Hurd (*8*). At 100° and 150° C. the Lewis and Randall rule was applied also in obtaining the fugacity of the methane in solution. This procedure should be quite accurate since the vapor phase composition was never less than 0.926 mole fraction of methane. The Henry's Law constants at the seven temperatures were plotted as logarithm of Henry's constant *vs*. reciprocal absolute temperature. The graph was linear in the range from −25° to 100° C., and the slope of the line gave an enthalpy change of methane upon solution of

$$\Delta H = (H_{2\,(\text{gas})} - \bar{H}_2) = 895 \pm 36 \text{ cal./gram mole}$$

The linearity of the Henry's Law plot indicates that the following thermodynamic statements are accurate approximations for methane in the temperature range of −25° to 100° C. and up to 30 atm. pressure

$$\bar{H}_2^* = \bar{H}_2^V = H_2^V$$

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

$$\Delta C_p = C_{p2}^V - \bar{C}_{p2} = 0$$

Table II gives temperature, liquid phase compositions, and liquid phase molar volumes along the three-phase (solid-liquid-vapor) line. The gas phase is substantially pure methane while the solid phase is regarded to be pure *n*-decane. The three phase data were compared with those obtained by Stalkup (*14*) who used a chromatographic technique. The Stalkup data are about 0.65° C. lower than this study at pressures above 8 atm. The probable error in temperature in establishing the solid line in the present study is ±0.05° C. The freezing point of air saturated *n*-decane is within 0.01° C. of Rossini's value (*11*).

Table II. Solid-Liquid-Vapor Phase Behavior

Pressure, Atm.	Temperature, °C.	Composition Liquid Phase, Mole Fraction of Methane	Molar Volume Liquid Phase, Ml./Gram Mole
1[a]	−29.67	. . .	184.95
5	−30.19	0.033	180.0
10	−30.72	0.065	175.2
15	−31.25	0.099	170.5
20	−31.77	0.132	166.2
25	−32.28	0.161	162.0
30	−32.79	0.190	157.7
35	−33.28	0.219	153.5
40	−33.78	0.250	149.1
45	−34.27	0.280	144.8
50	−34.76	0.307	140.8
60	−35.66	0.357	133.5
65	−36.05	0.381	130.2
70	−36.38	0.405	126.7

[a] Air saturated freezing point.

The lower pressure data of Table II were used to calculate the heat of fusion of *n*-decane by use of the Van't Hoff isochore and the triple point of *n*-decane reported by Rossini (*11*). The results of 6910 cal. per gram mole at 5 atm. and 7180 cal. per gram mole at 10 atm. are in good agreement with the value 6863 cal. per gram mole reported by Rossini *et al.* (*11*).

NOMENCLATURE

C_{p2}^V = molar heat capacity of pure 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.
H_2^V = molar enthalpy of pure methane in the gas phase at any pressure and temperature, cal./gram mole
$\bar{H}_2^V$ = partial molar enthalpy of methane in a gaseous solution of any dilution, cal./gram mole
$\bar{H}_2^\circ$ = Partial molar enthalpy of methane in an infinitely dilute liquid solution, cal./gram mole

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Three Phase Equilibria in the Binary Systems Ethane–*n*-Docosane and Ethane–*n*-Octacosane

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EXPERIMENTAL determination of volumetric and phase data on hydrocarbon mixtures continue to be of importance owing to the lack of sound theoretical predictive relationships. The phenomenon of partial miscibility in certain hydrocarbon mixtures has been of considerable interest recently.

Partial miscibility is a fairly common occurrence in binary liquid mixtures where one of the components is polar. However, studies have shown that certain binary paraffin mixtures exhibit a three phase (L_1 - L_2 - V) region over a short temperature range bounded below by the L.C.S.T. (Lower Critical Solution Temperature at which the two liquid phases are in critical equilibrium) and above by the Type *K* point (at which the lighter liquid phase is in critical equilibrium with the vapor phase). Rowlinson and coworkers have reported the occurrence of this phenomenon in several binary mixtures involving methane and ethane (*1, 9, 10*) with higher paraffins. Kohn (*3*) has reported partial miscibility in the system methane–*n*-heptane. Kim (*2, 5*) found that the systems ethane–*n*-

The binary system ethane–*n*-docosane exhibited partial miscibility behavior over a temperature range of 7.26° C. Pressures, compositions, and molar volumes of the two liquid phases are presented at selected temperatures. The binary system ethane–*n*-octacosane did not have two liquid phases owing to the formation of a solid phase. Pressures, compositions, and molar volumes of the liquid phase are presented along the solid-liquid-vapor lines near the critical point of pure ethane.

nonadecane and ethane–*n*-eicosane exhibited this behavior, but that it was absent in the ethane–*n*-octadecane system.

This study of the ethane–*n*-docosane and ethane–*n*-octacosane systems was undertaken since these systems would help illustrate any possible trends in the behavior of successive higher paraffins with ethane.

EXPERIMENTAL

The apparatus has been described in detail by Kohn (*4*), and has been used in several studies of binary hydrocarbon mixtures (*2*, *3*, *6*). The experimental technique for obtaining composition data in the three phase region has been described by Ma (*6*) and Rodrigues (*7*).

The ethane used was Matheson Co. pure grade material labeled as having 99% minimum purity and was purified further using the procedure described by Kohn (*5*). Isotherms on the purified gas at 25° C. indicated a difference of less than 0.21 atm. between the dew point and bubble point pressures. Thus, the authors believed that the purified ethane contained less than 0.4 mole % impurities. The heavy hydrocarbons were petroleum-derived Humphrey-Wilkinson products labeled as having 97% minimum purity and were used without further purification.

RESULTS

The system ethane–*n*-docosane exhibited partial miscibility phenomena over a temperature range of 7.26° C. Smoothed values of pressure, composition, and molar volume of the two liquid phases at 0.5° C. intervals are presented in Table I. The vapor phase was assumed to be pure ethane. Curves of the raw experimental data plotted against temperature had average absolute deviations of 0.143 atm. for pressure, 0.00037 mole fraction for composition, and 0.449 ml. per gram mole for molar volume. Temperature measurements are believed accurate to 0.02° C.

No partial miscibility region was observed in the ethane–*n*-octacosane system. In this system a solid phase appears which intersects the vapor-liquid region in the immediate pressure and temperature area of the expected partial miscibility.

The solid-liquid-vapor data are shown in Table II. The three-phase data are given to ±0.1° C., ±0.07 atm., ±0.002 mole fraction, and ±0.8 ml. per gram mole. The data at the lower pressures were used to calculate the heat of fusion of octacosane by using the Van't Hoff isochore. In the calculations, 60.05° C. was used as the freezing point of pure *n*-octacosane. The calculations gave a value of 21,200 cal. per gram mole for the heat of fusion of *n*-octacosane. This value is consistent with heat of fusion values of *n*-paraffins given in Rossini *et al.* (*8*). At the higher compositions of ethane the activity coefficients for *n*-octacosane were calculated from the equations below using the above value of the heat of fusion of octacosane.

$$\ln (\gamma_1 x_1) = -\frac{\Delta H_f}{R} \frac{(T_0 - T)}{T_0 T}$$

Table I. Smoothed Values of Pressure, Composition, and Molar Volume of the Three Phase (L_1-L_2-V) Region of the Ethane–*n*-Docosane System

		Liquid 1 Phase		Liquid 2 Phase	
Temp., ° C.	Pressure, Atm.	Mole fraction ethane	Mol. vol. ml./gram mole	Mole fraction ethane	Mol. vol. ml./gram mole
27.57[a]	43.31	0.9630	90.00	0.9630	90.00
28.00	43.75	0.9491	91.75	0.9795	89.63
28.50	44.26	0.9439	93.40	0.9849	89.97
29.00	44.77	0.9398	94.73	0.9879	90.68
29.50	45.28	0.9362	95.73	0.9894	91.62
30.00	45.79	0.9328	96.53	0.9906	92.77
30.50	46.31	0.9298	97.20	0.9918	94.23
31.00	46.83	0.9269	97.75	0.9928	95.95
31.50	47.35	0.9242	98.40	0.9936	97.90
32.00	47.86	0.9216	99.25	0.9945	99.88
32.50	48.37	0.9192	100.03	0.9951	101.95
33.00	48.88	0.9169	100.98	0.9959	104.20
33.50	49.40	0.9148	101.57	0.9967	106.88
34.00	49.91	0.9126	101.25	0.9975	110.40
34.50	50.43	0.9106	99.22	0.9985	116.15
34.83[b]	50.78	0.9093	95.90	0.9991	131.00

[a] L.C.S.T. point at which L_1 is identical with L_2. [b] Type *K* point at which two phases are in critical identity in the presence of a third noncritical phase.

Table II. Solid-Liquid-Vapor Equilibrium in the Ethane–*n*-Octacosane System

Pressure, Atm.	Temp., ° C.	Liquid Phase Composition, Mole Fraction Ethane	Molar Volume Liquid Phase, Ml./G. Mole
1[a]	60.05	...	503.2
5	58.5	0.135	443.0
10	56.6	0.267	384.0
15	54.6	0.382	332.2
20	52.6	0.477	290.6
25	50.6	0.562	252.1
30	48.6	0.634	219.9
35	46.6	0.692	193.6
40	44.6	0.740	175.8
45	42.4	0.788	156.4
50	40.8	0.820	144.2
55	39.6	0.840	137.0
76.6	38.7	...	...
48.81[b]	32.83		
45.0	28.90		
42.5	26.12		
40.0	23.21		
37.5	20.23		

[a] Air saturated freezing point. [b] Type *K* point.

A Type *K* point was found in the ethane–*n*-octacosane system. This point is reported in Table II, and it represents the point of critical identity of the vapor and liquid phases in the presence of a noncritical solid phase. The Type *K* point as expected is actually quite close to the vapor-liquid critical point of pure ethane. The other pressures given at the bottom of Table II are within 0.2 atm. of the vapor pressure curve of pure ethane. This appears to indicate that the vapor and liquid phases are quite pure ethane.

Table III gives the results of a vapor-liquid isotherm which was run at 61° C. This is reasonably close to the freezing point of pure *n*-octacosane. The vapor phase at any of the pressures studied was substantially pure ethane. The data of Table III were used to compute the vapor-liquid activity coefficients for *n*-octacosane based upon an integration of the Gibbs-Duhem equation using the activity

Table III. Vapor-Liquid Isotherm at 61° C. in the Ethane–*n*-Octacosane System

Pressure, Atm.	Composition of Liquid Phase, Mole Fraction Ethane	Molar Volume of Liquid Phase, Ml./G. Mole	Fugacity of Ethane, Atm.
[a]	...	504.9	...
1	0.028	492.1	0.9946
5	0.133	446.8	4.880
10	0.240	400.7	9.489
15	0.338	357.8	13.85
20	0.421	321.8	17.95
25	0.492	290.6	21.81
30	0.552	278.0	25.41
35	0.600	243.2	28.77
40	0.645	224.5	31.88

[a] Normal vapor pressure of *n*-octacosane.

coefficients for ethane. The standard state for ethane was taken as the hypothetical incompressible liquid of unit mole fraction which obeys Henry's Law. These calculated activity coefficients agreed within 0.2% with those calculated from data taken along the solid-liquid-vapor line at compositions up to 50 mole % ethane.

NOMENCLATURE

ΔH_f = heat of fusion of *n*-octacosane
L = liquid phase
L_1 = liquid phase rich in heavy hydrocarbon
L_2 = liquid phase rich in ethane
L.C.S.T. = point at which L_1 is identical with L_2
S = solid phase
Type K = point at which two phases are in critical identity in the presence of a third noncritical phase
V = vapor phase
γ = activity coefficient

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Thermodynamics of Solutions-Volume Change on Mixing for Four Systems

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Pure component densities and volume change on mixing were determined for four hydrocarbon systems: 2,2,4-trimethylpentane–toluene, 2,4-dimethylpentane–cyclohexane, cyclohexane–1,4-dioxane, and 2,4-dimethylpentane–1,4-dioxane over the temperature range 28° to 90° C. Maximum values for ΔV^M were 2,4,4-trimethylpentane–toluene, 0.087; 2,4-dimethylpentane–1,4-dioxane, 0.44; cyclohexane-1,4 dioxane, 1.0 ml. per gram mole. Measurements for 2,4-dimethylpentane–cyclohexane indicated that ΔV^M was less than 0.015 ml. per gram mole and within the margin of experimental error. The densities as a function of temperature, and ΔV^M as a function of composition were correlated by empirical functions.

AS PART of a program on thermodynamics of nonelectrolyte solutions, liquid density data were determined for 2,2,4-trimethylpentane, toluene, 2,4-dimethylpentane, cyclohexane, and 1,4-dioxane, and for mixtures of four binary systems of the components. The latter were measured to determine the isothermal volume change on mixing ΔV^M, in order that better energy change on mixing ΔE^M values could be calculated. This work was concurrent with enthalpy of mixing ΔH^M measurements, reported elsewhere (*4*).

EXPERIMENTAL APPARATUS

Pycnometers. Calibrated 25-ml. dual stem borosilicate glass pycnometers were used to determine the densities at 28.00° C.; each stem had a 2-mm. bore × 20-mm. long section, topped by a 0.5-mm. bore × 70-mm. long section with an etched scale to obviate the tedious adjustment of volume by bringing the miniscus exactly to some particular mark. The latter was determined by using a cathetometer.

In order to obtain 5×10^{-6} accuracy, Bureau of Standards Class S weights were used, and weighings on an analytical balance were made to the nearest 0.01 mg. Corrections were made for buoyancy, changes in the lengths of the balance arms, and adsorbed surface moisture. By these precautions densities were determined with a reproducibility of 1×10^{-4}

Expansion Pipet. At elevated temperatures, the density was determined by enclosing the material in a calibrated expansion pipet sealed off with a mercury filled U-tube which was raised and lowered to maintain equilibrium pressure. The pipet was surrounded by circulating water and insulated by a silvered vacuum jacket. The circulating

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[1] Deceased.