ACKNOWLEDGMENT

This paper presents results of a part of the research carried out for the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. DA-04-495 ORD-18 sponsored by the U. S. Army Ordnance Corps.

LITERATURE CITED

(1) Bridgeman, O. C., J. Am. Chem. Soc. 49, 1174 (1927).
(2) Corcoran, W. H., Reamer, H. H., Sage, B. H., Ind. Eng. Chem. 46, 2541 (1954).
(3) Duffy, C. H., Corcoran, W. H., Sage, B. H., Ibid., 48, 431 (1956).
(4) Forsythe, W. R., Giauque, W. F., J. Am. Chem. Soc. 64, 48 (1942).
(5) Kay, W. B., Stern, S. A., Ind. Eng. Chem. 47, 1463 (1955).
(6) Klemenc, A., Rupp, J., Z. anorg. Chem. 194, 51 (1930).
(7) Klemenc, A., Spiess, T., Monatsh. Chem. 77, 216 (1947).
(8) Kuster, F. W., Kremann, R., Z. anorg. Chem. 41, 1 (1904).
(9) Lewis, G. N., J. Am. Chem. Soc. 30, 668 (1908).
(10) Meyers, C. H., J. Research Natl. Bur. Standards 9, 807 (1932).
(11) Reamer, H. H., Corcoran, W. H., Sage, B. H., Ind. Eng. Chem. 45, 2699 (1953).
(12) Reamer, H. H., Mason, D. M., Sage, B. H., Ibid., 1094 (1953).
(13) Robertson, G. D., Jr., Mason, D. M., Sage, B. H., Ibid., 44, 2928 (1952).
(14) Sage, B. H., Lacey, W. N., "Volumetric and Phase Behavior of Hydrocarbons," Stanford University Press, Stanford, Calif., 1939.
(15) Sage, B. H., Lacey, W. N., Trans. Am. Inst. Mining Met. Engrs. 136, 136 (1940).
(16) Schlinger, W. G., Sage, B. H., Ind. Eng. Chem. 42, 2158 (1950).
(17) Sprague, R. W., Kaufman, E., Ibid., 47, 458 (1955).
(18) Stern, S. A., Kay, W. B., J. Am. Chem. Soc. 76, 5353 (1954).
(19) Taylor, G. B., Ibid., 17, 633 (1925).
(20) Whittaker, A. G., Sprague, R. W., Skolnick, S., "Thermal Decomposition Studies of Nitric Acid," Tech. Mem. 329, Naval Ordnance Test Station, February 1952.
(21) Wilson, G. L., Miles, F. D., Trans. Faraday Soc. 36, 356 (1940).

Received for review March 19, 1956 Accepted April 26, 1956

Phase Equilibria in Hydrocarbon Systems

Volumetric and Phase Behavior of the Methane–n-Heptane System

H. H. REAMER, B. H. SAGE, AND W. N. LACEY
California Institute of Technology, Pasadena, Calif.

Volumetric and phase behavior of binary hydrocarbon mixtures is of interest in predicting the behavior of fluids encountered in the production and refining of petroleum. Only limited information about the characteristics of the methane-n-heptane system is available.

Measurements of the molal volume of four mixtures of methane and n-heptane were made at pressures up to 10,000 pounds/square inch in the temperature interval between 40° and 460° F. The composition of the gas phase was determined throughout the heterogeneous region within the above-described temperature interval. The results of these measurements are presented in tabular and graphical form.

The present data are in fair agreement with earlier measurements for this system admixed with small percentages of nitrogen. The behavior was in accordance with expectations for this binary system.

In the production and refining of petroleum, use is frequently made of quantitative knowledge of the volumetric and phase behavior of hydrocarbon mixtures. Also, such information is necessary for evaluating measurements of molecular transport made under conditions which deviate from equilibrium. Mixtures of methane and n-heptane have not been intensively investigated. Boomer and Johnson (2, 3) studied this system at pressures up to approximately 3000 pounds/square inch for the temperature interval between 70° and 160° F. However, in order to approximate more closely the behavior of certain fields in Canada, these measurements were made with about 0.06 mole fraction of nitrogen present. The measurements of Boomer and Johnson were not made with the objective of establishing the partial volumetric behavior of the components and for this reason they did not furnish the data required for evaluating transient experimental measurements of diffusion coefficients. Because of the need for additional volumetric and phase equilibrium data, measurements were made of the volumetric behavior of four mixtures of methane and n-heptane at pressures up to 10,000 pounds/square inch for the temperature interval between 40° and 460° F. In addition, the composition of the gas phase in heterogeneous mixtures of the methane-n-heptane system was determined.

The volumetric behavior of each of the components has been well established. The influence of pressure and temperature upon the molal volume of methane was determined in detail (7, 8, 9) and summarized (11). These data are in good agreement with available Joule-Thomson (5) heat capacity measurements (21). The properties of n-heptane at atmospheric pressure were critically reviewed by Rossini (15). Beattie (1, 20) studied the volumetric behavior at pressures up to 4000 pounds/square inch and investigated the critical region in detail. Newitt (6) and coworkers investigated the volumetric behavior of the liquid phase at pressures up to 75,000 pounds/square inch for temperatures below 140° F. Further measurements of the volumetric behavior of n-heptane in the liquid phase, recently reported (10), were used as the basis of the volumetric behavior of n-heptane in the present study. It is believed that the volumetric and phase behavior of the two components was known with at least the accuracy for which the behavior of the four mixtures of methane and n-heptane was established.

MATERIALS

The methane employed in this study was obtained from a field in the San Joaquin Valley of California. When received at the laboratory it contained small quantities of carbon dioxide and was saturated with water. The sample was passed successively over calcium chloride, potassium hydroxide, activated charcoal, anhydrous calcium sulfate, and Ascarite at pressures in excess of 500 pounds/

square inch. Mass spectrographic analysis of methane from this source, purified in the above-mentioned fashion, indicated that the sample contained less than 0.001 mole fraction of material other than methane and less than 0.0002 mole fraction of other hydrocarbons.

The n-heptane was obtained as research grade from the Phillips Petroleum Co. which indicated it to contain 0.0009 mole fraction of impurities. The n-heptane was dried over metallic sodium and fractionated in a column containing 16 glass plates at a reflux ratio greater than 30. The initial and final 10% of the overhead was discarded. The partially purified sample was passed as a liquid over activated alumina. After deaeration by extended refluxing at reduced pressure, the n-heptane had a specific weight of 42.4430 pounds/cubic foot and a refractive index of 1.3852 relative to the D-lines of sodium at 77° F. These values may be compared with 42.4195 pounds/cubic foot and a refractive index of 1.3851 reported by Rossini (15) for an air saturated sample. The agreement of the specific weight and index of refraction of the sample with accepted values leads the authors to believe that the n-heptane used contained less than 0.0005 mole fraction of impurities.

APPARATUS AND PROCEDURES

The equipment employed in this investigation was described in some detail (19). In principle, it consisted of a stainless steel pressure vessel within which known quantities of methane and n-heptane were introduced. The volume of the chamber available to hydrocarbons was varied by the introduction and withdrawal of mercury. Equilibrium within and between the phases was hastened by a spiral mechanical agitator driven by a rotating electromagnet outside the pressure vessel. The quantity of n-heptane introduced into the vessel was determined by weighing bomb techniques (12) with an uncertainty of not more than 0.02%. The methane was introduced from another pressure vessel by a displacement technique at constant pressure, and the weight of methane so introduced was established with an uncertainty comparable to that with which the volumetric behavior of methane is known. It is estimated that the uncertainty in the weight of methane introduced was not more than 0.1%.

The temperature of the sample was determined by means of a strain-free platinum resistance thermometer which was compared with a similar instrument calibrated by the National Bureau of Standards. The temperature of the sample was related to the international platinum scale with an uncertainty of less than 0.03° F. Pressures were measured by a balance (19) which was calibrated against the vapor pressure of carbon dioxide at the ice point (4). The pressure of the sample was established with a probable error of 0.05% or 0.1 pound per square inch, whichever was the larger uncertainty. After a series of measurements at ascending temperatures the volumetric behavior of the mixture was again measured at 100° F. The two isotherms agreed with one another in every case with a probable error of less than 0.1%, except in the immediate vicinity of bubble points for the mixtures rich in n-heptane; a slight increase in bubble-point pressure was noted as a result of limited chemical rearrangement of the n-heptane at temperatures above 400° F. In these instances the initial measurements were adopted.

The bubble-point state was determined by the discontinuous change in the isothermal derivative of molal volume with respect to pressure which occurred at this state. The composition at dew point was obtained by withdrawal of the gas phase samples from a heterogeneous mixture under isobaric-isothermal conditions.

Composition of the gas phase samples was determined by a partial condensation procedure. The gas sample was withdrawn from the variable volume chamber under isobaric-isothermal conditions after equilibrium had been established at the chosen pressure and temperature. The gas was passed through a partial condenser (12) maintained near the temperature of solid carbon dioxide and acetone and the vapor pressure of methane at liquid nitrogen

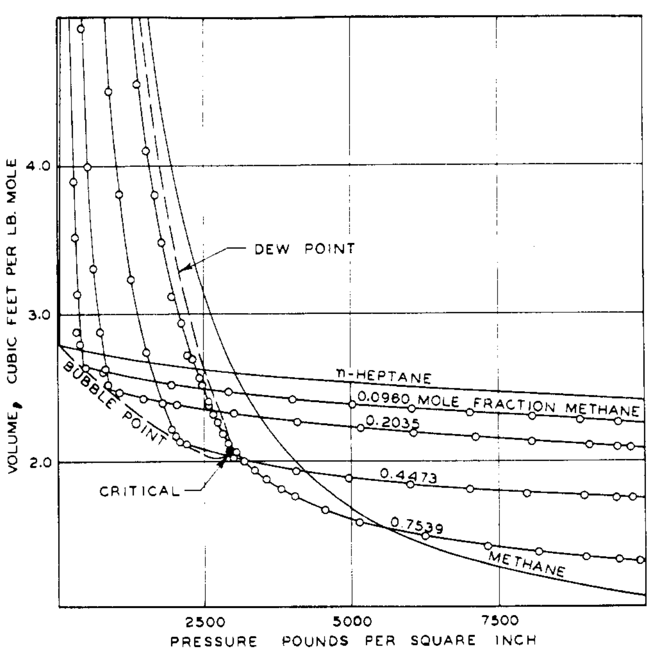

Figure 1. Experimental volumetric measurements at 280° F.

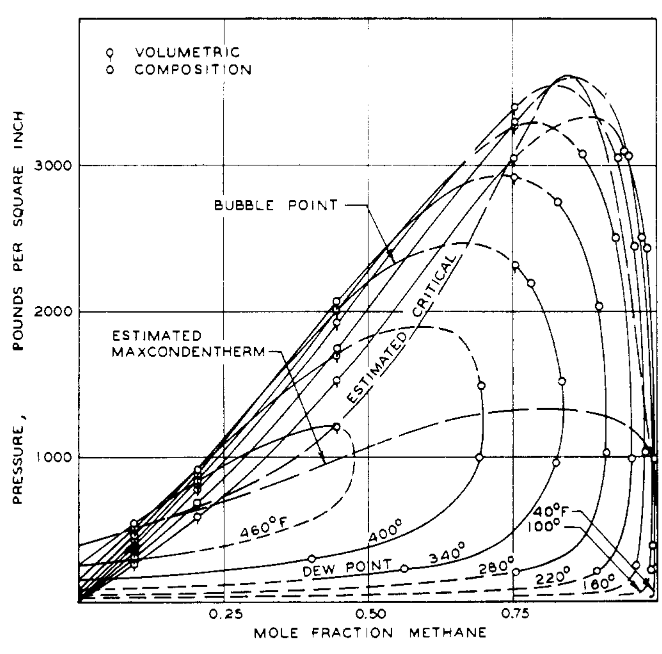

Figure 2. Compositions of coexisting gas and liquid phases

temperatures. The methane was condensed in a weighing bomb maintained at the temperature of liquid nitrogen and the quantity of methane was determined by the loss in weight of the bomb upon evacuation at the temperature of solid carbon dioxide and acetone. The total quantity of n-heptane was determined from the gain in weight of the partial condenser and the loss in weight of the weighing bomb upon evacuation at room temperature. The quantity of n-heptane accumulating in the weighing bomb was in nearly all cases less than 2% of the weight of n-heptane liquefied in the partial condenser. Some 30 measurements of the composition of the gas phase were made at different states throughout the temperature interval. Measurements upon duplicate samples withdrawn at the same equilibrium states indicated a probable error of 0.002 mole fraction n-heptane.

EXPERIMENTAL RESULTS

A sample of the experimental volumetric measurements is shown in Figure 1 for a temperature of 280° F. The data for methane and n-heptane have been included for comparison. The density of experimental points shown in Figure 1 is typical of those obtained at other temperatures. The detailed experimental data obtained in this investigation given in Table 1.

Experimental information such as is shown in Figure 1 was smoothed by residual graphical methods which have been described (13, 16). The smoothed values of the molal volume for even compositions are recorded in Table II. The corresponding values for pure methane and n-heptane are not included since these data are available (6, 10, 12).

TABLE I. EXPERIMENTAL VOLUMETRIC MEASUREMENTS FOR MIXTURES OF METHANE AND n-HEPTANE

Mole fraction methane = 0.0960

Sample wt. = 0.204269 lb.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.	Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.	Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.	Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
40° F.		100° F.		280° F.		340° F.	
9960.3	0.021878	9934.8	0.022596	10120.4	0.024570	10066.0	0.025266
9396.1	0.021931	9461.8	0.022651	9557.4	0.024721	9570.7	0.025419
8940.4	0.022007	8965.8	0.022723	8917.4	0.024887	9021.6	0.025585
8020.4	0.022114	8074.8	0.022860	8090.2	0.025072	8111.1	0.025859
7124.1	0.022245	7069.6	0.022992	7030.2	0.025364	7113.2	0.026157
6054.5	0.022426	6221.5	0.023139	6035.8	0.025656	6092.1	0.026498
5012.3	0.022572	5222.1	0.023336	5000.7	0.026008	5033.2	0.026966
3985.9	0.022725	4532.5	0.023474	4008.5	0.026408	4000.1	0.027471
2971.1	0.022890	3481.2	0.023705	2904.5	0.026884	3035.3	0.028074
1967.3	0.023070	2107.0	0.023999	1943.3	0.027449	1981.9	0.028936
882.8	0.023280	1006.0	0.024269	778.9	0.028344	1367.9	0.029535
346.1	0.023361	487.5	0.024414	481.2	0.028643	832.8	0.030282
304.4	0.023359	276.6	0.026529	391.2	0.030465	483.1	0.030901
248.1	0.023792	267.3	0.027336	377.6	0.031432	448.1	0.031657
220.1	0.026576	232.3	0.030783	343.1	0.034180	432.8	0.032807
193.3	0.030014	214.6	0.033048	303.7	0.038287	396.4	0.035745
168.8	0.034121	173.6	0.039950	273.0	0.042385	344.5	0.041397
143.1	0.040044	139.6	0.048861	214.1	0.054492	276.4	0.053691
130.5	0.043799	119.1	0.056711	177.3	0.067361	233.9	0.066596
100.9	0.056456	98.6	0.067980	155.5	0.078895	207.6	0.079190
82.9	0.068536	82.6	0.080785	138.9	0.091210	189.2	0.091809
71.0	0.079998	72.5	0.091762	126.5	0.103428	176.0	0.103794
61.9	0.091402	63.7	0.104448				
54.8	0.103650						
160° F.		220° F.		400° F.		460° F.	
9821.2	0.023268	9953.1	0.023932	9682.5	0.026121	9971.5	0.026762
9509.1	0.023308	9476.2	0.024048	9419.2	0.026221	9521.8	0.026916
9044.5	0.023398	8998.6	0.024157	9075.4	0.026334	8998.4	0.027128
8021.7	0.023572	8042.4	0.024362	8195.2	0.026619	8016.5	0.027510
7048.6	0.023751	7033.7	0.024571	7064.6	0.027050	7018.8	0.027983
6120.0	0.023954	6034.9	0.024828	6041.5	0.027521	6007.8	0.028539
5002.5	0.024199	5055.3	0.025090	5010.9	0.028059	5078.9	0.029154
4023.8	0.024422	4025.7	0.025407	3860.8	0.028833	4009.6	0.030041
3011.3	0.024688	2953.7	0.025734	2859.8	0.029692	3023.1	0.031124
1994.1	0.025018	2029.9	0.026111	1950.7	0.030772	1964.5	0.032893
865.8	0.025421	962.2	0.026706	1475.2	0.031520	1459.1	0.034181
402.4	0.025604	619.9	0.026869	897.0	0.032818	945.9	0.036475
339.7	0.026124	371.7	0.027738	543.5	0.034077	674.1	0.038786
326.9	0.026917	353.5	0.028874	506.7	0.034576	617.8	0.039568
296.6	0.029097	313.0	0.031956	494.5	0.035585	566.1	0.041042
258.6	0.032652	262.3	0.037204	466.3	0.038044	554.4	0.042375
187.0	0.043375	225.0	0.042736	412.9	0.044279	537.1	0.044506
142.3	0.055976	169.1	0.056157	361.0	0.053615	505.0	0.049363
111.1	0.071239	143.2	0.066837	315.8	0.066475	480.0	0.054313
100.2	0.078840	118.7	0.081135	284.8	0.080576	440.4	0.064509
87.2	0.090379	103.9	0.094069	268.1	0.091087	401.0	0.080181
76.3	0.103929	94.4	0.104578	254.2	0.102816	384.9	0.089388
						366.5	0.103514

TABLE I. EXPERIMENTAL VOLUMETRIC MEASUREMENTS FOR MIXTURES OF METHANE AND n-HEPTANE (Contd.)

Mole fraction methane = 0.2035

Sample wt. = 0.228610 lb.

40° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
9832.4	0.022407
9524.3	0.022446
9065.7	0.022510
8115.6	0.022643
7093.4	0.022786
6072.9	0.022930
5070.1	0.023080
4045.4	0.023258
2909.7	0.023517
1992.6	0.023710
947.9	0.023956
697.0	0.024017
597.9	0.024056
554.2	0.024832
541.2	0.025414
504.0	0.026974
430.4	0.031194
326.0	0.040626
251.8	0.055205
209.2	0.062694
182.7	0.072610
157.2	0.083345
141.3	0.092724

100° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
9604.1	0.023188
8932.3	0.023342
8149.1	0.023455
7085.7	0.023549
6086.2	0.023777
5142.8	0.023969
4145.1	0.024218
3004.7	0.024514
2053.8	0.024796
986.7	0.025105
735.1	0.025190
639.4	0.026700
605.0	0.027924
464.0	0.035032
375.6	0.042333
305.0	0.051315
250.9	0.061658
215.9	0.071252
177.1	0.086249
162.1	0.093844

160° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
9718.4	0.023833
9430.1	0.023922
8969.4	0.024001
8140.0	0.024164
7028.7	0.024387
5993.0	0.024621
5049.3	0.024867
4009.9	0.025156
3006.1	0.025547
1987.6	0.025894
1273.5	0.026237
771.6	0.026494
756.8	0.026895
731.3	0.027650
703.4	0.028487
609.6	0.031942
523.5	0.038116
395.3	0.046384
315.8	0.058391
253.8	0.070022
215.8	0.081872
189.2	0.093135

220° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
9691.4	0.024614
9566.3	0.024645
9079.0	0.024750
8133.6	0.024973
7091.7	0.025261
6043.0	0.025548
5126.5	0.025836
4019.9	0.026244
2983.8	0.026740
1989.3	0.027247
1258.7	0.027725
839.1	0.028029
794.3	0.029147
712.2	0.031764
542.9	0.039789
429.1	0.049054
345.7	0.059965
291.4	0.070671
251.3	0.081753
219.6	0.093696

280° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
9757.6	0.025346
9570.4	0.025402
9083.7	0.025530
8088.8	0.025808
7116.0	0.026110
6066.8	0.026484
5133.5	0.026856
4070.7	0.027375
3005.7	0.028032
2027.1	0.028721
1476.5	0.029254
1051.4	0.029681
864.8	0.030280
817.6	0.031696
731.1	0.034755
620.7	0.040011
506.4	0.048139
407.1	0.059316
344.0	0.070372
296.9	0.082027
264.5	0.092857

340° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
9746.8	0.026206
9498.7	0.026242
9070.7	0.026360
8095.8	0.026679
7083.1	0.027065
6106.0	0.027473
5162.5	0.027971
4049.5	0.028641
3065.7	0.029381
2058.6	0.030543
1455.0	0.031432
1191.1	0.031904
1022.9	0.032272
889.6	0.033073
869.6	0.033739
835.0	0.034917
753.2	0.038314
665.3	0.043020
543.4	0.052472
446.5	0.064588
361.0	0.082327
327.5	0.092794

400° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
9849.1	0.026930
9513.5	0.027069
8994.7	0.027253
8060.4	0.027620
7071.6	0.028071
6049.2	0.028594
5112.7	0.029201
4118.6	0.029999
3000.5	0.031189
1950.9	0.032906
1452.2	0.034227
1197.9	0.035119
1104.3	0.035537
1010.4	0.036019
889.6	0.037791
845.5	0.039685
726.2	0.045979
663.1	0.051233
583.0	0.059478
505.3	0.071084
455.2	0.081498
413.5	0.093450

460° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
9892.5	0.027700
9556.9	0.027861
9103.4	0.028055
8107.4	0.028525
7051.5	0.029110
6047.1	0.029777
5081.6	0.030537
4039.5	0.031615
3008.9	0.033166
2007.5	0.035595
1481.2	0.037973
1187.6	0.040281
1030.8	0.042272
915.2	0.044669
827.2	0.049525
772.6	0.054014
706.6	0.060977
630.0	0.072054
574.6	0.083518
533.3	0.095019

Mole fraction methane = 0.2035

Sample wt. = 0.076314 lb.

40° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
183.6	0.068135
173.8	0.075647
154.5	0.085096
124.2	0.106045
101.7	0.129775
84.9	0.155453
69.9	0.188756
60.1	0.219769
52.7	0.250897
46.5	0.284866

100° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
1897.6	0.024886
1519.3	0.025008
733.4	0.025334
719.6	0.025266
608.9	0.028019
496.7	0.033271
363.8	0.043936
215.8	0.071502
193.3	0.079582
172.7	0.088534
150.5	0.101805
127.6	0.119364
97.7	0.155885
81.5	0.186773
71.1	0.214316
59.4	0.257574
52.6	0.292381

160° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
212.6	0.083578
199.5	0.088975
185.0	0.095727
161.1	0.109920
130.6	0.135602
104.1	0.170974
87.3	0.205361
73.8	0.245377
65.7	0.278577

220° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
306.7	0.067692
281.4	0.073594
252.9	0.081637
208.4	0.099334
169.7	0.123169
143.0	0.147915
120.6	0.179401
103.5	0.213113
91.3	0.247658
82.6	0.279835

280° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
340.7	0.071557
320.1	0.076312
293.9	0.083311
262.1	0.094241
221.2	0.114434
170.2	0.156558
153.8	0.178616
135.8	0.211605
122.2	0.244667
111.5	0.280352

340° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
357.7	0.083705
340.4	0.089101
323.6	0.094660
298.5	0.105054
262.5	0.124792
228.5	0.152491
201.5	0.185162
182.7	0.219496
169.3	0.251967
159.3	0.284723

TABLE I. EXPERIMENTAL VOLUMETRIC MEASUREMENTS FOR MIXTURES OF METHANE AND n-HEPTANE (Contd.)

400° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
502.0	0.072059
477.4	0.077089
452.3	0.082844
410.8	0.095058
351.2	0.121217
315.7	0.146116
282.5	0.181509
263.6	0.211605
247.8	0.244409
236.6	0.276177

460° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
573.8	0.084156
548.2	0.091141
531.0	0.096441
501.4	0.107392
455.1	0.130922
412.9	0.164200
383.7	0.196499
359.6	0.223067
332.5	0.252875
326.9	0.259376
322.6	0.264973
317.7	0.270977
303.5	0.290084

Mole fraction methane = 0.4473

Sample wt. = 0.226878 lb.

40° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
9875.1	0.024312
9469.1	0.024350
8990.5	0.024464
8018.6	0.024618
6986.6	0.024819
5983.3	0.025041
5032.9	0.025175
3970.7	0.025327
2942.5	0.025587
2488.3	0.025731
1936.1	0.025910
1594.9	0.026065
1442.6	0.026974
1355.3	0.028289
1206.3	0.031101
1035.6	0.035596
863.2	0.042329
726.6	0.050736
599.0	0.060934
511.5	0.071599
452.2	0.081210
397.8	0.092704

100° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
10059.3	0.025207
9533.3	0.025333
9018.4	0.025381
8034.7	0.025605
7002.9	0.025849
6071.8	0.026096
5043.0	0.026432
4517.9	0.026526
4182.1	0.026615
3037.8	0.026922
2571.0	0.027151
1987.7	0.027429
1707.8	0.028323
1587.0	0.029918
1358.9	0.033790
1136.2	0.039416
877.1	0.049915
708.2	0.061206
595.8	0.072339
516.1	0.083378
455.5	0.094358

160° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
9886.4	0.026040
9463.9	0.026125
9013.5	0.026197
8105.9	0.026463
7077.7	0.026745
6065.8	0.027090
5048.3	0.027409
4018.4	0.027908
2972.3	0.028438
2554.2	0.028716
2155.9	0.028999
1923.9	0.029389
1852.2	0.030251
1634.9	0.033278
1277.2	0.040898
1059.9	0.048208
841.7	0.059610
700.9	0.070845
603.7	0.081737
529.9	0.092822

220° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
9983.9	0.026766
9519.3	0.026917
9005.1	0.027082
8044.2	0.027408
7002.9	0.027777
6025.7	0.028220
5051.0	0.028726
4042.4	0.029359
2965.5	0.030247
2486.5	0.030748
2071.5	0.031286
1999.8	0.031686
1937.0	0.032467
1756.7	0.035076
1505.6	0.039812
1194.7	0.048686
947.5	0.061909
770.2	0.073108
684.8	0.082095
598.4	0.093289

280° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
9805.1	0.028112
9507.5	0.028164
8989.2	0.028290
7981.5	0.028587
7010.0	0.029010
6013.3	0.029577
4964.1	0.030333
4077.4	0.031101
3000.2	0.032440
2182.7	0.033950
2053.0	0.034252
2003.5	0.034728
1950.9	0.035479
1777.1	0.038331
1514.7	0.043886
1251.0	0.051856
1058.5	0.060829
886.6	0.072005
765.7	0.083017
681.0	0.093435

340° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
10000.1	0.028818
9612.4	0.028997
9084.2	0.029265
8032.3	0.029762
7016.0	0.030367
6023.1	0.031096
4959.0	0.032069
3933.7	0.033355
2962.8	0.035121
2416.4	0.036654
2107.5	0.037897
2001.4	0.038439
1911.6	0.039389
1844.5	0.040631
1717.9	0.043243
1509.0	0.048687
1205.4	0.060175
1023.3	0.070686
888.9	0.081484
785.8	0.092582
739.3	0.098649

400° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
9884.3	0.029821
9500.8	0.030018
8941.1	0.030336
8163.6	0.030834
7202.7	0.031511
6269.6	0.032348
5118.4	0.033677
4180.7	0.035163
3115.0	0.037775
2567.1	0.039996
2286.6	0.041647
1984.8	0.044201
1793.1	0.046543
1694.0	0.048340
1450.6	0.056411
1198.1	0.068639
1026.5	0.080980
907.8	0.092771
856.3	0.099169

460° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
9931.6	0.030847
9506.9	0.031135
8970.5	0.031487
8007.5	0.032217
6991.2	0.033170
5967.8	0.034360
5016.9	0.035833
4006.2	0.038098
3435.7	0.039962
2984.8	0.042012
2649.7	0.044086
2410.8	0.046077
2224.7	0.048064
1911.9	0.052636
1555.6	0.061766
1308.1	0.072789
1135.3	0.085775
1015.5	0.098382

Mole fraction methane = 0.7539

Sample wt. = 0.290166 lb.

40° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
9508.0	0.029701
9200.0	0.029819
8913.7	0.029933
8135.1	0.030271
7071.6	0.030788
6084.9	0.031235
5116.4	0.031884
4144.8	0.032633
3515.4	0.033273
3282.7	0.033557
3046.0	0.033861
2964.2	0.034436
2838.6	0.035410
2612.2	0.037485
2274.2	0.041712
1871.6	0.049690
1635.4	0.056866
1456.2	0.064255
1331.0	0.070782
1259.1	0.075210

100° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
9671.6	0.031165
9379.5	0.031281
8974.9	0.031496
8068.2	0.032008
7030.3	0.032649
6043.8	0.033382
5060.4	0.034294
3980.0	0.035684
2951.6	0.040482
2185.2	0.052452
2183.0	0.052546
1944.5	0.058690
1711.0	0.066493
1516.8	0.075103
3948.1	0.035674
3286.9	0.037253
3148.0	0.038453
2778.7	0.042496
2484.7	0.046745

TABLE I. EXPERIMENTAL VOLUMETRIC MEASUREMENTS FOR MIXTURES OF METHANE AND n-HEPTANE (Contd.)

160° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
9653.7	0.032817
9273.3	0.032953
8934.5	0.033174
8057.0	0.033790
7064.3	0.034652
6055.9	0.035725
5101.0	0.036956
4556.3	0.037928
4059.0	0.039027
3836.0	0.039630
3610.0	0.040313
3404.5	0.041095
3237.3	0.042709
3171.4	0.043510
3048.2	0.045049
2927.7	0.046679
2705.0	0.050081
2360.4	0.056733
2039.0	0.065170
1792.3	0.073866

220° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
9889.8	0.034280
9519.9	0.034537
9001.7	0.034959
8030.9	0.035851
7085.4	0.036882
6005.7	0.038409
5054.7	0.040274
4532.6	0.041703
3994.0	0.043495
3789.0	0.044377
3584.8	0.045375
3322.9	0.046969
3175.5	0.048434
3067.7	0.050060
2961.7	0.051773
2861.1	0.053494
2674.9	0.056988
2330.0	0.064944
2012.9	0.074758

280° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
9932.4	0.035997
9579.9	0.036311
9000.4	0.036839
8176.4	0.037816
7326.3	0.038974
6273.9	0.040800
5138.0	0.043294
4565.0	0.045740
4045.6	0.048185
3815.9	0.049512
3564.5	0.051322
3360.2	0.053005
3184.2	0.054702
3037.1	0.056370
2908.4	0.058074
2815.0	0.059779
2738.1	0.061554
2664.0	0.063273
2593.4	0.065008
2454.0	0.068640
2289.5	0.073484

340° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
9984.4	0.037815
9432.5	0.038431
9014.2	0.038957
8127.2	0.040139
7069.8	0.042032
6183.4	0.044132
5183.2	0.047111
4700.4	0.049570
4443.5	0.051001
4229.7	0.052297
4017.5	0.053745
3790.3	0.055587
3594.2	0.057387
3484.4	0.058515
3351.0	0.060048
3221.3	0.061663
3077.5	0.063682
2951.9	0.065642
2799.9	0.068316
2627.7	0.071847
2482.1	0.075354
2395.0	0.077707

400° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
9867.6	0.039886
9498.7	0.040360
9066.1	0.041000
7228.7	0.044461
5181.8	0.051561
4113.7	0.058658
3394.4	0.066750
3172.1	0.070197
2940.4	0.074510

460° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
10001.6	0.041624
9575.0	0.042318
8951.4	0.043379
7159.4	0.047573
5284.9	0.055227
4318.2	0.062544
3735.9	0.069182
3385.8	0.074314

Mole fraction methane = 0.7539

Sample wt. = 0.068353 lb.

40° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
1433.2	0.065658
1328.0	0.071034
1238.0	0.077013
1101.3	0.087582
914.5	0.107709
765.9	0.130719
639.2	0.158994
530.9	0.194227
452.2	0.230396
382.2	0.275461
333.1	0.318548

100° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
4023.4	0.035448
3851.6	0.035737
3614.3	0.036246
3309.8	0.036873
3163.5	0.038238
2981.9	0.040113
2816.1	0.042122
1945.8	0.058743
1732.0	0.065979
1532.7	0.074774
1247.4	0.092460
906.5	0.129141
706.5	0.167514
585.0	0.204158
498.7	0.240937
436.8	0.276630
386.8	0.313794

160° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
2375.0	0.056384
2100.9	0.063470
1824.7	0.072986
1524.5	0.087236
1242.2	0.106488
1019.3	0.131462
836.2	0.161295
691.3	0.196071
568.2	0.240725
499.7	0.274491
434.0	0.316598
432.4	0.317921

220° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
2519.2	0.060473
2137.0	0.070887
1938.7	0.077947
1670.8	0.090386
1665.5	0.090624
1423.9	0.106058
1416.4	0.106743
1163.6	0.130168
1160.9	0.130412
952.8	0.159414
807.0	0.189112
683.0	0.224639
590.2	0.261243
492.3	0.315667

280° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
2572.5	0.065591
2411.9	0.069996
2266.4	0.074390
2101.0	0.080183
1963.3	0.085058
1780.2	0.094869
1632.6	0.103547
1514.9	0.111842
1364.8	0.124116
1207.7	0.140694
1062.4	0.160895
910.8	0.188729
773.6	0.223932
651.9	0.268545
557.3	0.317686

340° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
2597.1	0.072762
2437.4	0.076883
2321.8	0.080244
2214.5	0.084123
2093.9	0.089314
1983.6	0.094259
1808.0	0.103996
1589.9	0.117920
1408.5	0.134183
1217.8	0.157293
998.7	0.194779
813.2	0.243972
617.5	0.334540

400° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
3396.1	0.066937
3179.8	0.070284
2939.8	0.074749
2739.0	0.079429
2530.2	0.085134
2327.1	0.091618
2125.7	0.100003
1642.9	0.129810
1411.5	0.152628
1174.3	0.186677
990.7	0.224975
853.3	0.265094
738.4	0.310477

460° F.

Pressure, Lb./Sq.Inch Absolute	Volume, Cu.Ft./Lb.
4001.8	0.065703
3632.0	0.070501
3295.3	0.076031
3003.8	0.082147
2708.1	0.089827
2421.1	0.099486
2104.8	0.113636
1798.5	0.133132
1500.6	0.160522
1231.7	0.197949
1036.1	0.238106
891.8	0.279377
790.4	0.317972

TABLE II. MOLAL VOLUMES FOR MIXTURES OF METHANE AND n-HEPTANE

(Cu. ft. / lb. mole)

Pressure, Lb./Sq.Inch Absolute	Mole Fraction Methane 0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
					40° F.				
Dew point[a]	(4)	(6)	(8)	(9)	(10)	(11)	(18)	(21)	(28)
Estimated	1337	891	668	594	534	485	296	254	190
Bubble point[a]	(269)	(572)	(919)	(1319)	(1781)	(2302)	(2817)	(3198)	(3320)[b]
	2.149	2.002	1.850	1.699	1.559	1.425	1.298	1.207	1.184
200									
400	2.146								
600	2.143	2.001							
800	2.139	1.998							
1000	2.135	1.993	1.846						
1250	2.130	1.989	1.841						
1500	2.126	1.984	1.834	1.693					
1750	2.122	1.978	1.828	1.688					
2000	2.118	1.973	1.823	1.682	1.552				
2250	2.114	1.968	1.818	1.677	1.546				
2500	2.110	1.963	1.813	1.672	1.540	1.419			
2750	2.105	1.959	1.808	1.668	1.535	1.413			
3000	2.101	1.953	1.805	1.664	1.530	1.407	1.291		
3500	2.094	1.945	1.796	1.655	1.523	1.397	1.277	1.188	1.164
4000	2.085	1.936	1.789	1.649	1.515	1.387	1.264	1.164	1.116
4500	2.078	1.929	1.783	1.643	1.507	1.378	1.253	1.143	1.083
5000	2.072	1.921	1.775	1.636	1.501	1.371	1.243	1.125	1.056
6000	2.057	1.907	1.765	1.627	1.491	1.355	1.222	1.100	1.015
7000	2.045	1.897	1.756	1.617	1.479	1.338	1.200	1.077	0.980
8000	2.031	1.885	1.745	1.606	1.465	1.323	1.185	1.061	0.956
9000	2.019	1.874	1.733	1.595	1.455	1.313	1.173	1.045	0.934
10,000	2.009	1.863	1.721	1.583	1.443	1.299	1.159	1.029	0.913
					100° F.				
Dew point[a]	(7)	(9)	(11)	(18)	(21)	(25)	(31)	(40)	(46)
Estimated	848	659	539	329	282	237	191	148	128
Bubble point[a]	(318)	(669)	(1068)	(1518)	(2026)	(2549)	(3048)	(3490)	(3525)[b]
	2.247	2.100	1.948	1.795	1.650	1.511	1.391	1.313	1.374
200									
400	2.244								
600	2.240								
800	2.235	2.096							
1000	2.229	2.090							
1250	2.223	2.085	1.942						
1500	2.217	2.077	1.935						
1750	2.211	2.069	1.927	1.788					
2000	2.205	2.064	1.921	1.780					
2250	2.200	2.058	1.915	1.772	1.637				
2500	2.195	2.052	1.907	1.764	1.628				
2750	2.188	2.046	1.901	1.758	1.620	1.498			
3000	2.184	2.040	1.895	1.752	1.611	1.485			
3500	2.174	2.030	1.885	1.740	1.597	1.470	1.374	1.312	
4000	2.165	2.019	1.874	1.730	1.589	1.457	1.353	1.288	1.300
4500	2.157	2.009	1.865	1.719	1.581	1.449	1.334	1.263	1.250
5000	2.147	1.999	1.855	1.711	1.571	1.437	1.316	1.238	1.201
6000	2.129	1.981	1.838	1.697	1.555	1.417	1.289	1.185	1.118
7000	2.113	1.966	1.824	1.682	1.539	1.399	1.264	1.150	1.065
8000	2.100	1.951	1.808	1.665	1.524	1.384	1.247	1.121	1.022
9000	2.085	1.939	1.794	1.651	1.507	1.366	1.228	1.100	0.992
10,000	2.072	1.925	1.782	1.639	1.495	1.350	1.209	1.082	0.970
					160° F.				
Dew point[a]	(11)	(19)	(23)	(31)	(40)	(46)	(52)	(61)	(80)
Estimated	588	340	281	208	162	140	124	106	81
Bubble point[a]	(358)	(753)	(1199)	(1689)	(2202)	(2719)	(3178)	(3529)	(3325)[b]
	2.358	2.206	2.048	1.896	1.758	1.644	1.551	1.501	1.646
200									
400	2.352								
600	2.345								
800	2.339	2.204							
1000	2.330	2.194							
1250	2.323	2.183	2.045						
1500	2.313	2.173	2.035						

TABLE II. MOLAL VOLUMES FOR MIXTURES OF METHANE AND n-HEPTANE (Contd.)

Pressure, Lb./Sq.Inch Absolute	Mole Fraction Methane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
					160° F. (Contd.)				
1750	2.305	2.163	2.024	1.892					
2000	2.298	2.155	2.014	1.881					
2250	2.288	2.147	2.006	1.870	1.755				
2500	2.281	2.139	1.994	1.859	1.742				
2750	2.275	2.132	1.986	1.849	1.729	1.641			
3000	2.268	2.124	1.978	1.840	1.716	1.624			
3500	2.257	2.110	1.962	1.824	1.699	1.592	1.517		1.573
4000	2.243	2.096	1.949	1.808	1.678	1.567	1.474	1.426	1.453
4500	2.233	2.083	1.933	1.793	1.663	1.546	1.442	1.375	1.375
5000	2.225	2.072	1.921	1.781	1.648	1.526	1.414	1.338	1.315
6000	2.202	2.049	1.903	1.763	1.625	1.493	1.373	1.279	1.228
7000	2.183	2.032	1.883	1.742	1.604	1.465	1.336	1.231	1.155
8000	2.165	2.014	1.864	1.723	1.583	1.443	1.310	1.194	1.104
9000	2.150	1.999	1.850	1.704	1.563	1.422	1.288	1.166	1.062
10,000	2.133	1.981	1.833	1.691	1.551	1.409	1.269	1.143	1.036
					220° F.				
Dew point[a]	(24)	(33)	(45)	(56)	(64)	(74)	(88)	(103)	(212)
Estimated	287	209	153	123	108	93	79	67	33
Bubble point[a]	(399)	(818)	(1279)	(1777)	(2278)	(2754)	(3139)	(3286)[b]	(2883)[b]
	2.485	2.330	2.170	2.015	1.885	1.784	1.738	1.794	2.160
200									
400	2.484								
600	2.470								
800	2.457								
1000	2.447	2.319							
1250	2.437	2.305							
1500	2.424	2.290	2.158						
1750	2.411	2.278	2.144						
2000	2.400	2.264	2.130	2.003					
2250	2.390	2.253	2.118	1.988					
2500	2.379	2.242	2.105	1.974	1.870				
2750	2.370	2.232	2.090	1.960	1.850				
3000	2.362	2.220	2.078	1.946	1.830	1.760			
3500	2.348	2.204	2.058	1.922	1.797	1.715	1.675	1.715	1.837
4000	2.331	2.186	2.038	1.898	1.768	1.666	1.608	1.608	1.683
4500	2.316	2.170	2.021	1.881	1.745	1.629	1.557	1.527	1.554
5000	2.305	2.154	2.006	1.864	1.725	1.602	1.515	1.464	1.470
6000	2.280	2.127	1.980	1.838	1.694	1.565	1.460	1.378	1.345
7000	2.256	2.105	1.957	1.815	1.670	1.536	1.416	1.322	1.255
8000	2.235	2.084	1.935	1.790	1.644	1.507	1.381	1.272	1.188
9000	2.215	2.064	1.914	1.768	1.624	1.482	1.351	1.230	1.136
10,000	2.195	2.043	1.894	1.749	1.604	1.459	1.323	1.199	1.093
					280° F.				
Dew point[a]	(52)	(64)	(77)	(91)	(110)	(136)	(171)	(250)	(740)
Estimated	138	112	94	80	66	54	43	30	10.0
Bubble point[a]	(436)	(868)	(1349)	(1847)	(2304)	(2702)	(2912)	(2842)	(2012)
	2.643	2.489	2.333	2.193	2.088	2.020	2.048	2.226	3.38
200								38	39
400									19
600	2.623								12.4
800	2.603								
1000	2.587	2.472							
1250	2.568	2.452							
1500	2.551	2.430	2.318						
1750	2.535	2.409	2.293						
2000	2.520	2.390	2.271	2.177					3.40
2250	2.507	2.373	2.250	2.148					3.08
2500	2.489	2.357	2.232	2.123	2.054				2.798
2750	2.478	2.345	2.214	2.098	2.011				2.546
3000	2.466	2.331	2.196	2.076	1.985	1.952	2.014	2.149	2.335
3500	2.443	2.304	2.165	2.038	1.933	1.873	1.876	1.945	2.080

TABLE II. MOLAL VOLUMES FOR MIXTURES OF METHANE AND n-HEPTANE (Contd.)

Pressure, Lb./Sq.Inch Absolute	Mole Fraction Methane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
					280° F. (Contd.)				
4000	2.422	2.278	2.139	2.008	1.891	1.806	1.770	1.804	1.897
4500	2.408	2.260	2.116	1.981	1.858	1.756	1.699	1.698	1.751
5000	2.389	2.241	2.096	1.958	1.826	1.716	1.642	1.615	1.636
6000	2.357	2.209	2.061	1.921	1.781	1.655	1.555	1.500	1.481
7000	2.329	2.178	2.033	1.888	1.748	1.612	1.498	1.418	1.367
8000	2.303	2.152	2.004	1.856	1.712	1.574	1.450	1.356	1.283
9000	2.282	2.128	1.978	1.831	1.687	1.542	1.414	1.308	1.217
10,000	2.258	2.107	1.957	1.808	1.662	1.517	1.384	1.266	1.163
					340° F.				
Dew point[a]	(103)	(121)	(141)	(167)	(198)	(243)	(359)	(752)	
Estimated	69	60	52	44	38	31	21	10	
Bubble point[a]	(468)	(897)	(1351)	(1818)	(2198)	(2426)	(2448)[b]	(2041)[b]	
	2.843	2.704	2.569	2.445	2.355	2.382	2.566	3.38	
200									42.3
400									20.8
600	2.822								13.7
800	2.789								10.1
1000	2.758	2.682							8.0
1250	2.728	2.642							6.3
1500	2.702	2.608	2.546						5.18
1750	2.678	2.576	2.502						4.41
2000	2.658	2.547	2.461	2.406					3.86
2250	2.639	2.520	2.423	2.352	2.336			3.07	3.44
2500	2.622	2.492	2.388	2.302	2.273	2.350	2.532	2.809	3.12
2750	2.601	2.470	2.356	2.262	2.220	2.262	2.396	2.616	2.867
3000	2.580	2.452	2.328	2.228	2.176	2.198	2.292	2.467	2.674
3500	2.552	2.416	2.283	2.170	2.098	2.079	2.106	2.188	2.330
4000	2.522	2.385	2.248	2.126	2.032	1.972	1.960	2.004	2.100
4500	2.502	2.361	2.222	2.090	1.982	1.900	1.860	1.867	1.922
5000	2.478	2.335	2.193	2.061	1.939	1.839	1.780	1.767	1.794
6000	2.439	2.292	2.146	2.006	1.873	1.756	1.667	1.616	1.602
7000	2.404	2.254	2.102	1.960	1.822	1.694	1.590	1.511	1.466
8000	2.378	2.224	2.072	1.925	1.783	1.648	1.533	1.437	1.365
9000	2.351	2.195	2.043	1.895	1.750	1.612	1.490	1.383	1.292
10,000	2.328	2.173	2.023	1.872	1.721	1.576	1.448	1.336	1.239
					400° F.				
Dew point[a]	(169)	(197)	(236)	(294)	(373)	(540)			
Estimated	40	35	31	25	21	14			
Bubble point[a]	(524)	(898)	(1262)	(1586)	(1829)	(1904)[b]			
	3.15	3.04	2.976	2.964	3.03	3.37			
200			38	40	42	43	44.6	45.3	45.8
400						20	21.6	22.2	22.7
600	3.12						13.9	14.6	15.0
800	3.05						10.1	10.7	11.2
1000	2.992	2.995					7.80	8.46	8.92
1250	2.940	2.896					6.03	6.66	7.12
1500	2.894	2.831	2.858				4.92	5.50	5.92
1750	2.855	2.773	2.760	2.850			4.16	4.69	5.08
2000	2.822	2.724	2.677	2.701	2.839	3.19	3.62	4.06	4.45
2250	2.791	2.683	2.613	2.600	2.653	2.862	3.23	3.63	3.98
2500	2.763	2.651	2.565	2.523	2.544	2.655	2.943	3.29	3.60
2750	2.740	2.623	2.521	2.458	2.461	2.539	2.741	3.02	3.29
3000	2.718	2.593	2.482	2.403	2.386	2.437	2.581	2.792	3.04
3500	2.677	2.549	2.425	2.325	2.278	2.287	2.339	2.457	2.642
4000	2.643	2.506	2.375	2.264	2.183	2.155	2.161	2.230	2.358
4500	2.607	2.468	2.336	2.216	2.114	2.057	2.045	2.083	2.168
5000	2.576	2.435	2.298	2.170	2.057	1.984	1.950	1.965	2.015
6000	2.528	2.382	2.236	2.100	1.973	1.874	1.795	1.751	1.760
7000	2.488	2.338	2.191	2.046	1.914	1.796	1.696	1.630	1.605
8000	2.453	2.300	2.149	2.002	1.861	1.732	1.623	1.536	1.486
9000	2.418	2.267	2.113	1.963	1.819	1.682	1.567	1.467	1.398
10,000	2.390	2.239	2.086	1.932	1.786	1.647	1.522	1.413	1.333

TABLE II. MOLAL VOLUMES FOR MIXTURES OF METHANE AND n-HEPTANE (Contd.)

Pressure, Lb./Sq.Inch Absolute	Mole Fraction Methane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
					460° F.				
Dew point[a]	(302)	(353)	(428)	(558)					
Estimated	19	18	16	13					
Bubble point[a]	(541)	(822)	(1058)	(1193)					
	3.70	3.62	3.63	4.04					
200	31	38	42	44	46.2	47.4	48.2	48.7	49.0
400			18	20	21.6	22.7	23.51	23.04	24.38
600	3.62				13.4	14.6	15.34	15.02	16.18
800	3.46				9.29	10.4	11.24	11.12	12.08
1000	3.33	3.46			7.06	8.16	8.83	8.78	9.61
1250	3.22	3.29	3.45	3.85	5.48	6.36	6.93	6.95	7.66
1500	3.14	3.14	3.26	3.49	4.50	5.20	5.70	5.73	6.36
1750	3.08	3.04	3.11	3.28	3.78	4.38	4.83	4.90	5.46
2000	3.02	2.960	2.982	3.10	3.30	3.73	4.19	4.53	4.79
2250	2.980	2.898	2.884	2.936	3.09	3.40	3.75	4.03	4.28
2500	2.937	2.849	2.805	2.805	2.898	3.15	3.43	3.66	3.88
2750	2.897	2.801	2.735	2.705	2.758	2.916	3.15	3.37	3.55
3000	2.863	2.758	2.677	2.627	2.641	2.750	2.927	3.10	3.26
3500	2.807	2.692	2.578	2.504	2.484	2.519	2.605	2.715	2.838
4000	2.758	2.632	2.508	2.416	2.364	2.360	2.390	2.449	2.529
4500	2.719	2.585	2.454	2.348	2.274	2.234	2.227	2.253	2.305
5000	2.682	2.547	2.412	2.292	2.198	2.136	2.102	2.103	2.130
6000	2.620	2.480	2.337	2.202	2.084	1.989	1.921	1.885	1.876
7000	2.575	2.427	2.278	2.135	2.003	1.888	1.798	1.738	1.698
8000	2.528	2.378	2.226	2.081	1.943	1.815	1.709	1.630	1.568
9000	2.488	2.339	2.186	2.036	1.891	1.756	1.642	1.550	1.473
10,000	2.454	2.304	2.148	1.996	1.848	1.708	1.586	1.483	1.394

a Values in parentheses represent dew-point or bubble-point pressures.
b Retrograde dew point.

TABLE III. ANALYSIS OF GAS PHASE FROM HETEROGENEOUS EQUILIBRIUM

Temperature, ° F.	Pressure, Lb./Sq. Inch Absolute	Mole Fraction Methane
40	220.7	0.9972
	976.6	0.9972
	2433.7	0.9816
	3093.7	0.9428
100	375.2	0.9887
	371.9	0.9912
	212.0	0.9889
	1028.0	0.9926
	2512.3	0.9739
	3075.5	0.9495
160	241.7	0.9653
	1021.1	0.9821
	2444.0	0.9613
	3058.6	0.9310
220	200.7	0.8941
	981.3	0.9569
	2501.4	0.9289
	3097.0	0.8719
280	1021.8	0.9111
	2035.0	0.8990
	2752.1	0.8282
340	223.4	0.5606
	951.1	0.8256
	1515.3	0.8361
	2188.4	0.7830
400	297.2	0.4017
	989.9	0.6919
	1484.2	0.6956

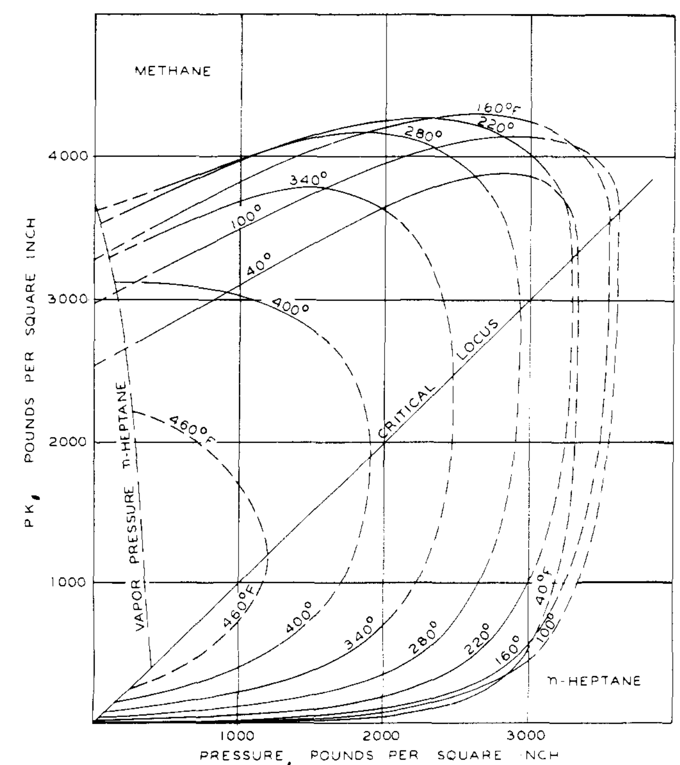

Figure 3. Equilibrium ratios for methane and n-heptane

The compositions of the coexisting liquid and gas phases were obtained from the experimentally measured composition of the gas phase (Table III) and the composition of the bubble-point states which were established from the volumetric data and which are shown in Figure 2. The properties of the bubble-point and dew-point states are recorded in Table IV for even values of pressure for each of the temperatures investigated. For the convenience of the reader, values of the equilibrium ratios for methane and n-heptane were included in Table IV. The critical volumes were obtained by extrapolation and involve much greater uncertainties than the other volumetric data. The product of the pressure and the equilibrium ratio is presented in Figure 3 as a function of pressure for both components of this binary system. The behavior was similar to that encountered with other binary systems containing methane (14, 17, 18).

Table V records a number of the properties at the unique states in the heterogeneous region. Pressure and temperature associated with the points of maximum pressure and temperature and the critical state are presented for a series of even-valued compositions. The information presented in Table V involves much larger uncertainties than that recorded in Tables II or IV since it resulted from interpolation of the volumetric and phase equilibrium data. Uncertainties in pressure may be as large as 5% and 30° F. in temperatures. The probable error is much smaller but cannot be established with certainty.

The compositions of the coexisting phases obtained from the measurements of Boomer and Johnson (3) have been compared with the present data in Table VI. The

TABLE IV. PROPERTIES OF THE COEXISTING GAS AND LIQUID PHASES

Pressure, Lb./Sq. Inch Absolute	Dew Point		Bubble Point		Equilibrium Ratio	
	Mole fraction methane	Volume, cu.ft./lb. mole[b]	Mole fraction methane	Volume, cu.ft./lb. mole	Methane	n-Heptane
			40° F.			
0.325[a]	0	-	0	2.302	-	1.0000
200	0.9964	26	0.0753	2.186	13.240	0.0039
400	0.9974	13	0.1445	2.083	6.900	0.0035
600	0.9971	8.1	0.2084	1.990	4.785	0.0037
800	0.9970	5.86	0.2670	1.902	3.734	0.0041
1000	0.9966	4.54	0.3215	1.819	3.100	0.0050
1250	0.9957	3.48	0.3840	1.723	2.593	0.0070
1500	0.9940	2.785	0.4410	1.640	2.254	0.0107
1750	0.9920	2.291	0.4930	1.569	2.012	0.0158
2000	0.9890	1.929	0.5425	1.501	1.823	0.0240
2250	0.9850	1.672	0.5900	1.440	1.670	0.0366
2500	0.9780	1.506	0.6373	1.375	1.535	0.0609
2750	0.9690	1.401	0.6870	1.315	1.410	0.0990
3000	0.9530	1.287	0.7400	1.254	1.288	0.1808
3328[c]	0.894	1.182	0.894	1.182	1.000	1.0000
897[d]	0.997	-	-	-		
3328[e]	-	-	0.894	-		
			100° F.			
1.58[a]	0	-	0	2.397	-	1.0000
200	0.9866	29[b]	0.0640	2.301	15.416	0.0143
400	0.9905	14	0.1240	2.212	7.988	0.0114
600	0.9911	9.3	0.1810	2.129	5.476	0.0111
800	0.9911	6.9	0.2340	2.048	4.235	0.0117
1000	0.9910	5.39	0.2842	1.972	3.487	0.0126
1250	0.9900	4.23	0.3425	1.884	2.891	0.0152
1500	0.9881	3.45	0.3963	1.802	2.493	0.0199
1750	0.9850	2.902	0.4470	1.725	2.204	0.0271
2000	0.9801	2.494	0.4950	1.658	1.980	0.0398
2250	0.9748	2.185	0.5435	1.591	1.794	0.0552
2500	0.9690	1.948	0.5905	1.525	1.641	0.0757
2750	0.9620	1.766	0.6400	1.459	1.503	0.1056
3000	0.9530	1.620	0.6910	1.400	1.379	0.1521
3500	0.9050	1.387	0.8030	1.312	1.127	0.4822
3609[c]	0.8550	1.315	0.8550	1.315	1.000	1.0000
989[d]	0.991	-	-	-		
3609[e]	-	-	0.8550	-		
			160° F.			
6.11[a]	0	-	0	2.508	-	1.0000
200	0.9597	32	0.0565	2.423	16.986	0.0427
400	0.9733	16	0.1110	2.338	8.768	0.0300
600	0.9780	10	0.1623	2.263	6.026	0.0263
800	0.9798	7.7	0.2107	2.186	4.650	0.0256
1000	0.9804	6.1	0.2567	2.117	3.819	0.0264
1250	0.9795	4.84	0.3108	2.032	3.152	0.0297
1500	0.9770	3.98	0.3620	1.953	2.699	0.0360
1750	0.9742	3.37	0.4125	1.878	2.362	0.0439
2000	0.9705	2.915	0.4620	1.809	2.101	0.0548
2250	0.9656	2.560	0.5090	1.746	1.897	0.0701
2500	0.9590	2.276	0.5580	1.688	1.719	0.0928
2750	0.9490	2.043	0.6070	1.637	1.563	0.1298
3000	0.9360	1.850	0.6610	1.586	1.416	0.1888
3500	0.8595	1.546	0.7870	1.501	1.092	0.6596
3549[c]	0.817	1.501	0.817	1.501	1.000	1.0000
1085[d]	0.981	-	-	-		
3452[e]	-	-	0.770	-		
			220° F.			
17.48[a]	0	-	0	2.644	-	1.0000
200	0.8942	35	0.0494	2.568	18.101	0.1113
400	0.9305	17	0.1003	2.484	9.277	0.0772
600	0.9449	11	0.1492	2.409	6.333	0.0648
800	0.9517	8.6	0.1960	2.338	4.856	0.0601
1000	0.9558	6.8	0.2410	2.267	3.966	0.0582
1250	0.9566	5.42	0.2940	2.183	3.254	0.0613
1500	0.9564	4.46	0.3450	2.101	2.772	0.0665
1750	0.9532	3.78	0.3957	2.024	2.409	0.0774
2000	0.9474	3.28	0.4457	1.954	2.126	0.0949
2250	0.9392	2.877	0.4944	1.891	1.900	0.1203
2500	0.9280	2.553	0.5450	1.834	1.703	0.1582

TABLE IV. PROPERTIES OF THE COEXISTING GAS AND LIQUID PHASES (Contd.)

Pressure, Lb./Sq. Inch Absolute	Dew Point		Bubble Point		Equilibrium Ratio	
	Mole fraction methane	Volume, cu.ft./lb. mole[b]	Mole fraction methane	Volume, cu.ft./lb. mole	Methane	n-Heptane
			220° F. (Contd.)			
2750	0.9120	2.285	0.5995	1.784	1.521	0.2197
3000	0.8864	2.056	0.6615	1.746	1.340	0.3356
3298[c]	0.778	1.766	0.778	1.766	1.000	1.0000
1182[d]	0.958	-	-	-		
2858[e]	-	-	0.623	-		
			280° F.			
40.96[a]	0	-	0	2.804	-	1.0000
200	0.7481	37	0.0405	2.735	18.472	0.2625
400	0.8628	19	0.0918	2.655	9.403	0.1511
600	0.8894	12	0.1390	2.584	6.399	0.1285
800	0.9037	9.2	0.1850	2.514	4.885	0.1182
1000	0.9100	7.3	0.2290	2.444	3.956	0.1167
1250	0.9120	5.72	0.2810	2.363	3.246	0.1224
1500	0.9107	4.69	0.3308	2.286	2.753	0.1334
1750	0.9073	3.96	0.3810	2.215	2.381	0.1498
2000	0.9000	3.40	0.4329	2.154	2.079	0.1763
2250	0.8900	2.972	0.4880	2.100	1.824	0.2148
2500	0.8660	2.621	0.5446	2.048	1.590	0.2942
2750	0.8280	2.330	0.6150	2.014	1.346	0.4468
2927[c]	0.732	2.091	0.732	2.091	1.000	1.0000
1281[d]	0.912	-	-	-		
2146[e]	-	-	0.464	-		
			340° F.			
83.2[a]	0	-	0	3.01	-	1.0000
200	0.5100	38	0.0305	2.953	16.721	0.5107
400	0.7220	19	0.0840	2.866	8.595	0.3045
600	0.7750	13	0.1317	2.798	5.882	0.2591
800	0.8060	9.6	0.1786	2.734	4.513	0.2386
1000	0.8260	7.6	0.2240	2.672	3.688	0.2242
1250	0.8369	6.0	0.2780	2.598	3.010	0.2259
1500	0.8360	4.88	0.3316	2.529	2.521	0.2454
1750	0.8250	4.07	0.3850	2.465	2.143	0.2846
2000	0.8040	3.46	0.4431	2.400	1.814	0.3519
2250	0.7730	2.977	0.5165	2.346	1.497	0.4695
2469[c]	0.6720	2.486	0.672	2.486	1.000	1.0000
1334[d]	0.8380	-	-	-		
1401[e]	-	-	0.315	-		
			400° F.			
151.4[a]	0	-	0	3.32	-	1.0000
200	0.2060	35[b]	0.0132	3.29	15.606	0.8046
400	0.5223	19	0.0670	3.20	7.796	0.5120
600	0.6210	13	0.1200	3.12	5.175	0.4307
800	0.6700	9.7	0.1740	3.06	3.851	0.3995
1000	0.6930	7.7	0.2290	3.02	3.026	0.3982
1250	0.6990	6.0	0.2980	2.975	2.354	0.4282
1500	0.6940	4.90	0.3725	2.962	1.863	0.4876
1750	0.6690	4.05	0.4620	2.981	1.448	0.6152
1906[c]	0.585	3.30	0.585	3.30	1.000	1.0000
1299[d]	0.699	-	0.699	-		
870[e]	-	-	-	-		
			460° F.			
257.8[a]	0	-	0	3.87	-	1.0000
400	0.2640	17[b]	0.0485	3.78	5.443	0.7735
600	0.4199	12	0.1205	3.68	3.485	0.6595
800	0.4670	8.8	0.1918	3.62	2.435	0.6595
1000	0.4750	6.7	0.2730	3.61	1.703	0.7282
1206[c]	0.441	4.50	0.441	4.50	1.000	1.0000
1025[d]	0.475	-	0.475	-		
517[c]	-	-	-	-		

[a] Vapor pressure of n-heptane.
[b] Volumes at dew point calculated.
[c] Critical state.
[d] Maximum two-phase temperature for a fixed composition.
[e] Maximum two-phase pressure for a fixed composition.

TABLE V. PROPERTIES AT THE UNIQUE STATES IN THE METHANE-n-HEPTANE SYSTEM[a]

Mole Fraction Methane	Critical Pressure, lb./sq.inch	Critical Temperature, °F.	Maxcondentherm Pressure, lb./sq.inch	Maxcondentherm Temperature, °F.	Maximum Pressure Pressure, lb./sq.inch	Maximum Pressure Temperature, °F.
0.0	396.7[b]	512.6[b]	396.7	512.6	396.7	512.6
0.1	510	506	510	506	542	454
0.2	648	497	640	498	898	396
0.3	830	486	795	486	1351	344
0.4	1070	469	920	474	1840	304
0.5	1459	440	1068	454	2315	267
0.6	2000	391	1199	431	2757	229
0.7	2675	315	1300	399	3178	189
0.8	3474	184	1335	359	3540	146
0.9	3250	31	1300	292		
1.0	673[b]	-116[b]	673	-116	673	-116

[a] These data are much more uncertain than the directly measured quantities.
[b] Taken from Rossini (16).

presence of nitrogen in their mixtures would be expected to cause a marked difference, as was found. These data were corrected to a nitrogen-free basis by C. A. Johnson and are also included for comparison in Table VI. The agreement is materially improved.

The measurements of Boomer and Johnson were interpolated to even values of pressure and temperature in order to permit a direct comparison with the data of Table IV. A limited number of values of specific volume were reported (3) although Boomer and Johnson did not indicate that their volumetric measurements were obtained with accuracy. The volumetric data indicate a large, although not unexpected, difference between the earlier measurements (3) and those of the present investigation when nitrogen was involved. The single mixture from Boomer and Johnson's work (3), containing only 0.005 mole fraction nitrogen, gave much better agreement of the volumetric data, as would be expected. No phase equilibrium data were obtained (3) for the mixture containing only traces of nitrogen. These measurements (3) were only obtained at a single temperature and therefore were not included in the comparison of Table VI.

ACKNOWLEDGMENT

This paper is a contribution from American Petroleum Institute Research Project 37 at the California Institute of Technology. Virginia Berry and June Gray assisted with the reduction of the experimental data to a form suitable for publication and E. E. Black with the experimental measurements. The information made available by C. A. Johnson and reported in Table VI is acknowledged.

TABLE VI. COMPARISON OF PRESENT DATA WITH MEASUREMENTS OF OTHER INVESTIGATORS

Pressure Lb./Sq.Inch	Mole Fraction Methane, Gas Phase: Authors	Boomer[a]	Boomer[b]	Liquid Phase: Authors	Boomer[a]	Boomer[b]
100° F.						
1000	0.991	0.927	0.983	0.284	0.273	0.275
1500	0.988	0.923	0.985	0.396	0.368	0.390
2000	0.980	0.917	0.982	0.495	0.451	0.488
2500	0.969	0.909	0.967	0.590	0.532	0.577
3000	0.953	0.895	0.944	0.691	0.611	0.672
3500	0.905	0.815	0.907	0.803	0.700	0.774
160° F.						
1000	0.980	0.919	0.963	0.257	0.267	0.242
1500	0.977	0.915	0.962	0.362	0.349	0.350
2000	0.970	0.907	0.950	0.462	0.427	0.445
2500	0.959	0.894	0.920	0.558	0.506	0.535
3000	0.936	0.876	0.875	0.661	0.584	0.655
3500	0.860	0.791		0.787	0.690	

[a] Boomer's measurements (3) involved a system containing significant quantities of nitrogen.
[b] Corrected by C. A. Johnson for the presence of nitrogen.

LITERATURE CITED

(1) Beattie, J. A., Kay, W. C., J. Am. Chem. Soc. 59, 1586 (1937).
(2) Boomer, E. H., Johnson, C. A., Argue, G. H. Can. J. Research, B, 15, 367 (1937).
(3) Boomer, E. H., Johnson, C. A., Piercey, A. G. A., Ibid., 396 (1938).
(4) Bridgeman, O. C., J. Am. Chem. Soc. 49, 1174 (1927).
(5) Budenholzer, R. A., Sage, B. H., Lacey, W. N., Ind. Eng. Chem. 32, 384 (1940).
(6) Eduljee, H. E., Newitt, D. M., Weale, K. E., J. Chem. Soc. 1951, 3086.
(7) Keyes, F. G., Burks, H. G., Ibid., 49, 1403 (1927).
(8) Kvalnes, H. M., Gaddy, V. L., Ibid., 53, 394 (1931).
(9) Michels, A., Nederbragt, G. W., Physica, 3, 569 (1936).
(10) Nichols, W. B., Reamer, H. H., Sage, B. H., Ind. Eng. Chem. 47, 2219 (1955).
(11) Olds, R. H., Reamer, H. H., Sage, B. H., Lacey, W. N., Ibid., 35, 922 (1943).
(12) Reamer, H. H., Olds, R. H., Sage, B. H., Lacey, W. N., Ibid., 34, 1526 (1942).
(13) Reamer, H. H., Sage, B. H., Lacey, W. N., Ibid., 41, 482 (1949).
(14) Ibid., 42, 534 (1950).
(15) Rossini, F. D., Pitzer, K. S., Arnett, R. L., Braun, R. M., Pimentel, G. C., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, 1953.
(16) Sage, B. H., Budenholzer, R. A., Lacey, W. N., Ind. Eng. Chem. 32, 1262 (1940).
(17) Sage, B. H., Lacey, W. N., "Some Properties of the Lighter Hydrocarbons, Hydrogen Sulfide, and Carbon Dioxide," American Petroleum Institute, New York, 1955.
(18) Sage, B. H., Lacey, W. N., "Thermodynamic Properties of the Lighter Paraffin Hydrocarbons and Nitrogen," Ibid., 1950.
(19) Sage, B. H., Lacey, W. N., Trans. AIME, 136, 136 (1940).
(20) Smith, L. B., Beattie, J. A., Kay, W. C., J. Am. Chem. Soc. 59, 1587 (1937).
(21) Vold, R. D., Ibid., 57, 1192 (1935).

Received for review December 20, 1955 Accepted May 7, 1956

Ethyl Alcohol–Water with 2,2,4-Trimethylpentane and with 1-Octene at 0° and 25° C.

JANINA NOWAKOWSKA, CARL B. KRETSCHMER, AND RICHARD WIEBE
Northern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture, Peoria, Ill.

In exploring the use of ethyl alcohol as a gasoline additive for preventing carburetor icing, it was desirable to obtain information on the amount of alcohol that would be extracted from the gasoline by water layer always present in the bottoms of storage tanks. The distribution of ethyl alcohol between water and the pure hydrocarbons 2,2,4-trimethylpentane and 1-octene was determined at temperatures of 0° and 25° C.

EXPERIMENTAL MATERIALS AND METHODS

2,2,4-Trimethylpentane of certified knock-rating grade was fractionated in an efficient column and, in order to remove olefins, was filtered through a long tube packed with silica gel. Its density at 25° C. was 0.68774 gram per ml. The accepted value is 0.68777 (1).

1-Octene, Phillips pure grade specified as better than 99 mole % pure, was used without further treatment. Its density was 0.71078 gram per ml. at 25° C. The accepted value is 0.71085 (1).

The commercial absolute ethyl alcohol had a density of 0.78597 gram per ml. at 25° C., corresponding to a water content of 0.30% by weight (4). This water content was taken into account in calculating the composition of the solutions.

Distilled water was taken from the laboratory supply.

The experimental procedure was adapted mainly from that used by Washburn and coworkers in their study of alcohol-water-hydrocarbon systems (8). We obtained solubility data for the ethyl alcohol–water-benzene system, not included here, which were in good agreement with those found by Washburn.

Points on the binodal curves were determined by titrating a known mixture of two components with the third component until turbidity appeared or disappeared. The mixtures were made by volume with calibrated pipets and burets, and their composition was converted to weight percent by using the densities previously mentioned. Over most of the composition range, ethyl alcohol–hydrocarbon mixtures were titrated with water. At the lower end of the water-rich part of the binodal curve, better results were obtained by titrating ethyl alcohol into a two-phase mixture of water and hydrocarbon until a homogeneous solution was obtained.

For the 25° C. isotherm, the end point was taken as that composition which would remain homogeneous in a bath maintained at 25.0°, but would become turbid when placed in a bath maintained at 24.8° C. The titrations at 0° C. were performed in small conical flasks supported in a bath of ice and water contained in a large unsilvered Dewar vessel. The solutions were stirred with a magnetic stirring apparatus, placed next to the Dewar vessel, with its rotating magnet in the same plane as the bottom of the titration flask which contained a small magnetized stirring bar. By this arrangement, enough power was transmitted to provide adequate stirring. The solution was observed

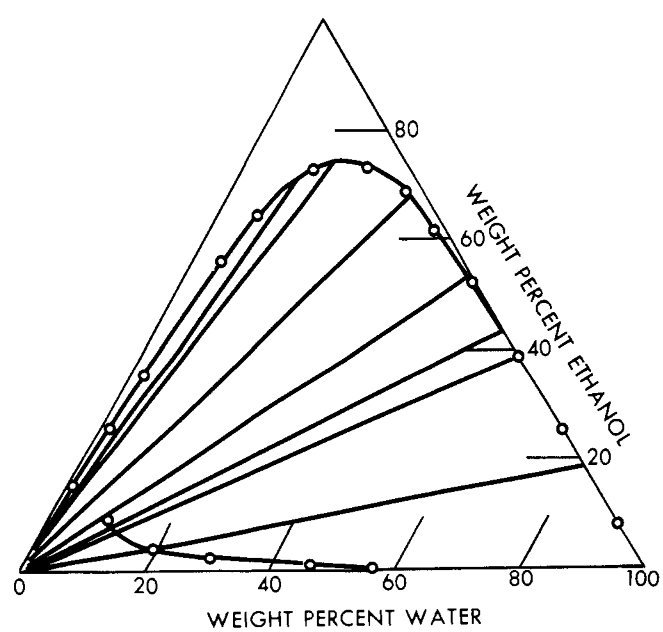

Figure 1. Triangular diagram for 2,2,4-trimethylpentane at 25° C.