presence of nitrogen from the data of this study was —0.009 mole fraction. The amount of nitrogen present in Boomer's system made any rigorous comparison of the results of little value.

No tabulation of saturated vapor compositions or volumes is presented. The study of Reamer presents these values at temperatures between 40° and 460°F. at pressures to 10,000 lb./sq. in. abs. The composition of the vapor state at 40°F. is approximately 0.996 mole fraction methane. At lower temperatures the vapor state may for all practical purposes be regarded as a gas having all the properties of pure methane.

The experimental dew-point compositions of this study agreed with those of Reamer with an average deviation of ±0.001 mole fraction. The saturated vapor molar volumes of the present study agreed with those of Reamer within 0.1 cu. ft./lb. mole. The molar volumes of Reamer were only reported to two significant figures at pressures below 1,000 lb./sq. in. abs.

It was found that the dew-point compositions could be interpolated and extrapolated at temperatures of 220°F. and below and at pressures up to 1,500 lb./sq. in. abs. by the following familiar thermodynamic equation:

$$y_1 = \frac{x_1 \gamma_1 \nu_{P1} P_1}{\nu_P P} \exp\left[\frac{V}{RT}(P - P_1)\right]$$

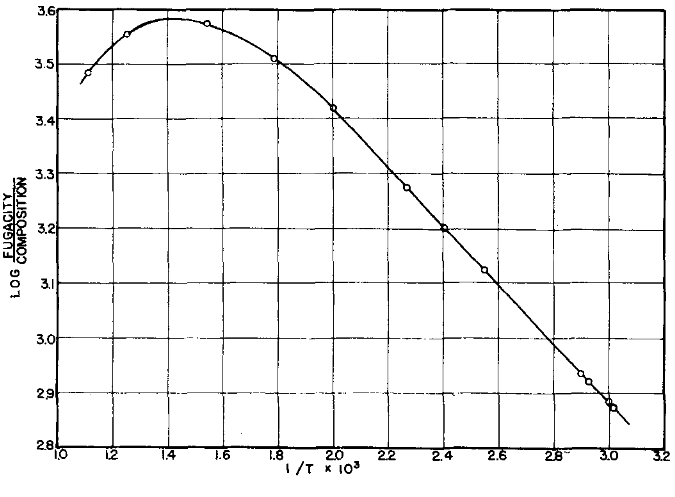

Fig. 7. Log fugacity/composition vs. reciprocal absolute temperature.

TABLE 2. SUMMARY OF THERMODYNAMIC PROPERTIES OF METHANE-*n*-HEPTANE SYSTEM

Temperature range of validity—
—130° to 75°F.

Compositional range of validity—
0 to 40 mole % CH_4

Thermodynamic property*	Function or numerical value, B.t.u./lb. mole
$\Delta H = H_2 \text{ (gas)} - \overline{H}_2$	$+ 2476$
$\Delta S = S_2 \text{ (gas)} - \overline{S}_2$	$+ \frac{2476}{T}$
$\Delta G = G_2 \text{ (gas)} - \overline{G}_2$	0
$\Delta C_P = C_{P2} \text{ (gas)} - \overline{C}_{P2}$	0

* Subscript 1 indicates solvent (*n*-heptane). Subscript 2 indicates solute (methane). The standard state of solute is the hypothetical liquid of unit mole fraction obeying Henry's Law. The standard state of solvent is the pure liquid under its own vapor pressure.

The activity coefficient was combined with the fugacity-coefficient ratio, and the resulting product was represented by an empirical function of the reduced temperature and pressure of the n-heptane. The resulting function is as follows:

$$\frac{\gamma_1 \nu_{P1}}{\nu_P} = \exp\left[A \frac{Pr^a}{Tr^b} \right]$$

The constants determined from the experimental data were found to be $A = 0.145$, $a = 0.80$, $b = 3.0$.

The equation agrees with the experimental data of both Reamer and this study with an average deviation of ±0.001 mole fraction at temperatures of 220°F. and below and pressures up to 1,500 lb./sq. in. abs.

Figure 6 shows the fugacity of methane as a function of the liquid composition along representative isotherms. As pointed out previously the gas phase is essentially pure methane at temperatures of 40°F. and below. The pure methane fugacity values of Matthews (*10*) in the low-temperature range were used to rigorously specify the fugacity of the dissolved methane at the various equilibrium pressures and temperatures. At temperatures higher than 40°F. the Lewis and Randall fugacity rule was employed along with the Matthews fugacity values to calculate the fugacity of the dissolved methane. Since the validity of the Lewis and Randall rule has not been completely checked for this system, no great accuracy is claimed for the fugacity values in the high-temperature range. The isotherms of Figure 6 indicate a high degree of linearity at compositions up to 0.400 mole fraction methane. At higher compositions there is noticeable curvature of the isotherms, so Henry's law does not hold accurately past 0.400 mole fraction methane.

The rigorous thermodynamic dependence of the Henry constant with temperature is given by the following equation:

$$\frac{d \ln f/x}{d\left(\frac{1}{T}\right)} = -\frac{\overline{H}_2^* - \overline{H}_2^0}{R}$$

In order to obtain information on the characteristic enthalpy difference the f/x values from a large scale plot of Figure 6 containing additional isotherms were plotted as log f/x vs. reciprocal absolute temperature. The results of this plot are shown in Figure 7. The linearity of the plot in the low-temperature range indicates that the following thermodynamic simplifications are true in this temperature range and at concentrations of methane up to 0.4 mole fraction:

$$\overline{H}_2^* = \overline{H}_{2(gas)}$$

$$\overline{H}_2^0 = \overline{H}_2$$

$$\Delta C_{P2} = C_{P2(gas)} - \overline{C}_{P2} = 0$$

At temperatures higher than 75°F. the f/x plot has considerable curvature indicating finite values for ΔC_P. In fact ΔC_P for methane is probably strongly temperature and pressure dependent in the temperature range from 75 to 400°F. The f/x data however can be reasonably well correlated when one assumes that ΔC_P is constant and employs an equation of the Valentiner-Lannung type (*16*). This treatment has not been presented here because of the doubt in the accuracy of the Lewis and Randall rule when applied in calculating fugacities in the methane-n-heptane system.

Table 2 summarizes the thermodynamic properties of the methane-n-heptane system in the temperature and composition ranges specified. These ideal thermodynamic values are believed to be sufficiently accurate to enable calculation of thermodynamic properties within ± 3% of the true values.

ACKNOWLEDGMENT

Sincere appreciation is expressed for the Esso Education Foundation Grant which made possible this study. Messers Charles C. Shockley and Joosup Shim assisted in various laboratory stages of the study and in the calculation of the numerical results.

NOTATION

$C_{P2(gas)}$ = molar heat capacity of methane in the gas phase at any temperature and pressure
$\overline{C}_{P2}$ = partial molar heat capacity of methane in a liquid solution of any dilution
exp = base of the Naperian logarithm system
f = fugacity of methane, lb./sq. in. abs.
$\overline{H}_2^*$ = partial molar enthalpy of methane in the ideal gas state at T
$\overline{H}_2^0$ = partial molar enthalpy of methane in an infinitely dilute solution at T
$\overline{H}_2$ = partial molar enthalpy of methane in a liquid solution of any dilution at T
$\overline{H}_{2(gas)}$ = molar enthalpy of methane in the gas phase at any T and P
L_1 = liquid phase having many of the properties of liquid n-heptane
L_2 = liquid phase having many of the properties of liquid methane
P_1 = normal vapor pressure of n-heptane at T
P = total pressure of the system
P_R = reduced pressure of n-heptane
R = universal gas constant
S_1 = solid n-heptane phase
T = absolute temperature of system, °R.
T_R = reduced temperature of n-heptane
Type k singular point = thermodynamic equilibrium point at which two phases are in critical identity in the presence of a third noncritical phase
V = vapor phase, molar volume
x_1 = mole fraction n-heptane in the liquid phase L_1
Y_1 = mole fraction n-heptane in the gas phase
γ_1 = activity coefficient of n-heptane in the liquid phase L_1
ν_{P_1} = fugacity coefficient of n-heptane in the liquid phase at the normal vapor pressure of n-heptane at T
ν_P = fugacity coefficient of n-heptane in the gas phase at the total pressure of the system and T

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