Multiphase and Volumetric Equilibria of Methane–*n*-Hexane Binary System at Temperatures between −110° and 150° C.

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THE VOLUMETRIC and phase behavior of binary hydrocarbon systems is not only of practical importance but also of considerable theoretical importance. The multiphase equilibrium properties are required for the design of separating units in the production and refining of petroleum. Accurate mixture data are valuable in the testing of theoretical mixture models. In addition, calculations involving molecular transport processes generally require particularly accurate values of equilibrium mixture properties. The present study was undertaken in view of the limited information on the low-temperature phase and volumetric behavior of this system.

A number of studies have been reported on the methane–*n*-hexane system. Frolich and others (*5*) measured the solubility of methane in *n*-hexane at 25° C. and at pressures as high as 88 atm. with an estimated accuracy of ±5.0%, but made no molar volume determinations. Bubble point and dew point densities and compositions at 25°, 55°, and 85° C., corresponding to pressures up to 230 atm., were reported by Boomer and Johnson (*2*) for methane–*n*-hexane mixtures which also contained a small amount of nitrogen. Sage (*17*) determined the solubility of methane in *n*-hexane at 37.8°, 71.1°, and 104.4° C. and at total pressures up to 204 atm. The solubility of methane in *n*-hexane corresponding to pressures up to critical and at temperatures of 37.9°, 71.1°, and 104.4° C. were determined by Schoch (*18*).

The data of Boomer (*2*), Sage (*17*), and Schoch (*18*) were compared with the data of the present study and reasonable agreement was obtained.

The volumetric behavior of the pure components has been extensively studied. Methane has been investigated by several groups of investigators (*2, 7, 13*) and data were summarized by Olds (*14*). Matthews (*13*) evaluated the thermodynamic properties from the *P-V-T* data previously mentioned (*7, 13*).

The properties of *n*-hexane have been established by several studies (*6, 16, 19*).

APPARATUS

The equipment is described by Kohn and Kurata (*11*). Pressures were determined by 16-inch dial Heiss Bourdon tube gages, which were compared during each experimental run to an Ashcroft dead weight piston gage. The pressures of the samples were determined with a probable error of 0.1% or 0.07 atm., whichever is the larger measure of uncertainty.

The volume of gas metered to the equilibrium cell was measured using 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 equilibrium cells were calibrated using a 10-ml. macroburet. The volumes were 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 using 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.

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 using an Aminco platinum resistance thermometer calibrated against primary and secondary standard fixed points. The calibration is probably within ±0.02° C. of the international platinum scale of temperature.

EXPERIMENTAL

Saturated liquid compositions and molar volumes were obtained using borosilicate 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 70 atm. without danger of glass failure. The 5-ml. cells were used at pressures up to 100 atm. In measuring bubble point composition and volume, the cell was charged with liquid *n*-hexane to a level which left a nominal volume above the liquid. The cell was put under a vacuum equal to the vapor pressure of the *n*-hexane 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 inside the cell. The pressure and liquid level of the material in the cell were noted. The concentration of methane in the liquid state and the molar volume of the liquid state were calculated at each equilibrium point from the pressure, temperature, and volumetric data taken. The initial liquid level of *n*-hexane 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*-hexane in the vapor state. These corrections were important only above 50° C. The information needed for the corrections was 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-mm. I.D. capillary tubing, very carefully marked and calibrated for small amounts of liquid. In measuring dew point composition and molar volume a small amount of *n*-hexane was injected into the dew point cell. The cell was flushed several times with gaseous methane to remove air, then was maintained at constant temperature while methane was added in incremental amounts from the variable level mercury bomb. Equilibrium at any pressure was obtained 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*-hexane 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 of calculating dew points and bubble points did not affect the accuracy of the results. The final calculations were made exact by residual correction techniques.

Solid-liquid vapor phase points were easily obtained by cooling the bubble point 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 0.1° C. A series of such points was obtained at different pressures by this technique.

MATERIALS

The methane and *n*-hexane were obtained from the Phillips Petroleum Co. Both components were "pure grade" materials, stated to have 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 100-atm. pressure, then passed at 100 atm. into a steel bomb containing activated charcoal. The bomb was maintained at −40° C. in a bath of dry ice and acetone. The molecular weight of the gas by gas density measurement was 16.13. The purity of the methane used is at least 99.5 mole %.

The *n*-hexane was de-aerated before each experimental run and used without further purification.

EXPERIMENTAL RESULTS

Selected experimental isotherms are presented in Figure 1. Ten experimental bubble point isotherms from −90° to 150° C. were determined in borosilicate glass equilibrium cells at pressures up to 100 atm. Five experimental dew point isotherms from 25° to 150° C. were determined in borosilicate glass dew point equilibrium cells at pressures up to 70 atm. The average deviation of the experimental points at pressures below 100 atm. and temperatures at −50° C. and higher was ±0.0015 mole fraction, ±0.07° C. and ±0.10 atm.; at lower temperatures it was ±0.003 mole fraction, ±0.1° C. and ±0.10 atm. The relatively few data points at pressures in excess of 100 atm. were taken in a stainless steel equilibrium cell and evaluated by graphical techniques. The average deviation of these data points is ±0.004 mole fraction, ±0.07° C. and ±0.2 atm.

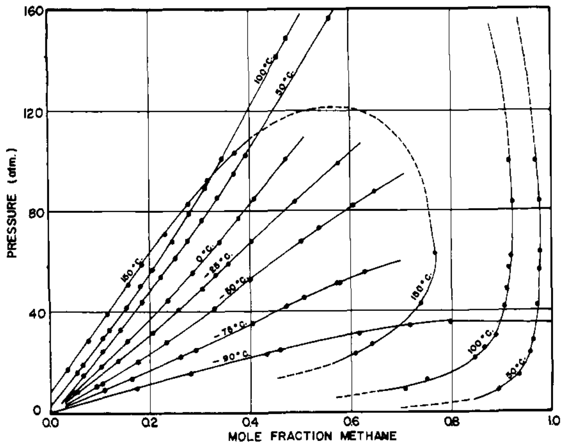

Figure 1. Selected experimental isotherms

Above −70° C. the isotherms of Figure 1 are typical of those of binary hydrocarbon systems which contain methane. The behavior along the −90° C. isotherm is unique. As the equilibrium pressure is increased to near that of the vapor pressure of pure methane, very large amounts of methane dissolve in the liquid phase. At liquid compositions in excess of 0.8 mole fraction methane the equilibrium pressure is constant. The phenomenon is exactly the same as that observed in systems which have two liquid phases (*8*, *9*). However, in the methane-*n*-hexane system two liquid phases were definitely not observed at any temperature or pressure.

Figures 2, 3, 4, and 5 present isobaric temperature-composition diagrams. Figure 2, which presents the behavior at 10 atm., shows that the vapor-liquid phase loop is intersected by a solid-vapor region. Such is to be expected in binary systems where one component has a triple point at a higher temperature than the critical point of the other component. Methane–carbon dioxide (*4*), methane–hydrogen sulfide (*9*), and methane–*n*-heptane (*8*) are systems containing methane which display this type of phase behavior.

Figure 2 shows the upper three-phase L-S_1-V line at −100.6° C. The liquid phase (L) has a composition of 0.236 mole fraction methane. The solid phase (S_1) is substantially pure *n*-hexane, while the vapor phase (V) is substantially pure methane. The lower three-phase line is at −125° C., which is imperceptibly close to the vapor pressure curve of pure methane. The three-phase line L-S_1-S_2 was not experimentally determined. It is shown at a temperature equal to the triple point of pure methane, which probably is within 2° C. of the true three-phase L-S_1-S_2 line.

Figure 3 is shown at a pressure of 19.2 atm., because this is the maximum pressure along the three-phase (L-S_1-V) line. At this pressure the two separate three-phase lines converge to a single temperature. The composition of the liquid phase is 0.600 mole fraction methane, but could be in error by several per cent, since the composition is extremely sensitive to temperature in this region. The temperature at the maximum pressure is indicated at −108.8° C. The probable error in this point is ±0.1° C. and ±0.2 atm. Several data points along the L-S_1-V line were taken at slightly lower temperatures than −108° C. at pressures as high as 20.0 atm. These points were disregarded in this study, because there was considerable doubt that equilibrium was attained during these specific determinations.

Figure 4 shows the phase behavior at 30 atm. At this pressure the phase behavior is normal in all respects to that of binary systems at pressures higher than the critical pressure of one of the components.

Figure 5 shows the phase behavior at 70 atm. This pressure is above the critical pressure of both pure components. The data in the critical regions were not experimentally determined and therefore are shown as dashed lines.

Table I presents the solid-liquid and the solid-liquid-vapor phase behavior. Only three two-phase points were determined, but these three points clearly indicate the effect of pressure on the freezing point of the S_1 phase. The freezing point is increased by increased pressure, which is consistent with the fact that the molar volume of the liquid exceeds that of the solid.

The three-phase data shown in Table I have been smoothed and shown at even pressure values. The calculated composition values of the liquid phase agree very well with the experimental values. These calculated values were obtained using an integration of the Van't Hoff isochore for solid solubility as a function of temperature with the heat of fusion considered constant. The measured experimental solubility points were used to calculate the heat of

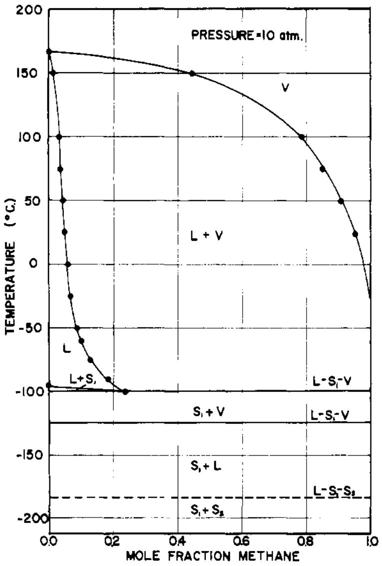

Figure 2. Isobaric temperature-composition diagram

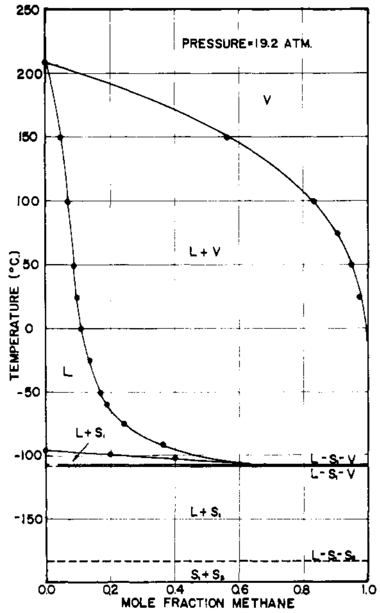

Figure 3. Isobaric temperature-composition diagram

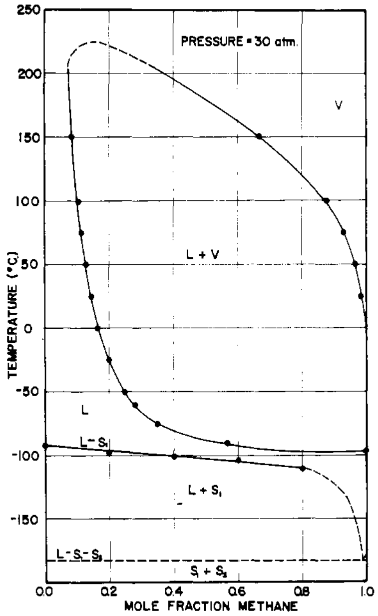

Figure 4. Isobaric temperature-composition diagram

Table I. Solid-Liquid and Solid-Liquid-Vapor Phase Behavior

Pressure, Atm.	Temp., ° C.	Compn. of Liquid Phase, Mole Fraction Methane	
	Solid-Liquid[a]		
18.9	−108.8	0.685	
48.1	−108.7	0.685	
65.5	−108.6	0.685	
	Solid-Liquid-Vapor[b]		
		Exptl.	Calcd.
<0.0026	−95.348	0.00	0.00
2.5	−96.60	0.056	0.058
5.0	−97.90	0.114	0.118
7.5	−99.27	0.174	0.178
10.0	−100.64	0.236	0.240
12.5	−102.03	0.300	0.295
15.0	−103.68	0.373	
17.5	−105.67	0.465	
19.2	−108.00	0.600	
18.0	−110.27	0.805	

[a] Locus of two-phase line L-S_1.
[b] Locus of three-phase line L-S_1-V.

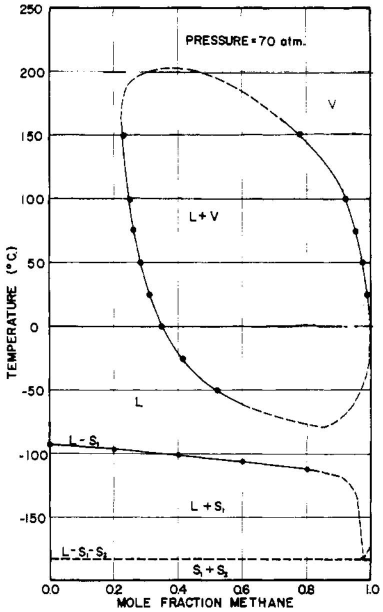

Figure 5. Isobaric temperature-composition diagram

fusion of *n*-hexane from the Van't Hoff isochore. The calculated heat of fusion was 3119 ± 69 cal. per gram mole, which agrees well with the literature value of 3114 cal. per gram mole (*16*).

The experimental vapor-liquid data demonstrated the validity of Raoult's law for *n*-hexane in the composition range exceeding 0.65 mole fraction *n*-hexane. The close agreement of the measured and calculated values of solubility is therefore strong evidence for the absence of a measurable amount of solid solution formation in this system and also indicates that ΔC_p [C_p(liquid) − C_p(solid)] is nominally small, probably close to 6 cal. per gram mole in ° K.

The smoothed values of composition and molar volume of the bubble point and dew point states are presented in Table II at even values of pressure for each temperature studied. The bubble point molar volumes are believed to be accurate to ±0.2% in the entire pressure and temperature ranges. The dew point compositions are believed to be accurate to ±0.002 mole fraction. The accuracy of the dew point molar volumes is very sensitive to pressure; below 40 atm. they are accurate to ±3.5% and between 50 and 70 atm. are accurate to ±0.4%.

To compare the data of this study with other investigations, large scale cross plots of bubble point pressures and saturated liquid molar volumes were prepared. The data of Boomer (*2*), Sage (*17*), and Schoch (*18*) were used in this comparison. Since these investigators studied only a limited temperature range, no extensive comparison could be made. The deviations of the Boomer values of bubble point composition from the data of this study are all negative and are approximately equal to 0.012 mole fraction. The deviations of Boomer's liquid molar volumes from the data of this study are also negative but are only 1.2 cc.

Table II. Properties of the Coexisting Gas and Liquid Phases

	Bubble Point		Dew Point[a]	
Pressure, Atm.	Mole fraction methane	Molar volume, cc./g. mole	Mole fraction methane	Molar volume, cc./g. mole
		Temp., 150° C.		
7.368[b]	0.000	163.51	0	
10	0.0110	162.75	0.4420	
20	0.0464	160.20	0.5625	1417.1
30	0.0826	157.48	0.6695	1036.3
40	0.1187	154.79	0.7220	830.3
50	0.1553	152.26	0.7520	692.9
60	0.1915	149.80	0.7675	605.5
70	0.2278	147.50	0.7780	530.6
80	0.2645	145.25	0.780	
90	0.3040	143.10	0.760	
100	0.3440	141.50	0.738	
120	0.6250[c]		0.6250	
		Temp., 100° C		
2.428[b]	0.000	147.95	0	
10	0.0300	145.52	0.7875	2010.2
20	0.0688	142.52	0.8316	1473.9
30	0.1065	139.59	0.8760	962.6
40	0.1440	136.72	0.8970	724.2
50	0.1810	133.97	0.9082	574.3
60	0.2160	131.29	0.9158	474.4
70	0.2490	129.10	0.9224	387.0
80	0.2807	126.73	0.9280	
90	0.3135	124.35	0.9321	
100	0.3434	122.36	0.9340	
120	0.4033	118.49		
140	0.4700	114.80		
160	0.5560	111.68		
		Temp., 75° C.		
1.211[b]	0.000	141.57	0	
10	0.0364	138.15	0.8460	
20	0.0767	134.90	0.9028	1317.2
30	0.1165	131.78	0.9267	874.0
40	0.1543	128.79	0.9385	699.2
50	0.1920	125.91	0.9457	561.8
60	0.2280	123.04	0.9492	449.5
70	0.2625	120.36	0.9524	362.1
80	0.2963	117.86	0.9555	
90	0.3295	115.36	0.9580	
100	0.3600	113.43	0.9605	
120	0.4192	109.50		
140	0.4830	105.75		
160	0.5530	102.20		
		Temp., 50° C.		
0.526[b]	0.000	136.29	0.000	
10	0.0422	133.53	0.9021	
20	0.0860	129.41	0.9465	1198.6
30	0.1290	126.04	0.9614	811.5
40	0.1690	122.86	0.9680	593.0
50	0.2080	119.80	0.9719	461.9
60	0.2458	116.74	0.9747	383.9
70	0.2820	113.93	0.9765	324.6
80	0.3186	111.06	0.9770	
90	0.3540	108.12	0.9768	
100	0.3850	105.88	0.9751	
120	0.4475	101.57		
140	0.5070	97.70		
160	0.5720	94.27		
		Temp., 25° C.		
0.198[b]	0.000	131.59	0.000	
10	0.0490	127.55	0.9530	
20	0.0978	123.74	0.9728	1061.3
30	0.1450	120.12	0.9795	736.7
40	0.1890	116.75	0.9830	543.1
50	0.2316	113.50	0.9850	427.6
60	0.2710	110.44	0.9863	374.6
70	0.3090	107.51	0.9871	312.1
		Temp. 25 ° C.		
80	0.3447	104.70	0.9868	
90	0.3810	101.83	0.9854	
100	0.4125	99.64	0.9833	
120	0.4740	94.95		
140	0.5370	90.70		
160	0.6090	86.03		
193.6[c]	0.7466	81.38	0.7466	81.38
		Temp., 0° C.		
0.0565[b]	0.000	127.29		
10	0.0560	122.92		
20	0.1108	118.67		
30	0.1637	114.74		
40	0.2135	111.00		
50	0.2590	107.44		
60	0.3045	104.07		
70	0.3493	100.57		
80	0.3910	97.51		
90	0.4300	94.45		
100	0.4720	91.27		
		Temp., −25° C.		
0.013[b]	0.000	123.26		
10	0.0695	117.49		
20	0.1366	112.56		
30	0.1995	108.00		
40	0.2570	103.82		
50	0.3120	99.76		
60	0.3643	95.83		
70	0.4140	92.08		
80	0.4660	88.15		
90	0.5245	83.84		
100	0.5825	79.80		
		Temp., −50° C.		
	0.000	119.64		
10	0.0880	112.56		
20	0.1705	106.44		
30	0.2473	101.00		
40	0.3197	95.64		
50	0.3865	90.90		
60	0.4560	85.84		
70	0.5225	80.92		
80	0.5880	77.23		
		Temp., −75° C.		
	0.000	116.28		
5	0.0630	111.06		
10	0.1240	106.63		
15	0.1844	102.20		
20	0.2405	98.01		
25	0.2930	94.27		
30	0.3480	90.46		
35	0.3970	86.77		
40	0.4455	83.40		
45	0.4953	79.72		
50	0.5610	75.45		
55	0.6225	70.50		
60	0.6870	67.30		
		Temp., −90° C.		
	0.000	114.35		
5	0.0920	107.06		
10	0.1820	100.51		
15	0.2740	93.77		
20	0.3648	87.52		
25	0.4550	81.28		
30	0.5675	73.54		
35	0.7120	63.11		
35.86[e]	1.0000	60.07		

[a] Dew point compositions and molar volumes at 0° C. and lower temperatures are accurately given by properties of pure methane.
[b] Vapor pressure of pure *n*-hexane.
[c] Critical composition estimated by extrapolation.
[d] Critical state.
[e] Vapor pressure of pure methane.

per gram mole, which is approximately a 1.0% deviation. Boomer's system contained nitrogen, so an accurate comparison was impossible.

The average deviation of the bubble point compositions reported by Sage (*17*) from those of this study was ±0.002 mole fraction. The liquid molar volume deviation of Sage from those of this study was ±1.5 cc. per gram mole. The data of Schoch (*18*) gave a particularly excellent comparison with the results of this study: composition deviation, ±0.0007 mole fraction and liquid molar volume deviation, +0.5 cc. per gram mole.

The volumetric measurements for pure *n*-hexane were compared with the data of several investigators (*6, 16, 19*). The agreement was excellent, with the single exception of the volume reported by Stuart (*19*) at 150° C.

The dew point composition and molar volume values were not determined below 25° C. The difficulty of measuring accurately a few tenths of a mole fraction and the initial limited purity of the materials used did not justify dew point determinations below 25° C. Since the dew point states at the lower temperatures contain methane in excess of 0.99 mole fraction except at very low pressures, the equilibrium properties at these states are regarded as identical to those of pure methane.

The dew point compositions were smoothed for purposes of interpolation and extrapolation at temperatures of 100° C. and below and at pressures up to 100 atm. by the following thermodynamic equation:

$$y_1 = \frac{P_1 x_1}{P}\left[\frac{\gamma_1 \nu_{p1}}{\nu_p}\right]\exp.\left\{\frac{V}{RT}(P - P_1)\right\} \tag{1}$$

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*-hexane:

$$\frac{\gamma_1 \nu_{p1}}{\nu_p} = \exp.\left\{A\,\frac{P_r^a}{T_r^b}\right\} \tag{2}$$

The constants for Equation 2 were determined by using a multiple statistical regression analysis on an IBM 1620 computer. The constants determined from the experimental data were: $A = 0.125$, $a = 0.50$, and $b = 4.20$.

Equation 2 agrees with the experimental dew point compositions of this study with an average deviation of ±0.002 mole fraction at pressures up to 100 atm. and at temperatures of 100° C. and below.

Figure 6 shows the effect of composition on the saturated liquid molar volumes of this study. Since at each temperature two phases are present, there is only one degree of freedom and composition is not independent of pressure. The linearity of the lines is marked in the composition range up to 0.50 mole fraction methane, except at the two highest temperatures. In a strictly rigorous thermodynamic sense the concept of partial molar volume is inapplicable to the two-phase region, where at constant temperature only one degree of freedom remains. However, in a practical sense it is very useful because the pure *n*-hexane volumetric data can be regarded as equal to the partial molar volume of *n*-hexane in solutions containing up to 0.50 mole fraction methane and thus only one measured experimental point fixes the molar volume line with good accuracy.

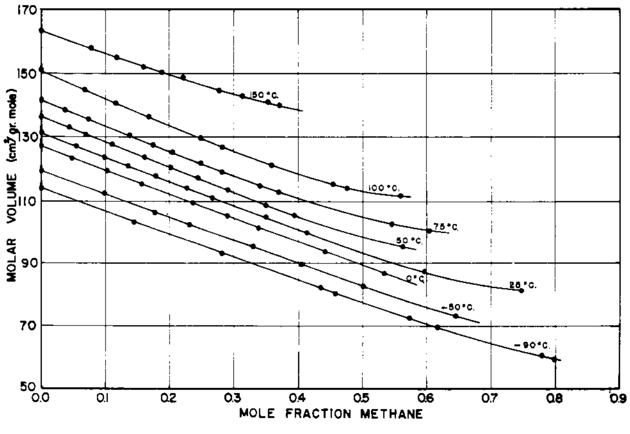

Figure 6. Saturated liquid molar volumes

Figure 7 shows the fugacity of methane as a function of liquid composition along representative isotherms. Below 25° C. the fugacity values of Matthews and Hurd (*13*) for pure methane were used to specify the fugacity of the dissolved methane at the various equilibrium pressures. These values are accurate, because the vapor phase in this temperature range and at pressure higher than a few atmospheres is substantially pure methane. At 25° C. or higher the Lewis and Randall fugacity rule was employed along with the Matthews fugacity values for pure methane to calculate the fugacity of the dissolved methane. While the Lewis and Randall rule holds for all gaseous systems in the composition range near each pure component, the ranges must be experimentally determined. This has not been done and therefore, even though the fugacity lines above 25° C. show good linearity, high accuracy of the calculated fugacity values in this temperature range is not claimed.

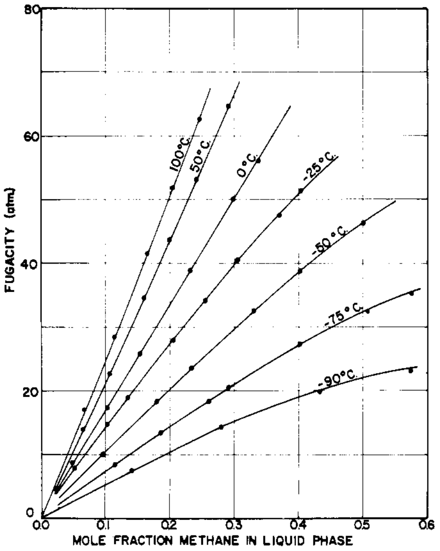

Figure 7. Fugacity-composition diagram

The slopes of the fugacity lines in Figure 7 are the Henry's law constants for the solute methane. These slopes are constant in the dilute range and only small deviations from constant slope are observed even at 0.40 mole fraction methane. The initial values of the fugacity deviation from straight lines were themselves found to be linear functions of the concentration of the dissolved methane. This was experimentally verified and found to hold accurately in the range from 0.35 to 0.50 mole fraction methane. This deviation phenomenon was described by Lewis and Randall (*12*). The experimental values of the deviation constants are not reported here because of the small concentration range and the limited utility of such values.

Figure 8 plots the logarithm of the Henry's law constant *vs.* reciprocal absolute temperature. The exact thermo-

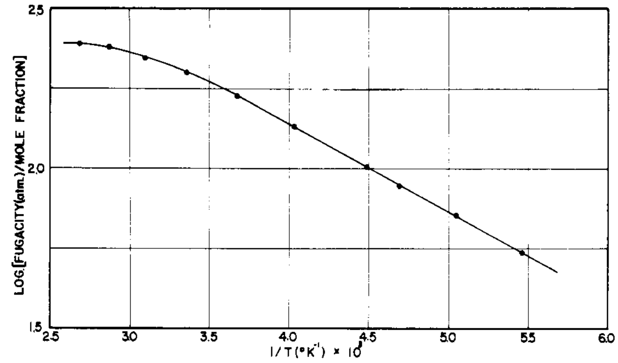

Figure 8. Log (fugacity/mole fraction) vs. reciprocal absolute temperature

dynamic dependence of the Henry's law constant upon temperature is given by

$$\frac{d \ln f/x}{d(1/T)} = -\frac{\bar{H}_2^* - \bar{H}_2^\circ}{R}$$

The slope of Figure 8 is linear in the temperature range from 25° to −102° C., where the solid n-hexane phase is observed. The linearity of the plot in this temperature range indicates that the following thermodynamic simplifications are true at concentrations of methane up to 0.40 mole fraction:

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

$$\bar{H}_2^\circ = \bar{H}_2$$

$$\Delta C_{p2} = C_{p2(gas)} - \bar{C}_{p2} = 0$$

From the slope of the curve the enthalpy change of methane upon solution $[(H_{2(gas)} - \bar{H}_2)]$ was calculated to be:

$$\Delta H = +\ 1237 \pm 31 \text{ cal. per gram mole}$$

The following thermodynamic properties of the methane-n-hexane system in the temperature range of validity, −102° to 25° C., and composition range of validity, 0 to 40 mole fraction methane, are believed to be accurate to within ±3% of the true values.

Thermodynamic Property	Function or Numerical Value, Cal./G. Mole
$\Delta H = H_{2(gas)} - \bar{H}_2$	1237 ± 31
$\Delta S = S_{2(gas)} - \bar{S}_2$	1237 ± 31/T
$\Delta G = G_{2(gas)} - \bar{G}_2$	0
$\Delta C_p = C_{p2(gas)} - \bar{C}_{p2}$	0
H_1(liq) − H_1(solid)	3119 ± 69
S_1(liq) − S_1(solid)	3119 ± 69/T

The thermodynamic behavior of the methane-n-hexane system is similar to that of the methane-light paraffin hydrocarbon binary systems. There is a gradual decrease in solubility of methane in the liquid phase of mixtures as the paraffin molecular weight increases. n-Hexane is the highest molecular weight paraffin which is completely miscible with methane. The higher homologs should all show limited miscibility in the liquid or solid phases.

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NOMENCLATURE

$C_{p2(gas)}$ = molar heat capacity of methane in gas phase at any temperature and pressure
$\bar{C}_{p2}$ = partial molar heat capacity of methane in liquid solution of any dilution
exp. = base of Naperian logarithm system
f = fugacity of methane, atm.
$\bar{H}_2^*$ = partial molar enthalpy of methane in ideal gas state at T
$\bar{H}_2^\circ$ = partial molar enthalpy of methane in an infinitely dilute solution at T
$\bar{H}_2$ = partial molar enthalpy of methane in a liquid solution of any dilution at T
$\bar{H}_{2(gas)}$ = molar enthalpy of methane in gas phase at any T and P
ln = Naperian logarithm
log = logarithm to base 10
L = liquid phase
P_1 = normal vapor pressure of n-hexane at T
P = total pressure of system
P_r = reduced pressure of n-hexane
R = universal gas constant
S_1 = solid n-hexane phase
T = absolute temperature of system, ° K.
T_r = reduced temperature of n-hexane
V = vapor phase; molar volume
x_1 = mole fraction n-hexane in liquid phase
y_1 = mole fraction n-hexane in gas phase

The standard state of the solute is the hypothetical incompressible liquid of unit mole fraction obeying Henry's law. The standard state of the solvent is the pure liquid under its own vapor pressure.

Greek Letters

γ_1 = activity coefficient of n-hexane in liquid phase
ν_{p1} = fugacity coefficient of n-hexane in liquid phase at normal vapor pressure of n-hexane at T
ν_p = fugacity coefficient of n-hexane in gas phase at total pressure of system at T

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