Table II. Smoothed Values of Composition of Three-Phase Region

Press., Atm.	Temp., °C.	Mole Fraction Ethane Comp., liquid 1	Comp., liquid 2	Comp., vapor phase
7.18	−40.00	0.360	0.957	0.992
10	−30.07	0.376	0.936	0.991
20	−5.65	0.410	0.934	0.990
30	10.80	0.357	0.936	0.989
40	23.78	0.354	0.941	0.988
50	35.25	0.348	0.962	0.986
51.08[a]	36.42	0.351	0.979	0.979

[a] Critical temperature and pressure of the liquid 2 and vapor phase.

the equilibrium properties at these states are regarded as identical to those of pure ethane.

The smoothed three-phase data (L_1-L_2-V) are shown at even pressures in Table II. In comparing those smoothed values presented in Table II with values of Kuenen (*5*), the average deviation of the pressure is 1% for temperatures below the critical point. At the critical point, the deviation is 3% and −3% in temperature and pressure, respectively. Kuenen's system contained air, which raised the critical pressure and lowered the critical temperature of the system.

From the compositions along the three-phase line given in Table II and illustrated by the dashed lines in Figure 1, there definitely does not seem to be a lower critical solution point for the system (L_1 = L_2 in the presence of a vapor phase). Rather it would appear that at a temperature in the region of −97.8° C. that the three-phase line terminates at a quadruple point. At this point solid methanol should be in equilibrium with the (L_1), (L_2) and vapor phases.

NOMENCLATURE

L_1 = liquid phase rich in methanol
L_2 = liquid phase rich in ethane
V = vapor phase

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

JAMES P. KOHN and WILLIAM F. BRADISH
University of Notre Dame, Notre Dame, Ind.

Vapor-liquid compositions and molar volumes were determined at eight temperatures between −50° and 150° C. Temperature, pressures, and compositions along the three phase (vapor-liquid-solid) lines are reported at temperatures between −107.6° and −56.7° C.

THIS STUDY was undertaken in view of the scarcity of information on the low temperature phase and volumetric behavior of the methane-*n*-octane system. Such information is desirable for its use in low temperature theoretical studies and for its value in assessing the economic feasibility of employing low temperature separation processes in systems involving light hydrocarbon mixtures.

No studies of the vapor-liquid behavior of the methane-*n*-octane system were found in the literature. Brewer (*1*) reported a study of the three phase (solid-liquid-vapor) locus and reported compositions of the liquid phase.

The *P-V-T* behavior of the pure components has been studied. Methane has been investigated by several groups of investigators (*3, 6, 8, 9, 10*). Matthews (*7*) evaluated the thermodynamic properties of methane from selected *P-V-T* data previously mentioned.

Young (*15, 16*) presented vapor pressures, specific volumes, and critical constants of *n*-octane from −3° to 296° C. Felsing (*2*) reported the compressibility of liquid *n*-octane at temperatures from 100° to 275° C. at pressures to 300 atm. Data on the liquid density, vapor pressures, critical constants, and heat of fusion of *n*-octane were reported by Rossini (*12*). Sage (*13*) summarized the *P-V-T-X* work done on the light hydrocarbon pure component, binary, and ternary systems to the year 1950.

EXPERIMENTAL

The equipment and the experimental techniques were described by Kohn (*5*) and were the same as those used in other studies on binary hydrocarbon systems (*4, 14*).

The methane and *n*-octane were obtained from the Phillips Petroleum Co. Both components were "pure grade" materials stated to have 99% minimum purity. The methane was processed as described by Kohn and the resulting gas used in the study was thought to have a purity in excess of 99.5%. The *n*-octane was de-aerated before each experimental run and used without further purification.

RESULTS

Eight experimental bubble point isotherms were determined for the range −57.22° C. to 150° C. Each isotherm was run in a small borosilicate glass equilibrium cell of 5 cc. volume and in a large borosilicate glass cell of 12 cc. volume at pressures to 70 atm. The average deviation of the experimental bubble points was ±0.0015 mole fraction, ±0.07° C. and ±0.10 atm.

Four experimental dew point isotherms were determined between 25° C. and 150° C. and at pressures to 70 atm. in a borosilicate glass equilibrium cell of 10 cc. volume. The dew point isotherms were run at least twice at each temperature with good reproducibility. At temperatures of 150° and 100° C., the average deviation of the experimental points was ±0.002 mole fraction, ±0.07° C. and ±0.1 atm. At 50° and 25° C., the average deviation of the experimental points was ±0.001 mole fraction, ±0.07° C. and ±0.07 atm. Vapor-liquid critical points were determined at 25° and 50° C. in a stainless steel equilibrium cell. Since these critical points were determined by graphical discontinuities in the mass *vs.* pressure relationships, they represent data of lower accuracy than that obtained in the borosilicate glass cells. The probable accuracy of the vapor-liquid critical points is ±0.07° C., ±6 atm. and ±0.02 mole fraction.

Table I presents the smoothed *P-V-T-X* properties in the vapor-liquid region at temperatures between −50° and 150° C. The saturated vapor properties were not measured below 25° C. because of the difficulty of accurately measuring concentrations of *n*-octane less than a few tenths of a mole per cent. The vapor volumes at 25° C. and above are reproducible to ±0.5%. The liquid molar volumes are reproducible to ±0.1%. The dew point composition were smoothed by use of the following thermodynamic equation:

Table I. Properties of the Coexisting Vapor and Liquid Phases

	Liquid		Vapor[a]	
Pressure, Atm.	Mole fraction, methane	Molar volume, ml./gram mole	Mole fraction methane	Molar volume, ml./gram mole
		T = 150° C.		
1.995[b]	0.000	193.8		
10	0.028	189.9		
20	0.063	185.8	0.881	1708
30	0.097	181.5	0.914	1133
40	0.131	177.5	0.930	846.4
50	0.164	173.6	0.939	675.7
60	0.196	170.0	0.945	562.5
70	0.229	166.3	0.949	481.6
		T = 100° C.		
0.463[b]	0.000	179.6		
10	0.033	175.6	0.947	3034
20	0.069	171.3	0.971	1505
30	0.104	167.0	0.979	996.2
40	0.139	162.8	0.982	742.5
50	0.173	158.6	0.984	590.3
60	0.207	154.5	0.985	488.9
70	0.240	150.1	0.986	416.9
		T = 75° C.		
0.186[b]	0.000	173.9		
10	0.038	169.0		2820
20	0.075	165.0	0.985	1395
30	0.112	160.6	0.990	920.8
40	0.148	156.5	0.992	682.1
50	0.183	152.5	0.993	540.5
60	0.218	148.5	0.994	446.6
70	0.251	144.8	0.994	379.5
		T = 50° C.		
0.065[b]	0.000	168.4		
10	0.043	162.8	0.991	2604
20	0.083	158.2	0.995	1281
30	0.122	154.1	0.996	841.5
40	0.161	149.8	0.997	622.5
50	0.188	145.6	0.997	491.6
60	0.234	141.8	0.997	404.8
70	0.265	138.0	0.997	342.8
269.8[c]	0.787	86.1	0.787	86.1
		T = 25° C.		
0.020[b]	0.000	163.5		
10	0.047	158.2	0.998	2385
20	0.094	153.0	0.999	1167
30	0.136	148.5	0.999	763.2
40	0.178	143.4	0.999	562.7
50	0.220	138.7	0.999	442.8
60	0.255	134.9	0.999	362.5
70	0.287	131.4	0.999	305.1
263[c]	0.798	81.5	0.798	81.5
		T = 0° C.		
	0.000	158.9		
10	0.054	153.0		
20	0.106	147.4		
30	0.155	142.2		
40	0.201	137.2		
50	0.244	132.5		
60	0.285	128.0		
70	0.319	124.3		
		T = −25° C.		
	0.000	154.6		
10	0.065	147.7		
20	0.128	140.6		
30	0.187	134.4		
40	0.238	128.9		
50	0.288	123.6		
60	0.337	118.2		
70	0.373	114.1		
		T = −50° C.		
	0.000	150.5		
10	0.086	141.4		
20	0.168	132.5		
30	0.244	124.4		
40	0.312	117.0		
50	0.370	110.6		
60	0.424	105.0		
70	0.472	100.0		

[a] Vapor compositions and molar volumes at 0° C. and lower temperatures are accurately given by properties of pure methane.

[b] Vapor pressure of pure *n*-octane. [c] Vapor-liquid critical state.

$$Y_1 = \frac{x_1 \gamma_1 \nu_{P1} P_1}{\nu_P P} \exp\left[\frac{V}{RT} (P - P_1) \right]$$

The activity coefficient was combined with the fugacity-coefficient ratio to give an empirical function of the reduced temperature and pressure of the n-octane. The resulting function is

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

The constants determined from the experimental data were $A = 0.09$, $a = 1.0$, $b = 2.0$. The equation with the constants given agrees with the experimental data of this study within ± 0.003 mole fraction at temperatures above 100° C. and within ±0.001 mole fraction below 100° C. at pressures to 70 atm.

Table II presents data along the solid-liquid-vapor, three-phase lines. The air-saturated freezing point of n-octane reported here is within 0.06° C. of that reported by Rossini (*12*). The measured experimental solubility points were used to calculate the heat of fusion of n-octane from the Van't Hoff isochore. The calculated heat of fusion was 4953 ± 60 cal. per gram mole which agrees with the literature value of 4957 cal. per gram mole (*12*). Because the Van't Hoff isochore regarding ΔH_f as constant does not allow accurate calculation of the solubility of methane in n-octane in excess of 0.20 mole fraction, Raoult's law does not hold accurately for n-octane past 0.20 mole fraction methane. This was definitely demonstrated by the results of the low temperature vapor-liquid equilibrium study which showed that methane solubility up to about 0.20 mole fraction accurately followed Henry's law.

Table II. Smoothed Solid-Liquid-Vapor, Three-Phase Lines

Pressure, Atm.	Temperature, ° C.	Liquid Phase Comp., Mole Fraction Methane	
		Exptl.	Calcd.[a]
1 atm.[b]	−56.73	0	0
5.20	−57.77	0.05	0.05
10.25	−58.75	0.10	0.10
20.60	−60.71	0.20	0.192
31.25	−62.67	0.30	0.275
43.20	−64.62	0.40	0.352
57.30	−66.56	0.50	0.420
70.50	−67.65	0.56	0.454
46.07	−82.46[c]		
45.00	−83.21b		
40.00	−88.80		
35.00	−91.30		
30.00	−96.10		
25.00	−101.50		
20.00	−107.60		

[a] Calculated from simple Van't Hoff isochore regarding $\Delta H_f = (H_L - H_S) = 4953$ cal./gram mole. [b] Air-saturated freezing point. [c] Type k singular point. (Vapor is identical with the liquid in the presence of the solid phase.)

The three-phase, solid-liquid-vapor line, which is actually a three-phase surface in three dimensions intersects the vapor-liquid critical locus. This was positively shown by the observation of a type-k singular point at −82.46° C. and 46.07 atm. At this point, the vapor phase is in critical identity with the liquid phase in the presence of the solid phase. The singular point is quite close in temperature and pressure to the critical point of pure methane. The three-phase, solid-liquid-vapor line below −82.46° C. appears to parallel the vapor pressure curve of pure methane. The equilibrium pressures average about 0.5 atm. higher than those of pure methane when measured at the same temperature. This effect may result from using values of the vapor pressures of methane which have never been measured accurately. The small deviation in the vapor pressure of methane indicates that the composition of both the liquid and the vapor phases is reasonably pure methane.

There are two separate type-k singular points in this system. The second one was not found because of the pressure limitation of the borosilicate glass cells. All evidence would indicate that this point should be found at pressures in excess of 100 atm. and temperatures between −70° and −80° C. The extrapolated value of the second type-k point is 200 atm., −72° C. and 0.90 mole fraction methane.

The higher temperature solid-liquid-vapor line was compared with that of Papahronis (*11*) which was reported by Brewer (*1*). Papahronis' three-phase temperatures are about 0.8° C. higher than those reported in Table II. Since there is only one degree of thermodynamic freedom along this line, the 0.8° C. higher temperature is equivalent to concentrations which are 0.04 mole fraction methane higher, and pressures which are approximately 3.5 atm. higher than those in Table II. It is highly likely that the Papahronis results are in error because the three-phase line does not extrapolate to the literature value of the triple point of pure n-octane but to a value 0.7° C. higher, and the heat of fusion of n-octane cannot be calculated accurately employing Papahronis data in the Van't Hoff isochore even in the low concentration methane region.

Figure 1 presents a temperature-composition diagram at 20 atm. pressure showing that the solid-vapor region cuts through the vapor-liquid region. The upper solid-liquid-vapor line is shown at −61.60° C. and the lower solid-liquid-vapor line is shown at −107.60° C. The vapor phase at these temperatures contains more than 0.999 mole fraction methane.

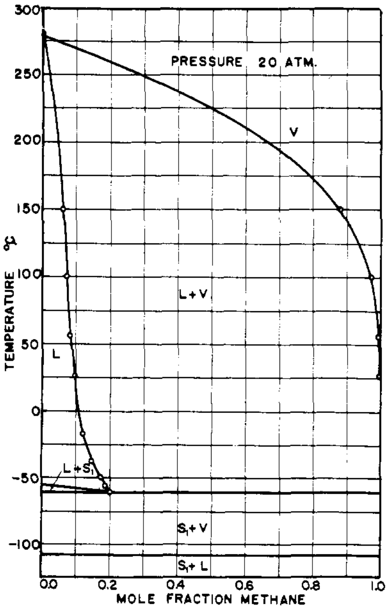

Figure 1. Isobaric temperature composition 20 atm. pressure

Figure 2 presents the fugacities of methane in solution in the low temperature range.

The fugacities of pure methane as given in Matthews (*7*) were used to compute the fugacities of the methane in solution at temperatures of 25° C. and lower. The calculation is valid since, at these low temperatures, the vapor state at all pressures studied was methane containing less than 0.001 mole fraction n-octane. Large scale graphs of fugacity of dissolved methane *vs.* composition in mole fraction were linear in the composition range below 0.20 mole

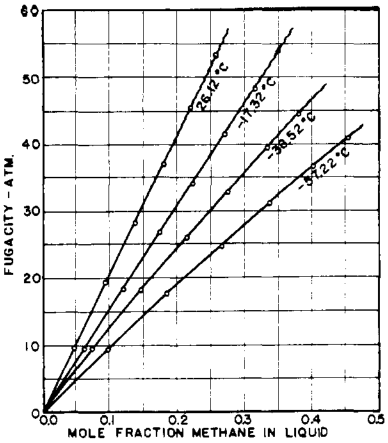

Figure 2. Fugacity of methane in *n*-octane

fraction methane. Thus methane in solution in *n*-octane at temperatures below 25° C. definitely follows Henry's law at concentrations up to 0.20 mole fraction methane.

The thermodynamic dependence of the Henry's law constant with temperature is given by:

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

The slopes of the lines of the large scale fugacity-composition diagram were plotted as logarithm of f/x *vs.* reciprocal absolute temperatures. The graph was a straight line indicating that the following thermodynamic simplifications are true at concentrations of methane to 0.20 mole fraction and from 25° C. to the freezing point of *n*-octane:

$$\bar{H}_2^* = \bar{H}_2(\text{gas}) = H_2(\text{gas})$$

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

$$\Delta C_P = C_{P2}(\text{gas}) - \bar{C}_{P2} = 0$$

From the slope of the straight line the enthalpy change of methane on solution $[H_2(\text{gas}) - \bar{H}_2]$ was

$$\Delta H = +1240 \pm 50 \text{ cal./gram mole}$$

The following thermodynamic properties of the methane–*n*-octane system in the temperature range −60 to 25° C. and in the composition range 0 to 0.20 mole fraction methane are accurate within the designated levels.

Thermodynamic Property	Function or Numerical Value, Cal./Gram Mole
$\Delta H = H_2(\text{gas}) - \bar{H}_2$	1240 ± 50
$\Delta S = S_2(\text{gas}) - \bar{S}_2$	$\frac{1240 \pm 50}{T}$
$\Delta G = G_2(\text{gas}) - \bar{G}_2$	0
$\Delta C_P = C_{P2}(\text{gas}) - \bar{C}_{P2}$	0
$H_1(\text{liq}) - H_1(\text{solid})$	4953 ± 31
$S_1(\text{liq.}) - S_1(\text{solid})$	$\frac{4953 \pm 31}{T}$

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NOMENCLATURE

C_{P2}(gas) = molar heat of methane in the gas phase at any temperature and pressure, cal./gram mole × ° K.
$\bar{C}_{P2}$ = partial molar heat capacity of methane in a liquid solution of any dilution, cal./gram mole × ° K.
exp. = base of the Naperian logarithm system
f = fugacity of methane (atm.)
G = Gibbs free energy, cal./gram mole
$\bar{H}_2^*$ = partial molar enthalpy of methane in the ideal gas state at T, cal./gram mole
$\bar{H}_2^\circ$ = partial molar enthalpy of methane in an infinitely dilute solution at T, cal./gram mole
$\bar{H}_2$ = partial molar enthalpy of methane in a liquid solution of any dilution at T, cal./gram mole
$\bar{H}_2$(gas) = molar enthalpy of methane in the gas phase any T and P. cal./gram mole
L = liquid phase
P_1 = normal vapor pressure of *n*-octane at T, atm.
P = total pressure of the system, atm.
P_r = reduced pressure of *n*-octane
R = universal gas constant
S_1 = solid *n*-octane phase, molar entropy of *n*-octane. cal./gram mole × ° K.
T = absolute temperature of system, ° K.
T_r = reduced temperature of *n*-octane
V = vapor phase; molar volume of liquid, ml./gram mole
x_1 = mole fraction *n*-octane in the liquid phase
y_1 = mole fraction *n*-octane in the gas phase
γ_1 = activity coefficient of *n*-octane in the liquid phase
ν_{P1} = fugacity coefficient of *n*-octane in the liquid phase at the normal vapor pressure of *n*-hexane at T
ν_P = fugacity coefficient of *n*-octane in the gas phase at the total pressure of the system at T

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.

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