reaction—as copper metal, thereby giving low solubility values. The plated copper, in contrast to that deposited from supersaturated solution, largely as the oxide, is difficult to remove by flushing with $2N$ nitric acid. Since the Pocock and Stewart equipment was constructed of stainless steel, this plating process probably occurred at all points downstream of their equilibrator, and may well have contributed significantly to the low solubility values that they reported.

The solubility diagram of cupric oxide obtained in this work is qualitatively similar to that of silica (4) and germanium dioxide (2), as shown by Figure 4 (3). This similarity suggests that the type of solubility equation proposed by Frank (1), Martynova (6), and others is generally applicable to aqueous high-temperature metal oxide solubilities. The equations are of the basic form

$$\log S = A - \frac{B}{T} - n \log V$$

where S is the solubility, T is the temperature in $°K.$, n is the hydration number of the solvated solute, V is the specific volume of the solvent, and A and B are constants. They are derived from the initial assumption that the solute exists in solution as un-ionized molecules hydrated with an average number, n, of solvent molecules. The experimental results can be described by this equation over a limited temperature range above the critical temperature, but not over the whole temperature range. While it is likely that at supercritical temperatures un-ionized molecules may be in solution, at lower temperatures, where the dielectric constant of water is high, copper ions probably exist in solution, and a more complex equilibrium situation would occur, one that would not be described by the above equation.

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Phase Equilibria in Hydrocarbon Systems
Volumetric Behavior in the Methane–Propane–n-Decane System

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The results of an experimental investigation of the volumetric behavior of 22 mixtures of methane, propane, and n-decane are reported. The experimental measurements were carried out at pressures between 200 and 10,000 p.s.i. in the temperature interval between 40° and 460° F. Some 5500 states were investigated. The compositions of the mixtures studied were selected to permit the direct evaluation of the partial volumetric behavior of each of the components.

THE VOLUMETRIC behavior of ternary hydrocarbon mixtures has not been investigated extensively. The only experimental investigation known to the authors, covering a wide range of pressures and temperatures, is a study of the volumetric behavior of the methane–n-butane–n-decane system (7, 8, 10, 12, 13). Studies of the volumetric behavior of binary hydrocarbon systems are more extensive. Examples of related binary systems include the methane-propane (11), methane-decane (9, 19) and propane–n-decane (3, 15) systems. In addition, five of the binary systems associated with the quaternary system, methane–propane–n-butane–n-decane, have been investigated throughout the pressure interval between 200 and 10,000 p.s.i. at temperatures between 40° and 460° F.

To complete a study of a second ternary system of the quaternary system, methane–propane–n-butane–n-decane, an investigation of the volumetric and phase behavior of the methane–propane–n-decane system was undertaken. The results of the phase behavior measurements are available (20). The data presented earlier (20) include the volumetric behavior of the coexisting liquid phase. These latter data were based upon the volumetric measurements reported here.

A systematic study of 22 mixtures of methane, propane, and n-decane was carried out at pressures between 200 and 10,000 p.s.i. and at eight temperatures between 40° and 460° F. The compositions investigated are shown in Figure 1 and recorded in Table I. These compositions were so chosen as to permit each composition to fall at the intersection of three straight lines representing fixed ratios of the mole fractions of each of three pairs of the components. For example, the line AB in Figure 1 represents a ratio of the mole fraction of propane to the sum of the mole fractions of n-decane and propane of 0.6806. The choice of compositions was made to yield fixed values of the following composition parameters.

$$C_{3, 10} = x_3 / (x_3 + x_{10}) \tag{1}$$

$$C_{10, 1} = x_{10} / (x_{10} + x_1) \tag{2}$$
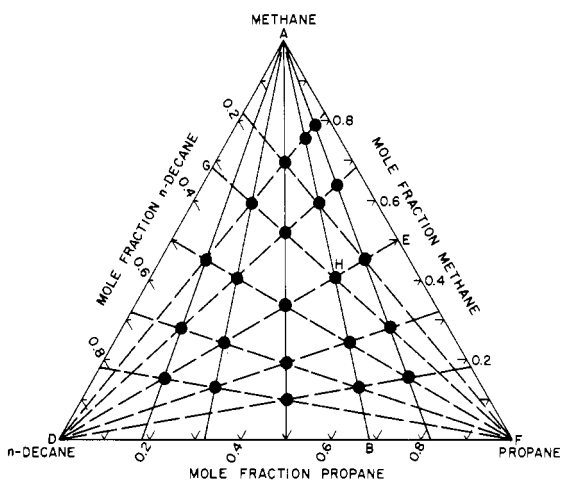
$$C_{1, 3} = x_1 / (x_1 + x_3) \tag{3}$$

Figure 1. Composition of mixtures investigated

Table I. Composition of Mixtures Investigated

Composition Parameter[a]			Mole Fraction			Sample
$C_{3,10}$	$C_{10,1}$	$C_{1,3}$	Methane	Propane	n-Decane	Studied[b]
0.1806	0.8194	0.5000	0.1529	0.1531	0.6939	L
	0.6806	0.6806	0.2762	0.1308	0.5929	L, S
	0.5000	0.8194	0.4510	0.0992	0.4498	L, S
0.3194	0.8194	0.3194	0.1311	0.2778	0.5911	L
	0.6806	0.5000	0.2430	0.2420	0.5150	L
	0.5000	0.6806	0.4049	0.1902	0.4048	L, S
	0.3194	0.8194	0.5917	0.1305	0.2778	L, S
0.5000	0.8194	0.1806	0.1000	0.4500	0.4500	L
	0.6806	0.3194	0.1799	0.4099	0.4102	L
	0.5000	0.5000	0.3340	0.3329	0.3331	L
	0.3194	0.6806	0.5162	0.2419	0.2419	L, S
	0.1806	0.8194	0.6920	0.1539	0.1541	L, S
0.6806	0.6806	0.1806	0.1312	0.5912	0.2776	L
	0.5000	0.3194	0.2429	0.5150	0.2421	L
	0.3194	0.5000	0.4050	0.4049	0.1901	L, S
	0.1806	0.6806	0.5908	0.2783	0.1309	L, S
	0.0935	0.8194	0.7556	0.1663	0.0782	L, S
0.8194	0.5000	0.1806	0.1528	0.6945	0.1527	L
	0.3194	0.3194	0.2756	0.5936	0.1308	L, S
	0.1806	0.5000	0.4510	0.4500	0.0990	L, S
	0.0935	0.6806	0.6357	0.2985	0.0658	L
	0.0464	0.8194	0.7880	0.1737	0.0383	L, S

[a] Nominal composition parameters defined by Equations 1, 2, and 3. Uncertainty in parameter C ±0.0005. [b] L denotes "large" sample and S "small" sample.

Sets of compositions which yield fixed values of these composition parameters were chosen so that the partial volumetric behavior (4, 17) of the components may be established directly, without the need of extensive interpolation with respect to composition. The values of the three composition parameters for each of the components are also presented in Table I.

Figure 2 shows the variation in the molal volume with respect to the mole fraction of each of the three components passing through point H. The locus of the three curves in Figure 2 corresponds to the lines AB, DE, and FG in Figure 1. The partial molal volume of the three components may be established at point H or at any other point along the curves by the following expressions.

$$\bar{V}_1 = V + (1 - n_1) \left(\frac{\partial V}{\partial n_1} \right)_{T, P, [n_3/(n_3 + n_{10})]} \tag{4}$$
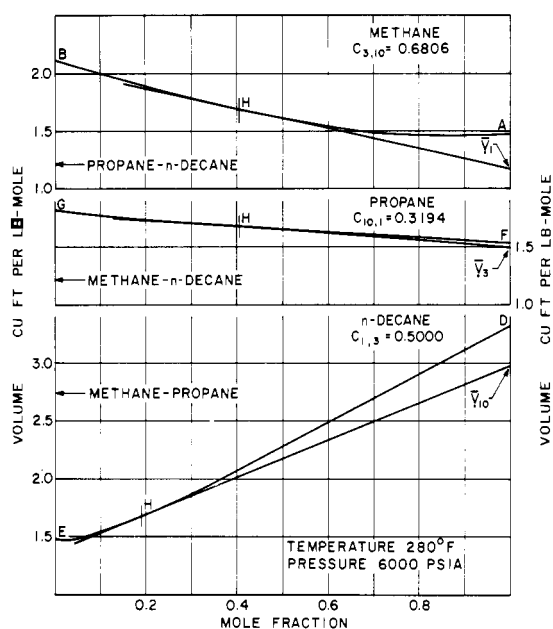

Figure 2. Effect of mole fraction of each component on molal volume for fixed values of related composition parameters

$$\bar{V}_3 = V + (1 - n_3) \left(\frac{\partial V}{\partial n_3} \right)_{T, P, [n_{10}/(n_1 + n_{10})]} \tag{5}$$

$$\bar{V}_{10} = V + (1 - n_{10}) \left(\frac{\partial V}{\partial n_{10}} \right)_{T, P, [n_1/(n_1 + n_3)]} \tag{6}$$

The graphical operations corresponding to Equations 4 to 6 are shown in Figure 2 for each of the three components, at a composition corresponding to point H of Figure 1. The foregoing explanation has been presented to indicate the reason the compositions were chosen as indicated in Figure 1. Since the volumetric behavior of the three binary systems associated with the ternary system, methane–propane–n-decane, have already been investigated (8, 11–13, 15), no further experimental work was carried out at the boundaries of the ternary system.

EXPERIMENTAL METHODS

The equipment employed in this investigation has been described in detail (18). Essentially, it consists of a stainless steel vessel within which hydrocarbons of known composition and weight are confined over mercury. This vessel forms one arm of a U-tube, while the second arm contains a movable electrical contact that permits the elevation of the mercury in the second arm of the U-tube to be determined with accuracy. Air was introduced into the second chamber to adjust the level of the mercury to the desired value. A magnetically driven agitator is provided in the arm of the U-tube wherein the sample was confined to hasten attainment of physical equilibrium. Suitable valves were provided to permit the introduction and withdrawal of hydrocarbon samples. The desired weights of n-decane and propane were introduced gravimetrically by weighing bomb techniques (18). Methane was introduced by isobaric, isothermal volumetric displacement, and the weight determined from the known volumetric behavior of methane (6). The accuracy of this method was checked by displacement of a known weight of methane into a weighing bomb, and the agreement between the gravimetric techniques and the volumetric method was within 0.002 fraction.

It should be recognized that it was desired to prepare mixtures of known composition, as well as of known weight. The accuracy with which the weight of each of the hydrocarbons within the apparatus was known is indicated in a portion of Table II. It is believed that the compositions were known within 0.001 mole fraction, and the weight of sample was within 0.0015 fraction.

The pressures were measured by means of a balance involving a piston-cylinder combination (18). This balance was calibrated periodically (14, 16) against the vapor pressure of carbon dioxide at the ice point. The vapor pressure of carbon dioxide at this state has been established (2) with accuracy. As indicated in Table II, the pressures were known within 0.1 p.s.i. or 0.1%, whichever is the larger measure of uncertainty. The chamber within which the hydrocarbon sample was confined was immersed in an agitated oil-bath, the temperature of which was controlled by means of a modulating circuit (18), and this temperature remained constant both with respect to time and spatial position in the bath within 0.05° F. The relation of the temperature to the international platinum scale was established by means of a strain-free, platinum resistance thermometer (5) which was compared with the indications of similar instruments which had been calibrated by the National Bureau of Standards. The consistency of temperature measurements and the reproducibility of the calibrations of the standardized instrument indicate that the temperatures were known relative to the international platinum scale within 0.03° F. throughout the temperature interval between 40° and 460° F. At 32.00° F., it was assumed that the absolute temperature was 491.688° R. From a consideration of the accuracy with which various primary variables were established, the molal volume was believed established within 0.2% at pressures below 5000 p.s.i., and the uncertainty may have been as large as 0.4% on an absolute basis at pressures between 5000 and 10,000 p.s.i.

Measurements were carried out with descending pressures under isothermal conditions. After the initial investigations at the higher pressures had been completed, approximately 75% of the sample was withdrawn from the equipment in a homogeneous region and another set of isotherms established. The weight of material remaining in the pressure vessel was determined from comparisons of the volumetric behavior of the smaller and the original larger sample at states where direct comparison could be made. This comparison process probably did not introduce more than 0.1% additional uncertainty in the measurements upon the smaller sample.

MATERIALS

The propane and n-decane were obtained as research grade from the Phillips Petroleum Co. The propane was reported by the vendor to contain only 0.0001 mole fraction of materials other than propane. The n-decane contained less than 0.005 mole fraction of impurities and there were, for the most part, aliphatic hydrocarbons containing ten carbon atoms per molecule. The methane was obtained through the courtesy of Texaco, Inc., from a well in the San Joaquin Valley, and was passed over calcium chloride, activated charcoal, ascarite, and drierite at pressures in excess of 500 p.s.i. The properties of the n-decane, propane, and methane which were measured are recorded in a part of Table II. It is believed that none of the components in the "as used" condition contained more than 0.001 mole fraction of impurities. The index of refraction and the specific weight of the n-decane at 77° F. and atmospheric pressure is believed to represent the best measure of the purity of this compound. Good agreement with critically chosen values (1) is indicated in Table II. Consistency with respect to quality of the value of the vapor pressure of the sample of propane is considered the most sensitive indication of its purity. A special chromatographic analysis of methane was considered the best measure of the purity of this component.

The information in Table II gives what is believed to be a realistic appraisal of the precision and accuracy of the measurement, as well as the purity of the hydrocarbons employed. The lack of thermal rearrangement of n-decane at 460° F. was established from the absence of any measurable change in composition of the homogeneous phase withdrawn for analysis after a significant period at a temperature of 460° F.

At the time each of the original large samples was withdrawn to permit investigations with a smaller sample, the analysis of the material withdrawn was checked by means of partial condensation (12) at the temperature of a mixture of trichlorethylene and carbon dioxide to remove the n-decane, followed by a chromatographic determination of the relative amounts of methane and propane. The total quantity of the sample and the quantity of n-decane was established gravimetrically by use of a condensation weighing bomb technique (18). The investigation of the 22 samples studied was carried out on a semicontinuous basis over a period of some four years, ending in August 1967. The composition of each of the samples investigated is given in Table I.

EXPERIMENTAL RESULTS

Figure 3 shows a typical set of experimental measurements for a mixture lean in methane, showing the discontinuity in the first derivative of the molal volume vs. pressure at bubble point and the extent of the measurements in the two-phase region. The standard error of estimate for the data shown in Figure 3 from the smooth curves was 0.002 cubic feet per pound-mole. A similar set of data in the homogeneous region for a mixture rich in methane is shown in Figure 4. In this case, the results have been expressed as the compressibility factor, defined as follows

$$Z = PV/RT \tag{8}$$

The standard error of estimate in the compressibility factor was 0.0009.

Table II. Physical Properties and Uncertainties of Measurement

Quantity	Authors	Reference (1)	Uncertainty[a]
Specific weight[b], lb./cu. ft.			
n-Decane	45.346	45.337	
Index of refraction[c]			
n-Decane	1.4094	1.40967	
Composition, mole fraction			0.001
Methane	0.9977[d]		
Propane		0.9999[e]	
n-Decane		0.9949[e]	
Vapor pressure[f], p.s.i.a.			
Propane, 100° F.	0.15		
Temperature, ° F.			0.03
Pressure, p.s.i.a.			0.1
Molal volume, %			
Pressures below 5000 p.s.i.a.			0.2
Pressure above 5000 p.s.i.a.			0.4

[a] Estimated uncertainties in experimental measurements. [b] Specific weight at 77° F. and atmospheric pressure. [c] Index of refraction relative to D-line of sodium at 77° F. [d] Chromatographic analysis. [e] Sample purity reported by vendor. [f] Change in vapor pressure with change in quality from 0.1 to 0.8.

Table III. Comparison of Volumes Smoothed by Several Methods

Mole Fraction Methane	Number of Points	Method 1[a] Average Deviation		Standard error[f]	Method 2[b] Average Deviation		Standard error[f]	Method 3[c] Average Deviation		Standard error[f]
		Algebraic[d]	Fraction[e]		Algebraic[d]	Fraction[e]		Algebraic[d]	Fraction[e]	
100° F.										
Composition Parameter,[g] $C = 0.1806$										
0.1529	18	0.0051	0.0025	0.0088	0.0072	0.0033	0.0109	0.0167	0.0068	0.0183
0.2762	24	0.0028	0.0014	0.0046	0.0036	0.0017	0.0049	0.0097	0.0044	0.0109
0.4510	13	0.0024	0.0014	0.0029	0.0024	0.0014	0.0030	0.0035	0.0018	0.0039
	55	0.0034	0.0018	0.0059	0.0045	0.0021	0.0071	0.0105	0.0046	0.0126
Composition Parameter, $C = 0.3194$										
0.1311	12	0.0027	0.0012	0.0031	0.0055	0.0024	0.0061	0.0036	0.0017	0.0052
0.2430	13	−0.0011	0.0028	0.0069	−0.0059	0.0028	0.0071	−0.0043	0.0020	0.0055
0.4049	12	0.0016	0.0014	0.0031	0.0021	0.0017	0.0037	−0.0043	0.0024	0.0059
0.5917	9	0.0004	0.0010	0.0025	−0.0001	0.0010	0.0024	−0.0002	0.0013	0.0030
	46	0.0009	0.0017	0.0043	0.0003	0.0021	0.0052	−0.0015	0.0019	0.0050
Composition Parameter, $C = 0.5000$										
0.1000	15	0.0010	0.0009	0.0023	−0.0009	0.0008	0.0023	0.0037	0.0020	0.0046
0.1799	14	0.0024	0.0012	0.0035	0.0039	0.0020	0.0052	0.0137	0.0071	0.0147
0.3340	13	0.0015	0.0012	0.0028	−0.0010	0.0013	0.0027	0.0017	0.0016	0.0034
0.5162	14	−0.0007	0.0010	0.0018	−0.0009	0.0010	0.0019	−0.0029	0.0021	0.0042
0.6920	9	−0.0022	0.0022	0.0037	−0.0009	0.0018	0.0026	0.0087	0.0091	0.0274
	65	0.0006	0.0012	0.0027	0.0001	0.0014	0.0031	0.0047	0.0040	0.0122
Composition Parameter, $C = 0.6806$										
0.1312	14	0.0007	0.0020	0.0065	−0.0017	0.0017	0.0039	−0.0021	0.0015	0.0031
0.2429	16	0.0067	0.0041	0.0077	0.0116	0.0071	0.0130	0.0117	0.0072	0.0133
0.4050	13	−0.0009	0.0010	0.0020	−0.0018	0.0015	0.0029	−0.0015	0.0014	0.0027
0.5908	10	−0.0018	0.0025	0.0068	0.0018	0.0028	0.0051	0.0050	0.0053	0.0080
0.7556	8	−0.0019	0.0018	0.0028	−0.0029	0.0029	0.0040	−0.0006	0.0026	0.0034
	61	0.0012	0.0024	0.0057	0.0022	0.0034	0.0073	0.0030	0.0038	0.0077
Composition Parameter, $C = 0.8194$										
0.1528	18	0.0021	0.0015	0.0032	0.0016	0.0013	0.0031	0.0036	0.0025	0.0044
0.2756	17	0.0017	0.0014	0.0025	0.0019	0.0015	0.0027	0.0048	0.0033	0.0055
0.4510	15	−0.0001	0.0011	0.0021	0.0005	0.0015	0.0026	−0.0001	0.0011	0.0024
0.6357	15	0.0020	0.0017	0.0031	0.0019	0.0018	0.0027	0.0020	0.0017	0.0028
0.7880	8	0.0001	0.0006	0.0010	0.0001	0.0010	0.0015	0.0012	0.0012	0.0016
	73	0.0013	0.0013	0.0026	0.0015	0.0014	0.0026	0.0025	0.0021	0.0038
Over-all	300	0.0015	0.0016	0.0043	0.0017	0.0020	0.0052	0.0040	0.0033	0.0089
220° F.										
Composition Parameter,[g] $C = 0.1806$										
0.1529	16	0.0007	0.0005	0.0019	0.0033	0.0014	0.0046	0.0145	0.0054	0.0152
0.2762	12	−0.0089	0.0038	0.0100	−0.0092	0.0038	0.0102	−0.0079	0.0033	0.0093
0.4510	11	0.0020	0.0010	0.0027	0.0015	0.0008	0.0021	0.0025	0.0013	0.0035
	43	−0.0025	0.0018	0.0062	−0.0018	0.0022	0.0068	0.0031	0.0036	0.0108
Composition Parameter, $C = 0.3194$										
0.1311	13	0.0024	0.0010	0.0033	0.0039	0.0018	0.0055	0.0028	0.0014	0.0042
0.2430	12	0.0012	0.0016	0.0051	0.0032	0.0015	0.0039	−0.0027	0.0012	0.0034
0.4049	12	−0.0008	0.0005	0.0017	0.0005	0.0006	0.0020	−0.0042	0.0023	0.0054
0.5917	14	−0.0002	0.0011	0.0022	0.0000	0.0005	0.0017	0.0001	0.0006	0.0018
	51	0.0006	0.0011	0.0032	0.0019	0.0011	0.0035	−0.0009	0.0013	0.0037
Composition Parameter, $C = 0.5000$										
0.1000	14	0.0034	0.0017	0.0066	0.0018	0.0014	0.0038	0.0000	0.0000	0.0000
0.1799	12	−0.0020	0.0013	0.0035	−0.0024	0.0023	0.0073	0.0037	0.0018	0.0050
0.3340	12	0.0023	0.0018	0.0055	0.0020	0.0017	0.0056	−0.0001	0.0023	0.0062
0.5162	15	0.0007	0.0022	0.0049	0.0020	0.0015	0.0035	−0.0021	0.0020	0.0039
0.6920	12	0.0002	0.0006	0.0013	−0.0002	0.0003	0.0007	0.0011	0.0008	0.0017
	65	0.0010	0.0016	0.0047	0.0007	0.0014	0.0045	0.0004	0.0014	0.0038
Composition Parameter $C = 0.6806$										
0.1312	15	0.0007	0.0018	0.0046	0.0007	0.0016	0.0045	0.0001	0.0020	0.0050
0.2429	12	0.0028	0.0018	0.0056	0.0080	0.0045	0.0092	0.0082	0.0056	0.0108
0.4050	13	0.0008	0.0023	0.0052	−0.0009	0.0015	0.0039	0.0012	0.0020	0.0048
0.5908	14	0.0011	0.0015	0.0039	0.0024	0.0016	0.0040	0.0035	0.0030	0.0052
0.7556	11	−0.0021	0.0026	0.0051	−0.0015	0.0028	0.0054	−0.0025	0.0026	0.0053
	65	0.0007	0.0020	0.0047	0.0017	0.0023	0.0055	0.0021	0.0030	0.0063
Composition Parameter, $C = 0.8194$										
0.1528	16	−0.0001	0.0012	0.0027	0.0015	0.0013	0.0031	0.0007	0.0009	0.0020
0.2756	13	0.0008	0.0009	0.0018	0.0011	0.0011	0.0022	0.0019	0.0016	0.0030
0.4510	15	0.0010	0.0012	0.0027	−0.0005	0.0013	0.0026	0.0005	0.0013	0.0032
0.6357	15	0.0003	0.0012	0.0031	−0.0003	0.0014	0.0044	0.0015	0.0024	0.0048

(Continued)

Table III. (Continued)

Mole Fraction Methane	Number of Points	Method 1[a] Average Deviation Algebraic[d]	Method 1[a] Average Deviation Fraction[e]	Method 1[a] Standard error[f]	Method 2[b] Average Deviation Algebraic[d]	Method 2[b] Average Deviation Fraction[e]	Method 2[b] Standard error[f]	Method 3[c] Average Deviation Algebraic[d]	Method 3[c] Average Deviation Fraction[e]	Method 3[c] Standard error[f]
					220° F.					
				Composition Parameter,[g] $C = 0.1806$						
0.7880	13	−0.0008	0.0015	0.0025	0.0014	0.0017	0.0031	0.0025	0.0020	0.0039
	72	0.0002	0.0012	0.0025	0.0006	0.0014	0.0031	0.0014	0.0017	0.0034
Over-all	296	0.0002	0.0015	0.0043	0.0008	0.0017	0.0047	0.0040	0.0033	0.0089

[a] Volumes smoothed as function of temperature and pressure. [b] Volumes smoothed as function of temperature, pressure and mole fraction methane. [c] Volumes smoothed as function of temperature, pressure and mole fractions methane, propane, and n-decane.

[d] Average deviation expressed in cu. ft. per lb.-mole and defined by $s = \sum_1^N (V_e - \underset{\cdot}{v}_s)/N$

[e] Average fractional deviation defined by $S_f = \sum_1^N [(V_e - \underset{\cdot}{V}_s)/V_e]/N$. [f] Standard error of estimate expressed in cu. ft. per lb.-mole and

defined by $\sigma = \left\{ \left[\sum_1^N (V_e - \underset{\cdot}{V}_s)^2 \right] / (N-1) \right\}^{1/2}$ [g] Composition parameter defined by $C = \underset{\cdot}{x}_3/(\underset{\cdot}{x}_3 + \underset{\cdot}{x}_{10})$.

Table IV. Sample of Experimental Volumetric Data

Composition Parameter, $C_{3,10}$	0.6806	Mole Fraction Propane	0.4049	Average Molecular Weight	51.401
Mole Fraction Methane	0.4050	Mole Fraction n-Decane	0.1901		

Pressure, p.s.i.a.	Compressibility factor	Volume, cu.ft./lb.	Pressure, p.s.i.a.	Compressibility factor	Volume, cu.ft./lb.	Pressure, p.s.i.a.	Compressibility factor	Volume cu.ft./lb.
100° F.			280° F.			400° F.		

Sample Weight = 0.221560 lb.

Pressure, p.s.i.a.	Compressibility factor	Volume, cu.ft./lb.	Pressure, p.s.i.a.	Compressibility factor	Volume, cu.ft./lb.	Pressure, p.s.i.a.	Compressibility factor	Volume cu.ft./lb.
9851.6	2.2471	0.026653	9698.9	1.8914	0.030116	9867.5	1.7926	0.032606
9436.5	2.1618	0.026770	9481.6	1.8574	0.030252	9515.2	1.7430	0.032879
9041.8	2.0774	0.026848	9093.2	1.7928	0.030447	9004.7	1.6681	0.033248
8068.2	1.8766	0.027178	8093.7	1.6273	0.031050	8005.3	1.5237	0.034163
7031.6	1.6566	0.027529	6986.3	1.4363	0.031750	6997.6	1.3744	0.035252
6037.6	1.4385	0.027840	6041.5	1.2718	0.032509	6010.6	1.2274	0.036653
5023.8	1.2162	0.028287	5035.8	1.0956	0.033599	5049.5	1.0815	0.038443
4046.2	0.9964	0.028774	4025.8	0.9149	0.035097	4004.6	0.9233	0.041381
2768.0	0.6991	0.029513	3211.0	0.7657	0.036828	3202.1	0.8077	0.045271
2328.0	0.5942	0.029824	2505.7	0.6373	0.039279	2316.6	0.6986	0.054123
2021.4	0.5203	0.030077	2405.1	0.6196	0.039785	2202.7	0.6886	0.056108
1885.4	0.4878	0.030233	2353.8	0.6109	0.040077	2080.8	0.6789	0.058539
1747.5	0.4539	0.030350	2294.9	0.6013	0.040466	2021.0	0.6754	0.059979
1625.8	0.4323	0.031069	2225.0	0.5903	0.040972	1966.6	0.6725	0.061380
1593.9	0.4310	0.031595	2171.4	0.5909	0.042023	1913.6	0.6706	0.062898
1549.2	0.4292	0.032373	2162.4	0.5925	0.042314	1865.5	0.6733	0.064785
1482.6	0.4275	0.033696	2082.6	0.5785	0.042898	1820.8	0.6768	0.066711
1402.5	0.4252	0.035427	1929.0	0.5932	0.047489	1776.3	0.6797	0.068676
1299.1	0.4248	0.038209	1834.6	0.5947	0.050057	1699.4	0.6843	0.072275
1195.8	0.4254	0.041575	1686.5	0.5981	0.054765	1560.6	0.6924	0.079629
1097.3	0.4277	0.045544	1463.1	0.6044	0.063793	1451.4	0.6991	0.086457
1019.7	0.4307	0.049357	1303.3	0.6142	0.072781	1385.7	0.7038	0.091166
935.7	0.4353	0.054357	1162.3	0.6251	0.083053	1318.8	0.7085	0.096418
868.1	0.4401	0.059240	1077.7	0.6326	0.090660			
798.2	0.4463	0.065329	1023.0	0.7382	0.096341			
737.2	0.4518	0.071613						
664.2	0.4612	0.081146						
625.0	0.4673	0.087372						
598.3	0.4719	0.092158						
576.2	0.4760	0.096535						

Sample Weight = 0.065878 lb.

Pressure, p.s.i.a.	Compressibility factor	Volume, cu.ft./lb.	Pressure, p.s.i.a.	Compressibility factor	Volume, cu.ft./lb.	Pressure, p.s.i.a.	Compressibility factor	Volume cu.ft./lb.
2413.2	0.6031	0.029202	1104.4	0.6271	0.087683	1498.4	0.6934	0.083053
2113.4	0.5327	0.029455	1052.2	0.6303	0.092508	1414.4	0.6982	0.088597
1814.8	0.4605	0.029649	1000.9	0.6361	0.098150	1335.6	0.2034	0.094531
1693.6	0.4323	0.029824	901.6	0.6481	0.10992	1270.6	0.7090	0.10015
1625.5	0.4227	0.030389	704.5	0.6666	0.13292	1189.0	0.7164	0.10815
1568.9	0.4216	0.031400	625.9	0.6910	0.17048	1092.8	0.7257	0.11920
1515.7	0.4197	0.032353	525.3	0.7098	0.20869	942.9	0.7412	0.14109
1459.0	0.4166	0.033365	423.0	0.7312	0.26692	754.0	0.7646	0.18202
1299.7	0.4159	0.037392	390.3	0.7383	0.29215	640.8	0.7810	0.21875
1058.2	0.4232	0.046731	372.7	0.7423	0.30756	551.6	0.7972	0.25941
809.9	0.4396	0.063423	355.5	0.7464	0.32425	532.2	0.8023	0.27523
686.5	0.4534	0.077177				499.9	0.8068	0.28968
641.6	0.4595	0.083695				476.5	0.7907	0.29782
611.7	0.4649	0.088812				454.6	0.8174	0.32270

Table V. Molal Volumes in the Methane–Propane–n-Decane System

Composition Parameter[a]	0.5000
Mole Fraction Methane	0.1799
Mole Fraction Propane	0.4099
Mole Fraction n-Decane	0.4102
Average Molecular Weight	79.321

Pressure, P.S.I.A.	Temperature, ° F.							
	40	100	160	220	280	340	400	460
Bubble point[b]	(531)	(720)	(870)	(1025)	(1180)	(1305)	(1370)	(1390)
	1.928	2.020	2.132	2.260	2.414	2.606	2.920	3.328
200	...	...	...	...	...	...	...	...
400	...	...	...	...	...	...	...	...
600	1.927[c]	...	...	...	...	...	...	...
800	1.924	2.018	...	...	...	...	...	...
1000	1.920	2.014	2.128	...	...	...	...	...
1250	1.917	2.008	2.119	2.245	2.407[c]	...	...	...
1500	1.911	2.003	2.110	2.230	2.382	2.572	2.857	3.250
1750	1.907	1.998	2.100	2.218	2.355	2.535	2.774	3.097
2000	1.902	1.991	2.091	2.205	2.334	2.502	2.713	2.979
2250	1.897	1.986	2.081	2.193	2.316	2.472	2.661	2.893
2500	1.894	1.980	2.074	2.180	2.298	2.446	2.618	2.831
2750	1.890	1.975	2.066	2.168	2.284	2.420	2.579	2.773
3000	1.886	1.970	2.058	2.156	2.270	2.398	2.550	2.727
3500	1.879	1.958	2.043	2.136	2.243	2.358	2.494	2.642
4000	1.872	1.948	2.030	2.119	2.217	2.325	2.450	2.578
4500	1.864	1.938	2.016	2.102	2.195	2.296	2.413	2.527
5000	1.855	1.929	2.003	2.085	2.174	2.273	2.378	2.488
6000	1.843	1.913	1.983	2.060	2.142	2.227	2.320	2.416
7000	1.831	1.897	1.965	2.040	2.112	2.191	2.275	2.359
8000	1.821	1.881	1.947	2.017	2.086	2.159	2.235	2.312
9000	1.810	1.869	1.930	1.996	2.063	2.130	2.197	2.271
10000	1.801	1.857	1.912	1.976	2.040	2.103	2.166	2.237
σ[d]	0.001	0.002	0.001	0.003	0.002	0.003	0.001	0.003

Composition Parameter[a]	0.5000
Mole Fraction Methane	0.6920
Mole Fraction Propane	0.1539
Mole Fraction n-Decane	0.1541
Average Molecular Weight	39.812

Pressure, P.S.I.A.	Temperature, ° F.							
	40	100	160	220	280	340	400	460
Bubble point[b]	(3155)	(3485)	(3660)	(3706)	(3520)			
	1.262	1.378	1.502	1.662	1.884			
200	...	...	...	...	...	...	...	...
400	...	...	...	...	...	...	...	...
600	...	...	...	...	...	...	...	...
800	...	...	...	...	...	...	...	...
1000	...	...	...	...	...	...	...	...
1250	...	...	...	...	...	...	...	...
1500	...	...	...	...	...	...	...	...
1750	...	...	...	...	...	...	...	...
2000	...	...	...	...	...	...	...	...
2250	...	...	...	...	...	...	...	...
2500	...	...	...	...	...	...	...	3.458
2750	...	...	...	...	...	...	2.855	3.188
3000	...	...	...	...	...	...	2.660	2.974
3500	...	...	...	...	...	2.137	2.380	2.646
4000	1.240[c]	1.343	1.466	1.615	1.786[c]	1.982	2.194	2.414
4500	1.226	1.319	1.426	1.555	1.706	1.874	2.056	2.243
5000	1.214	1.298	1.399	1.515	1.645	1.789	1.949	2.112
6000	1.191	1.267	1.352	1.449	1.556	1.670	1.792	1.923
7000	1.172	1.245	1.318	1.401	1.488	1.585	1.687	1.798
8000	1.157	1.223	1.290	1.362	1.444	1.529	1.615	1.706
9000	1.142	1.206	1.266	1.332	1.404	1.482	1.563	1.638
10000	1.131	1.190	1.243	1.305	1.370	1.440	1.508	1.578
σ[d]	0.001	0.001	0.002	0.001	0.002	0.001	0.003	0.003

[a] Nominal composition parameter defined by $C = x_3/(x_3 + x_{10})$. [b] Values in parentheses represent bubble point pressure expressed in pounds per square inch absolute. [c] Volume expressed in cubic feet per pound-mole.

[d] Standard error of estimate defined by $\sigma = \left[\sum_{1}^{N} (V_e - V_s)/(N - 1) \right]^{1/2}$
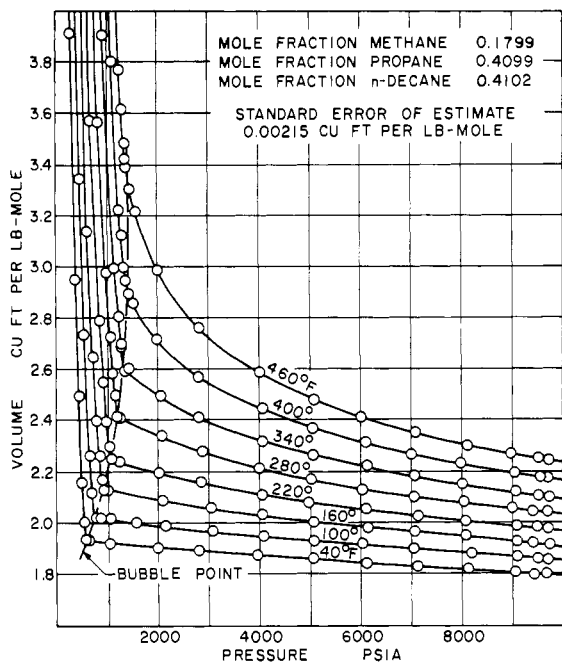
Figure 3. Experimental results for
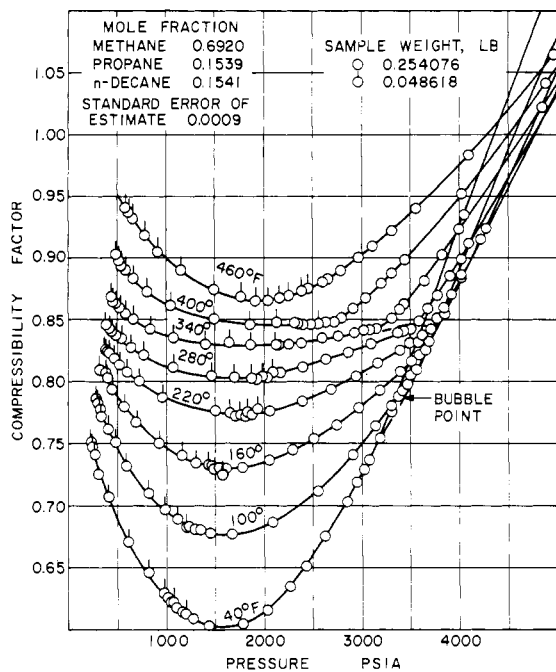a mixture lean in methane

Figure 4. Experimental results for
a mixture rich in methane

The experimental data for each mixture were smoothed
with respect to pressure and temperature. The standard
error of estimate of all of the experimental volumetric data
from the smooth curves drawn through them was 0.003
cubic feet per pound-mole. These values were then plotted
with respect to mole fraction of methane along the set
of parametric lines shown in Figure 1. A typical set of
curves along the composition locus AB is shown in Figure
5. Smoothed values for five temperatures were also plotted
with respect to mole fraction of propane and mole fraction
of n-decane. A comparison of the deviations for the three
methods of smoothing for two temperatures constitutes
Table III. After a review of the information in Table
III, it was deemed desirable to smooth the experimental
data only with respect to temperature, pressure and mole

fraction of methane. Detailed experimental data involving
some 5500 equilibrium states are available from American
Society for Information Science (ASIS). An example of
the experimental data for one mixture at three temperatures
is shown in Table IV.

Smooth volumetric data for two of the 22 experimental
mixtures are set forth in Table V. The values for the
other 20 mixtures are available from ASIS. The standard
error of estimate of each of the mixtures from this final
smoothing also is set forth in Table V. For each state
investigated for the two mixtures, the molal volume is
listed in Table V. In addition, the composition and average
molecular weight for converting molal to specific volumes
have been included. The bubble-point pressures are pre-
sented, along with the corresponding molal volumes at bubble
point. Considering the information in Tables I to III, for
the most part, the smooth values probably reflect the actual
volumetric behavior of the methane–propane–n-decane sys-
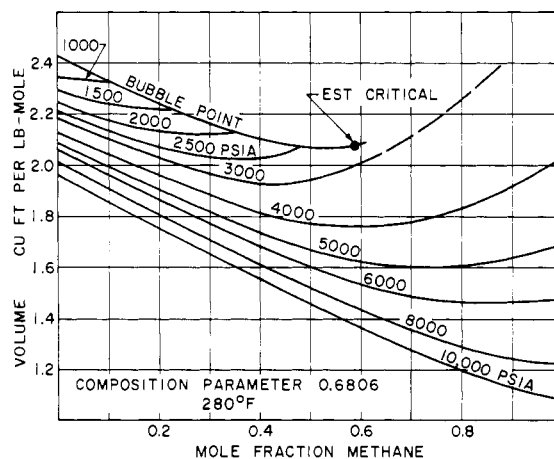

Figure 5. Effect of mole fraction of methane on
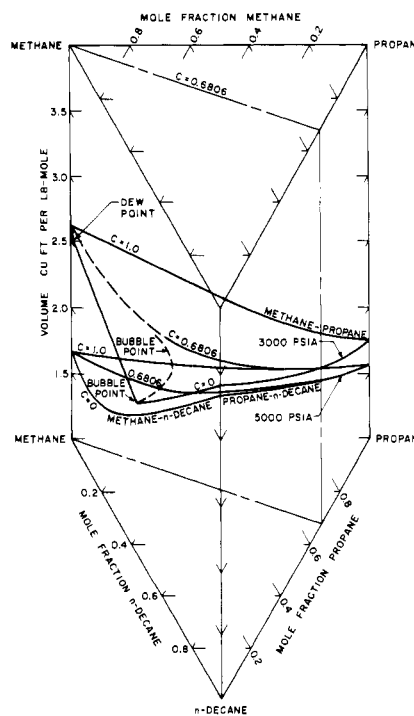molal volume for a fixed-composition parameter,
$C_{3.10}$

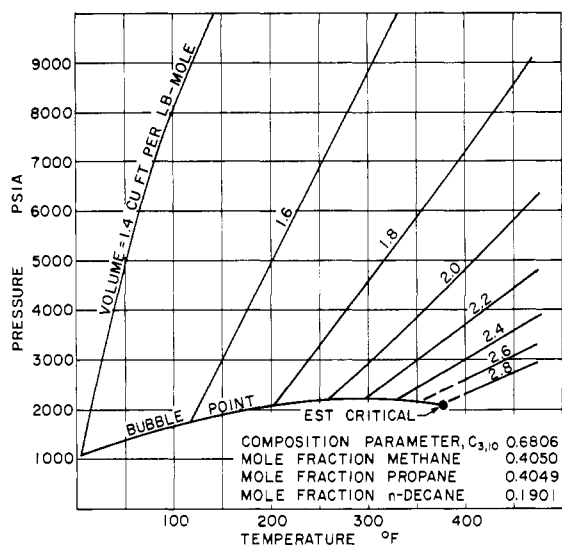Figure 6. Volume-composition
diagram for 280° F.

Figure 7. Pressure-temperature diagram for a
mixture of methane, propane, and n-decane

tem with an uncertainty of 0.2% at pressures below 5000
p.s.i. and 0.4% for the higher pressure.

BEHAVIOR OF SYSTEM

A large number of diagrams can be prepared from the
information submitted in Table V and that available from
ASIS. For example, Figure 6 shows an isometric projection
of the molal volume as a function of composition for two
different pressures at 280°F. The locus of bubble point
states has been indicated (20). A pressure-temperature
diagram for mixture H of Figure 1 is presented in Figure
7. Lines of constant molal volume have been presented
as a parametric variable. No information concerning be-
havior in the heterogeneous region has been included, in
the interest of clarity. The estimated location of the critical
state has been indicated.

There are a large number of additional diagrams which
could be prepared to depict the behavior of this system,
particularly those showing the effects of changes in tem-
perature. However, the ones which have been presented
give an indication of the nature of the volumetric behavior
of this system. The information presented in Table V and
available from ASIS is in agreement with the information
concerning the phase behavior of the methane–propane–
n-decane system which has been presented earlier (20).
For example, the molal volumes for the bubble point liquid
reported earlier (20) are in agreement with the corre-
sponding values of molal volume given for the two of the
22 mixtures investigated that are tabulated in Table V.

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Lorine Faris carried out the graphical and numerical
operations associated with the reduction of the experimental
data.

NOMENCLATURE

C = composition parameter, defined by Equations 1, 2, and
3
N = number of points
n = mole fraction
P = pressure, p.s.i.
R = universal gas constant, (p.s.i.)(cu.ft.)/(lb.-mole)(° R.)
s = average deviation, defined in Table III
s_f = average fractional deviation, defined in Table III

T = thermodynamic temperature, ° R.
V = molal volume, cu. ft. per lb.-mole
$\bar{V}$ = partial molal volume, cu. ft. per lb.-mole, defined by
Equations 4, 5, and 6
x = mole fraction in liquid phase
Z = compressibility factor, defined by Equation 7

Greek

Σ = summation operator
σ = standard error of estimate, defined in Tables III and
V

Subscripts

e = experimental
n = mole fraction
P = pressure
s = smoothed
T = temperature
$1, 3, 10$ = components methane, propane, and n-decane, respec-
tively

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