Part I

PHASE EQUILIBRIA
MOLECULAR TRANSPORT
THERMODYNAMICS

Partial Volumetric Behavior in Hydrocarbon Systems

Methane and *n*-Heptane in the Liquid Phase of the Methane–*n*-Heptane System

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The concept of a partial quantity was originally proposed by G. N. Lewis (*2*) in connection with a system of thermodynamics. A graphical method for the evaluation of partial volume was first developed by Roozeboom (*8*) and later described by Lewis (*3*). The significance of the partial volume with especial reference to the concept of variable weight systems was discussed in an earlier paper (*9*).

For present purposes the partial volume is defined by the equation,

$$\bar{V} = \left(\frac{\partial \underline{V}}{\partial m_k}\right)_{T,P,m_j} \tag{1}$$

It is convenient in the case of the liquid phase of binary systems to evaluate the partial molal volume (hereafter referred to as partial volume) directly from the volumetric information concerning a system of unit weight by the following relationship:

$$\bar{V}_k = V + (1 - n_k)\left(\frac{\partial V}{\partial n_k}\right)_{T,P,m_j} \tag{2}$$

Equation 2 is particularly useful at mole fractions approaching unity for the component in question and becomes more difficult to apply with precision at compositions approaching infinite dilution for that component. For this reason, in the present instance the partial volumetric data for methane at mole fractions of methane greater than 0.5 were obtained by direct evaluation from Equation 2. A similar procedure was followed to determine the partial volume of *n*-heptane. Partial volumetric data for methane and *n*-heptane, when the respective mole fractions were less than 0.5, were established from the relation,

$$\bar{V}_k = \frac{V - n_j \bar{V}_j}{n_k} \tag{3}$$

In addition, the values of the partial quantities were checked for consistency by use of the conventional Gibbs-Duhem equation, written for partial volumes as

$$n_k\left(\frac{\partial \bar{V}_k}{\partial n_k}\right)_{T,P} = n_j\left(\frac{\partial \bar{V}_j}{\partial n_j}\right)_{T,P} \tag{4}$$

In a number of cases it proved advantageous to integrate Equation 4 over a range of compositions in order to obtain more accurate values of one or the other partial volume. These integrations were carried out for isobaric, isothermal conditions.

An over-all check of the graphical method indicates that for the most part the results satisfy Equations 2, 3, and 4 with an uncertainty of 1%, except for partial volumes of components near infinite dilution, when the uncertainty may be as large as 2.5%. The foregoing discussion of accuracy relates only to the graphical procedure utilized in evaluating the partial quantities. The measures of uncertainty indicated do not include errors other than those directly associated with the graphical operations. Specifically they do not include uncertainties associated with the experimental data.

The volumetric behavior of methane has been carefully investigated by Michels and Nederbragt (*4*), and by Reamer and others (*6*), and probably does not involve uncertainties greater than 0.2% throughout the range of conditions covered in this evaluation. Recently the volumetric behavior of *n*-heptane in the liquid phase was studied within the same range of temperatures and pressures (*5*). The agreement of these measurements with those of other investigators (*1*, *10*) indicates that the probable uncertainty in values of the molal volume of *n*-heptane in the liquid phase is not more than 0.2% throughout the range of temperatures and pressures of interest.

An investigation of the volumetric and phase behavior of the methane–*n*-heptane system has been made (*7*) recently. It is probable that the molal volumes of the four mixtures of methane and *n*-heptane investigated do not involve uncertainties in the molal volume greater than 0.3% over the range of temperatures and pressures of interest. These data, together with the volumetric behavior of methane and *n*-heptane, yield a consistent basis for establishing the partial volumes of methane and *n*-heptane in the liquid phase.

The data were plotted upon large-scale diagrams representing the isothermal, isobaric change in molal volume with respect to mole fraction of methane. By the application of Equation 2, the appropriate values of partial volumes of methane and *n*-heptane were established graphically. In the region where Equation 2 was not particularly effective, Equation 3 was employed. The final values appear to correspond to the actual partial volumetric behavior of the system with probable uncertainties of not more than 1.5%

for compositions containing more than 0.5 mole fraction of the compound of interest and with uncertainties progressively increasing to as much as 3% for states corresponding to infinite dilution. The data, however, are consistent as far as Equation 2 is concerned within 0.2%. Smoothed values of the partial volume of methane are set forth in Table I for the entire composition interval, for temperatures from 40° to 460°F. and at pressures up to 10,000 pounds per square inch. The partial volume of *n*-heptane in the liquid phase of the methane-*n*-heptane system is presented in Table II for the same ranges of states. The probable error for states adjacent to the heterogeneous regions or near the critical state of the system is larger than that indicated above. The detail of the experimental data was not such as to permit the partial volumes to be

Table I. Partial Volume of Methane in Liquid Phase of Methane–*n*-Heptane System

Pressure, P.S.I.A.	Mole Fraction Methane 0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
40° F.									
Bubble Point	(269)[a] 0.85[b]	(572) 0.85	(919) 0.86	(1319) 0.871	(1781) 0.898	(2302) 0.942	(2817) 1.010	(3198) 1.108	(3320) 1.252
200	...	...	...	...	...	...	...	...	...
400	0.84[b]	...	...	...	...	...	...	...	...
600	0.83	0.85	...	...	...	...	...	...	...
800	0.82	0.84	...	...	...	...	...	...	...
1,000	0.81	0.83	0.85	...	...	...	...	...	...
1,250	0.80	0.82	0.84	...	...	...	...	...	...
1,500	0.80	0.81	0.83	0.862	...	...	...	...	...
1,750	0.79	0.80	0.82	0.854	...	...	...	...	...
2,000	0.78	0.80	0.82	0.846	0.891	...	...	...	...
2,250	0.78	0.79	0.81	0.839	0.883	...	...	...	...
2,500	0.77	0.78	0.80	0.832	0.875	0.934	...	...	...
2,750	0.77	0.78	0.80	0.827	0.868	0.925	...	...	...
3,000	0.76	0.77	0.79	0.821	0.861	0.917	0.998	...	...
3,500	0.75	0.76	0.78	0.812	0.851	0.903	0.973	1.080	1.192
4,000	0.75	0.76	0.77	0.804	0.842	0.890	0.951	1.034	1.102
4,500	0.74	0.75	0.77	0.797	0.832	0.878	0.932	0.995	1.046
5,000	0.73	0.74	0.76	0.789	0.824	0.868	0.915	0.963	1.004
6,000	0.72	0.73	0.75	0.778	0.808	0.848	0.883	0.916	0.941
7,000	0.70	0.72	0.74	0.764	0.793	0.826	0.851	0.877	0.893
8,000	0.69	0.71	0.73	0.753	0.779	0.807	0.829	0.849	0.860
9,000	0.68	0.70	0.72	0.741	0.767	0.792	0.812	0.824	0.831
10,000	0.67	0.69	0.71	0.730	0.753	0.776	0.790	0.800	0.805
100° F.									
Bubble Point	(318)[a] 0.96[b]	(669) 0.96	(1068) 0.97	(1518) 0.981	(2026) 1.014	(2549) 1.075	(3048) 1.179	(3490) 1.348	(3525) ...
200	...	...	...	...	...	...	...	...	...
400	0.96[b]	...	...	...	...	...	...	...	...
600	0.95	...	...	...	...	...	...	...	...
800	0.94	0.96	...	...	...	...	...	...	...
1,000	0.93	0.95	...	...	...	...	...	...	...
1,250	0.92	0.94	0.96	...	...	...	...	...	...
1,500	0.91	0.92	0.95	...	...	...	...	...	...
1,750	0.90	0.91	0.93	0.962	...	...	...	...	...
2,000	0.89	0.90	0.92	0.946	...	...	...	...	...
2,250	0.88	0.89	0.91	0.933	0.993	...	...	...	...
2,500	0.88	0.88	0.90	0.924	0.974	...	...	...	...
2,750	0.87	0.88	0.89	0.912	0.958	1.060	...	...	...
3,000	0.86	0.87	0.88	0.903	0.945	1.041	...	...	...
3,500	0.85	0.86	0.87	0.890	0.924	1.007	1.134	1.345	...
4,000	0.84	0.85	0.86	0.880	0.909	0.975	1.087	1.232	1.322
4,500	0.83	0.84	0.85	0.870	0.898	0.950	1.044	1.166	1.225
5,000	0.82	0.83	0.84	0.861	0.885	0.927	1.004	1.109	1.161
6,000	0.81	0.82	0.83	0.845	0.864	0.887	0.941	1.013	1.063
7,000	0.80	0.81	0.82	0.830	0.844	0.858	0.890	0.946	0.990
8,000	0.79	0.79	0.80	0.815	0.826	0.838	0.863	0.898	0.933
9,000	0.78	0.78	0.79	0.799	0.804	0.819	0.838	0.866	0.892
10,000	0.77	0.77	0.78	0.786	0.791	0.800	0.816	0.842	0.863
160° F.									
Bubble Point	(358)[a] 1.11[b]	(753) 1.12	(1199) 1.094	(1689) 1.126	(2202) 1.193	(2719) 1.299	(3178) 1.440	(3529) 1.617	(3325) 1.823
200	...	...	...	...	...	...	...	...	...
400	1.11[b]	...	...	...	...	...	...	...	...
600	1.09	...	...	...	...	...	...	...	...
800	1.08	1.12	...	...	...	...	...	...	...
1,000	1.07	1.10	...	...	...	...	...	...	...
1,250	1.06	1.08	1.09	...	...	...	...	...	...
1,500	1.04	1.07	1.07	...	...	...	...	...	...
1,750	1.03	1.05	1.06	1.117	...	...	...	...	...
2,000	1.01	1.04	1.04	1.092	...	...	...	...	...
2,250	1.00	1.02	1.03	1.070	1.184	...	...	...	...
2,500	0.99	1.02	1.01	1.051	1.151	...	...	...	...
2,750	0.97	1.00	1.00	1.035	1.121	1.297	...	...	...
3,000	0.96	0.99	0.99	1.020	1.095	1.263	...	...	...
3,500	0.94	0.96	0.96	0.994	1.051	1.199	1.369	...	1.745
4,000	0.92	0.94	0.94	0.973	1.017	1.139	1.275	1.431	1.547
4,500	0.90	0.92	0.93	0.953	0.989	1.084	1.196	1.329	1.414
5,000	0.89	0.90	0.92	0.935	0.965	1.039	1.134	1.252	1.323
6,000	0.86	0.88	0.89	0.908	0.930	0.977	1.046	1.129	1.190
7,000	0.84	0.85	0.87	0.885	0.903	0.933	0.982	1.047	1.090
8,000	0.81	0.83	0.85	0.863	0.879	0.900	0.937	0.985	1.020
9,000	0.80	0.81	0.82	0.838	0.855	0.873	0.901	0.936	0.964
10,000	0.78	0.79	0.81	0.819	0.833	0.847	0.870	0.900	0.927
220° F.									
Bubble Point	(399)[a] 1.24[b]	(818) 1.25	(1279) 1.27	(1777) 1.319	(2278) 1.446	(2754) 1.614	(3139) 1.820	(3286) 2.122	(2883) ...
200	...	...	...	...	...	...	...	...	...
400	1.24[b]	...	...	...	...	...	...	...	...
600	1.22	...	...	...	...	...	...	...	...
800	1.20	...	...	...	...	...	...	...	...
1,000	1.18	1.23	...	...	...	...	...	...	...
1,250	1.16	1.21	...	...	...	...	...	...	...
1,500	1.14	1.18	1.24	...	...	...	...	...	...
1,750	1.13	1.16	1.22	...	...	...	...	...	...
2,000	1.11	1.14	1.19	1.284	...	...	...	...	...
2,250	1.09	1.12	1.17	1.252	...	...	...	...	...
2,500	1.07	1.11	1.15	1.224	1.403	...	...	...	...
2,750	1.05	1.09	1.13	1.196	1.356	...	...	...	...
3,000	1.04	1.07	1.11	1.170	1.310	1.561	...	...	...
3,500	1.02	1.04	1.07	1.125	1.227	1.447	1.669	1.868	1.996
4,000	0.99	1.01	1.04	1.085	1.158	1.343	1.508	1.656	1.782
4,500	0.97	0.99	1.02	1.052	1.106	1.244	1.393	1.522	1.613
5,000	0.96	0.97	0.99	1.024	1.066	1.170	1.300	1.414	1.493
6,000	0.92	0.94	0.96	0.982	1.012	1.091	1.178	1.262	1.324
7,000	0.90	0.91	0.93	0.948	0.972	1.023	1.091	1.157	1.201
8,000	0.88	0.89	0.90	0.919	0.938	0.980	1.028	1.078	1.116
9,000	0.86	0.87	0.88	0.892	0.908	0.938	0.976	1.015	1.051
10,000	0.84	0.85	0.85	0.866	0.880	0.898	0.929	0.965	0.998
280° F.									
Bubble Point	(436)[a] 1.55[b]	(868) 1.56	(1349) 1.58	(1847) 1.631	(2304) 1.841	(2702) 2.134	(2912) 2.351	(2842) ...	(2012) ...
200	...	...	...	...	...	...	...	...	...
400	...	...	...	...	...	...	...	...	...
600	1.53[b]	...	...	...	...	...	...	...	...
800	1.49	...	...	...	...	...	...	...	...
1,000	1.46	1.53	...	...	...	...	...	...	...
1,250	1.42	1.48	...	...	...	...	...	...	...
1,500	1.38	1.44	1.54	...	...	...	...	...	...
1,750	1.35	1.40	1.48	...	...	...	...	...	...
2,000	1.31	1.36	1.43	1.582	...	...	...	...	...
2,250	1.28	1.32	1.39	1.514	...	...	...	...	...
2,500	1.25	1.29	1.35	1.458	1.769	...	...	...	...
2,750	1.22	1.26	1.31	1.405	1.656	2.094	...	...	...
3,000	1.20	1.22	1.28	1.360	1.583	1.953	2.313	...	...
3,500	1.15	1.17	1.22	1.286	1.446	1.729	1.974	2.149	2.253
4,000	1.12	1.14	1.17	1.230	1.344	1.553	1.759	1.928	2.011
4,500	1.09	1.10	1.13	1.181	1.269	1.423	1.611	1.749	1.819
5,000	1.07	1.08	1.10	1.140	1.201	1.331	1.492	1.610	1.675
6,000	1.03	1.04	1.06	1.079	1.118	1.201	1.312	1.416	1.462
7,000	0.99	1.00	1.01	1.030	1.055	1.114	1.196	1.282	1.321
8,000	0.96	0.97	0.98	0.990	1.008	1.053	1.117	1.184	1.220
9,000	0.93	0.94	0.94	0.956	0.972	1.007	1.055	1.110	1.139
10,000	0.91	0.91	0.92	0.928	0.940	0.962	1.006	1.047	1.074
340° F.									
Bubble Point	(468)[a] 2.32[b]	(897) 2.35	(1351) 2.39	(1818) 2.450	(2198) 2.597	(2426) 2.992	(2448) 3.40	(2041) ...	... ...
200	...	...	...	...	...	...	...	...	...
400	...	...	...	...	...	...	...	...	...
600	2.23[b]	...	...	...	...	...	...	...	...
800	2.08	...	...	...	...	...	...	...	...
1,000	1.94	2.19	...	...	...	...	...	...	...
1,250	1.82	2.02	...	...	...	...	...	...	...
1,500	1.71	1.88	2.27	...	...	...	...	...	...
1,750	1.61	1.77	2.09	...	...	...	...	...	...
2,000	1.54	1.68	1.93	2.222	...	...	...	...	...
2,250	1.47	1.60	1.80	2.048	2.448	...	...	...	...
2,500	1.42	1.52	1.68	1.904	2.239	2.907	3.26	3.43	...
2,750	1.38	1.48	1.58	1.791	2.079	2.624	2.889	3.09	...
3,000	1.34	1.42	1.51	1.694	1.952	2.396	2.652	2.840	...
3,500	1.28	1.34	1.41	1.543	1.749	2.066	2.277	2.432	2.503
4,000	1.23	1.28	1.33	1.438	1.586	1.815	2.014	2.177	2.227
4,500	1.19	1.23	1.27	1.353	1.467	1.649	1.830	1.974	2.014
5,000	1.16	1.19	1.23	1.278	1.371	1.516	1.678	1.811	1.841
6,000	1.10	1.12	1.15	1.183	1.237	1.343	1.457	1.566	1.600
7,000	1.04	1.06	1.08	1.106	1.149	1.234	1.316	1.400	1.434
8,000	1.00	1.01	1.04	1.056	1.087	1.152	1.215	1.282	1.313
9,000	0.97	0.98	1.00	1.014	1.037	1.087	1.143	1.198	1.225
10,000	0.94	0.95	0.98	0.981	0.999	1.025	1.083	1.128	1.155
400° F.									
Bubble Point	(524)[a] 3.66[b]	(898) 3.71	(1262) 3.81	(1586) 3.96	(1829) 4.22	(1904) ...	... ...	... ...	... ...
200	...	...	...	...	...	...	...	...	...
400	...	...	...	...	...	...	...	...	...
600	3.24[b]	...	...	...	...	...	...	...	...
800	2.84	...	...	...	...	...	...	...	...
1,000	2.58	3.50	...	...	...	...	...	...	...
1,250	2.36	2.93	...	...	...	...	...	...	...
1,500	2.16	2.56	3.33	...	...	...	...	...	...
1,750	2.02	2.25	2.87	3.63	...	...	...	...	...
2,000	1.91	2.04	2.51	3.06	3.74	...	...	...	...
2,250	1.82	1.90	2.26	2.700	3.18	...	...	...	...
2,500	1.75	1.80	2.09	2.444	2.837	3.43	3.66	...	...
2,750	1.69	1.73	1.93	2.238	2.587	3.09	3.30	...	...
3,000	1.64	1.64	1.82	2.073	2.381	2.803	3.02	...	...
3,500	1.55	1.54	1.66	1.840	2.083	2.384	2.598	2.707	2.739
4,000	1.47	1.44	1.54	1.678	1.857	2.087	2.278	2.401	2.434
4,500	1.41	1.37	1.46	1.553	1.689	1.878	2.052	2.171	2.202
5,000	1.35	1.30	1.37	1.447	1.559	1.722	1.871	1.978	2.011
6,000	1.25	1.21	1.25	1.308	1.381	1.497	1.607	1.701	1.739
7,000	1.17	1.14	1.18	1.214	1.272	1.358	1.444	1.516	1.580
8,000	1.10	1.09	1.11	1.142	1.183	1.251	1.321	1.386	1.417
9,000	1.05	1.06	1.06	1.078	1.115	1.175	1.238	1.286	1.314
10,000	1.01	1.02	1.03	1.034	1.060	1.102	1.161	1.214	1.232

Table I. (*Continued*)

Pressure, P.S.I.A.	Mole Fraction Methane 0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
460° F.									
Bubble	(541)[a]	(822)	(1058)	(1192)	...	...	...	...	...
Point	6.33[b]	6.46	6.67	7.08	...	...	...	...	...
200	...	...	...	...	...	...	...	...	...
400	...	...	...	...	...	...	...	...	...
600	5.93[b]	...	...	...	...	...	...	...	...
800	4.69	...	...	...	...	...	...	...	...
1,000	4.00	5.66	...	...	...	...	...	...	...
1,250	3.09	4.56	5.83	7.05	...	...	...	...	...
1,500	2.68	3.63	4.82	5.79	...	...	...	...	...
1,750	2.44	3.06	4.06	4.97	...	...	...	...	...
2,000	2.25	2.68	3.44	4.24	4.85	...	...	...	...
2,250	2.10	2.44	3.00	3.63	4.22	4.72	...	...	...
2,500	1.97	2.23	2.67	3.16	3.68	4.14	...	...	...
2,750	1.87	2.07	2.41	2.838	3.27	3.62	...	...	...
3,000	1.78	1.94	2.22	2.584	2.940	3.25	3.46	...	...
3,500	1.65	1.76	1.93	2.212	2.519	2.745	2.912	2.997	...
4,000	1.55	1.63	1.75	1.958	2.202	2.401	2.541	2.621	2.645
4,500	1.48	1.53	1.63	1.775	1.971	2.140	2.261	2.341	2.380
5,000	1.42	1.46	1.54	1.631	1.789	1.939	2.051	2.130	2.172
6,000	1.32	1.34	1.37	1.438	1.546	1.660	1.756	1.828	1.874
7,000	1.24	1.24	1.27	1.320	1.393	1.475	1.567	1.629	1.665
8,000	1.17	1.17	1.19	1.229	1.287	1.351	1.427	1.485	1.514
9,000	1.12	1.12	1.13	1.150	1.198	1.254	1.325	1.378	1.403
10,000	1.08	1.08	1.08	1.093	1.123	1.179	1.241	1.287	1.311

[a] Bubble point pressure expressed in pounds per square inch.
[b] Partial volume expressed in cubic feet per pound mole.

established with the same accuracy in these regions as at other states remote from the phase boundaries or the critical state of the system.

To illustrate the influence of pressure, temperature, and composition upon the partial volumetric behavior of the components, several diagrams are presented. Figure 1 shows the influence of the mole fraction of methane upon the partial volume of this component at a temperature of

Table II. Partial Volume of *n*-Heptane in Liquid Phase of Methane-*n*-Heptane System

Pressure, P.S.I.A.	Mole Fraction *n*-Heptane 0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
40° F.									
Bubble	(3320)[a]	(3198)	(2817)	(2302)	(1781)	(1319)	(919)	(572)	(269)
Point	0.91[b]	1.57	1.97	2.149	2.214	2.250	2.274	2.289	2.296
200	...	...	...	...	...	...	...	...	...
400	...	...	...	...	...	...	...	...	2.294
600	...	...	...	...	...	...	...	2.289	2.290
800	...	...	...	...	...	...	...	2.288	2.286
1,000	...	...	...	...	...	...	2.272	2.284	2.283
1,250	...	...	...	...	...	...	2.269	2.282	2.278
1,500	...	...	...	...	...	2.247	2.263	2.278	2.273
1,750	...	...	...	...	...	2.244	2.258	2.272	2.269
2,000	...	...	...	...	2.213	2.240	2.254	2.267	2.265
2,250	...	...	...	...	2.209	2.236	2.250	2.262	2.261
2,500	...	...	...	2.147	2.205	2.232	2.245	2.258	2.256
2,750	...	...	...	2.145	2.202	2.229	2.241	2.254	2.253
3,000	...	...	1.98	2.142	2.199	2.226	2.238	2.248	2.249
3,500	0.91[b]	1.62	1.99	2.138	2.194	2.217	2.230	2.240	2.241
4,000	1.24	1.68	1.99	2.133	2.188	2.212	2.224	2.231	2.233
4,500	1.42	1.73	2.00	2.128	2.182	2.207	2.218	2.224	2.226
5,000	1.53	1.77	2.01	2.125	2.178	2.201	2.210	2.216	2.219
6,000	1.68	1.83	2.01	2.115	2.174	2.193	2.201	2.202	2.205
7,000	1.76	1.88	2.01	2.106	2.165	2.184	2.193	2.192	2.194
8,000	1.82	1.91	2.02	2.097	2.151	2.174	2.181	2.180	2.182
9,000	1.86	1.93	2.02	2.095	2.143	2.161	2.168	2.168	2.171
10,000	1.89	1.94	2.02	2.082	2.135	2.152	2.156	2.157	2.160
100° F.									
Bubble	(3525)[a]	(3490)	(3048)	(2549)	(2026)	(1518)	(1068)	(669)	(318)
Point	...	1.22	1.90	2.141	2.249	2.330	2.365	2.379	2.389
200	...	...	...	...	...	...	...	...	...
400	...	...	...	...	...	...	...	...	2.387
600	...	...	...	...	...	...	...	...	2.383
800	...	...	...	...	...	...	...	2.378	2.379
1,000	...	...	...	...	...	...	...	2.375	2.373
1,250	...	...	...	...	...	...	2.359	2.372	2.368
1,500	...	...	...	...	...	...	2.353	2.365	2.362
1,750	...	...	...	...	...	2.326	2.346	2.357	2.357
2,000	...	...	...	...	...	2.322	2.341	2.352	2.352
2,250	...	...	...	...	2.254	2.318	2.335	2.348	2.346
2,500	...	...	...	...	2.258	2.313	2.330	2.343	2.342
2,750	...	...	...	2.155	2.262	2.310	2.325	2.337	2.336
3,000	...	...	...	2.151	2.263	2.306	2.320	2.332	2.331
3,500	...	1.18	1.94	2.164	2.264	2.299	2.311	2.323	2.323
4,000	0.99[b]	1.49	1.97	2.180	2.262	2.290	2.303	2.312	2.313
4,500	1.28	1.66	2.01	2.198	2.257	2.284	2.296	2.302	2.305
5,000	1.43	1.75	2.04	2.202	2.253	2.277	2.288	2.293	2.295
6,000	1.61	1.87	2.10	2.212	2.243	2.264	2.273	2.275	2.278
7,000	1.74	1.96	2.14	2.210	2.232	2.250	2.259	2.259	2.263
8,000	1.83	2.02	2.14	2.203	2.221	2.236	2.248	2.245	2.249
9,000	1.89	2.04	2.14	2.186	2.210	2.223	2.229	2.230	2.234
10,000	1.93	2.04	2.13	2.175	2.200	2.213	2.217	2.217	2.220

Table II. (*Continued*)

Pressure, P.S.I.A.	Mole Fraction *n*-Heptane 0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
160° F.									
Bubble	(3325)[a]	(3529)	(3178)	(2719)	(2202)	(1689)	(1199)	(753)	(358)
Point	...	0.36	1.78	2.087	2.282	2.408	2.457	2.474	2.493
200	...	...	...	...	...	...	...	...	...
400	...	...	...	...	...	...	...	...	2.492
600	...	...	...	...	...	...	...	...	2.485
800	...	...	...	...	...	...	...	2.473	2.479
1,000	...	...	...	...	...	...	...	2.469	2.472
1,250	...	...	...	...	...	...	2.455	2.463	2.464
1,500	...	...	...	...	...	...	2.448	2.455	2.457
1,750	...	...	...	...	...	2.406	2.441	2.448	2.450
2,000	...	...	...	...	...	2.402	2.433	2.442	2.442
2,250	...	...	...	...	2.283	2.398	2.426	2.436	2.435
2,500	...	...	...	...	2.296	2.394	2.418	2.430	2.428
2,750	...	...	...	2.102	2.308	2.388	2.413	2.423	2.422
3,000	...	...	...	2.138	2.318	2.384	2.406	2.417	2.415
3,500	0.02[b]	...	1.86	2.188	2.331	2.375	2.394	2.405	2.404
4,000	0.68	1.48	1.97	2.220	2.333	2.367	2.385	2.394	2.395
4,500	1.02	1.61	2.04	2.240	2.331	2.358	2.375	2.383	2.385
5,000	1.24	1.72	2.08	2.250	2.326	2.349	2.365	2.371	2.374
6,000	1.57	1.86	2.14	2.259	2.313	2.335	2.347	2.349	2.353
7,000	1.74	1.97	2.16	2.258	2.298	2.317	2.330	2.330	2.334
8,000	1.86	2.03	2.18	2.253	2.286	2.303	2.313	2.315	2.316
9,000	1.94	2.08	2.19	2.250	2.275	2.290	2.294	2.296	2.301
10,000	2.02	2.12	2.20	2.250	2.265	2.275	2.278	2.280	2.284
220° F.									
Bubble	(2883)[a]	(3286)	(3139)	(2754)	(2278)	(1777)	(1279)	(818)	(399)
Point	...	0.80	1.60	2.032	2.310	2.486	2.550	2.588	2.618
200	...	...	...	...	...	...	...	...	...
400	...	...	...	...	...	...	...	...	2.618
600	...	...	...	...	...	...	...	...	2.607
800	...	...	...	...	...	...	...	...	2.596
1,000	...	...	...	...	...	...	...	2.580	2.586
1,250	...	...	...	...	...	...	...	2.569	2.575
1,500	...	...	...	...	...	...	2.544	2.558	2.565
1,750	...	...	...	...	...	...	2.535	2.549	2.555
2,000	...	...	...	...	...	2.483	2.526	2.546	2.546
2,250	...	...	...	...	...	2.478	2.518	2.531	2.538
2,500	...	...	...	...	2.329	2.473	2.510	2.523	2.529
2,750	...	...	...	...	2.346	2.468	2.503	2.514	2.521
3,000	...	...	...	2.058	2.360	2.463	2.495	2.506	2.513
3,500	0.41[b]	1.10	1.67	2.105	2.376	2.453	2.481	2.491	2.497
4,000	0.79	1.42	1.84	2.151	2.385	2.444	2.467	2.476	2.482
4,500	1.02	1.54	1.94	2.192	2.389	2.434	2.455	2.463	2.468
5,000	1.26	1.67	2.02	2.228	2.387	2.424	2.442	2.450	2.455
6,000	1.53	1.84	2.12	2.276	2.377	2.406	2.419	2.426	2.429
7,000	1.74	1.98	2.18	2.292	2.365	2.386	2.398	2.403	2.407
8,000	1.84	2.05	2.20	2.298	2.351	2.366	2.378	2.383	2.386
9,000	1.90	2.09	2.23	2.300	2.339	2.351	2.360	2.363	2.367
10,000	1.95	2.13	2.24	2.301	2.328	2.338	2.342	2.343	2.349
280° F.									
Bubble	(2012)[a]	(2842)	(2912)	(2702)	(2304)	(1847)	(1349)	(868)	(436)
Point	...	...	...	1.860	2.316	2.543	2.635	2.713	2.760
200	...	...	...	...	...	...	...	...	...
400	...	...	...	...	...	...	...	...	...
600	...	...	...	...	...	...	...	...	2.745
800	...	...	...	...	...	...	...	...	2.728
1,000	...	...	...	...	...	...	...	2.707	2.713
1,250	...	...	...	...	...	...	...	2.690	2.697
1,500	...	...	...	...	...	...	2.631	2.678	2.683
1,750	...	...	...	...	...	...	2.624	2.662	2.669
2,000	...	...	...	...	...	2.541	2.617	2.650	2.657
2,250	...	...	...	...	...	2.539	2.610	2.638	2.645
2,500	...	...	...	...	2.339	2.536	2.603	2.626	2.633
2,750	...	...	...	1.876	2.366	2.533	2.595	2.617	2.622
3,000	...	...	1.32	1.950	2.387	2.530	2.587	2.603	2.611
3,500	0.52[b]	1.13	1.65	2.089	2.420	2.523	2.571	2.584	2.590
4,000	0.87	1.31	1.80	2.186	2.438	2.516	2.554	2.563	2.571
4,500	1.14	1.49	1.90	2.256	2.447	2.508	2.538	2.547	2.553
5,000	1.28	1.64	1.99	2.305	2.451	2.500	2.522	2.531	2.536
6,000	1.48	1.84	2.12	2.360	2.444	2.478	2.496	2.500	2.506
7,000	1.71	1.96	2.20	2.372	2.432	2.456	2.471	2.477	2.480
8,000	1.85	2.04	2.24	2.368	2.416	2.435	2.447	2.454	2.457
9,000	1.92	2.10	2.25	2.361	2.402	2.416	2.426	2.431	2.434
10,000	1.97	2.14	2.26	2.354	2.390	2.401	2.406	2.409	2.413
340° F.									
Bubble	...	(2041)[a]	(2448)	(2426)	(2198)	(1818)	(1351)	(897)	(468)
Point	...	...	0.69	1.342	2.195	2.506	2.656	2.808	2.917
200	...	...	...	...	...	...	...	...	...
400	...	...	...	...	...	...	...	...	...
600	...	...	...	...	...	...	...	...	2.903
800	...	...	...	...	...	...	...	...	2.880
1,000	...	...	...	...	...	...	...	2.805	2.861
1,250	...	...	...	...	...	...	...	2.797	2.837
1,500	...	...	...	...	...	...	2.665	2.790	2.813
1,750	...	...	...	...	...	...	2.677	2.778	2.796
2,000	...	...	...	...	...	2.529	2.687	2.765	2.780
2,250	...	...	...	...	2.224	2.550	2.691	2.751	2.767
2,500	...	0.31	0.84	1.538	2.307	2.567	2.692	2.739	2.748
2,750	...	0.71	1.25	1.737	2.361	2.576	2.689	2.727	2.737
3,000	...	0.98	1.45	1.902	2.400	2.584	2.683	2.711	2.718
3,500	0.76[b]	1.25	1.71	2.098	2.447	2.588	2.662	2.686	2.693
4,000	1.01	1.45	1.86	2.214	2.478	2.585	2.641	2.663	2.670
4,500	1.21	1.60	1.96	2.276	2.497	2.577	2.625	2.642	2.647
5,000	1.38	1.71	2.04	2.323	2.507	2.567	2.607	2.622	2.625
6,000	1.62	1.89	2.15	2.378	2.509	2.548	2.577	2.586	2.588
7,000	1.75	2.01	2.23	2.399	2.495	2.526	2.541	2.555	2.556
8,000	1.89	2.09	2.28	2.406	2.479	2.504	2.520	2.527	2.530
9,000	1.96	2.15	2.30	2.406	2.463	2.482	2.495	2.500	2.501
10,000	2.02	2.18	2.31	2.403	2.451	2.466	2.479	2.477	2.478

Table II. (*Continued*)

Pressure, P.S.I.A.	Mole Fraction n-Heptane 0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
400° F.									
Bubble	...	...	...	(1904)[a]	(1829)	(1586)	(1262)	(898)	(524)
Point	...	...	...	1.305	1.781	2.225	2.590	2.861	3.120
200	...	...	...	...	...	...	...	...	...
400	...	...	...	...	...	...	...	...	...
600	...	...	...	...	...	...	...	...	3.105
800	...	...	...	...	...	...	...	...	3.071
1,000	...	...	...	...	...	...	...	2.870	3.038
1,250	...	...	...	...	...	...	...	2.887	3.005
1,500	...	...	...	...	...	...	2.656	2.898	2.975
1,750	...	...	...	...	...	2.327	2.711	2.903	2.948
2,000	...	...	0.76	1.359	1.939	2.459	2.750	2.894	2.923
2,250	...	...	1.06	1.610	2.125	2.533	2.776	2.878	2.903
2,500	...	...	1.27	1.796	2.251	2.576	2.785	2.864	2.878
2,750	...	...	1.43	1.938	2.335	2.605	2.784	2.847	2.861
3,000	...	...	1.56	2.026	2.391	2.623	2.775	2.831	2.842
3,500	0.87[b]	1.23	1.74	2.178	2.458	2.648	2.753	2.801	2.807
4,000	1.12	1.41	1.87	2.262	2.509	2.655	2.733	2.772	2.775
4,500	1.32	1.56	1.97	2.319	2.539	2.658	2.713	2.743	2.747
5,000	1.46	1.68	2.05	2.357	2.555	2.652	2.694	2.719	2.721
6,000	1.66	1.86	2.16	2.403	2.565	2.628	2.660	2.675	2.674
7,000	1.81	1.99	2.24	2.428	2.556	2.601	2.626	2.637	2.636
8,000	1.93	2.09	2.30	2.437	2.539	2.575	2.594	2.602	2.603
9,000	2.02	2.16	2.34	2.452	2.523	2.553	2.566	2.570	2.570
10,000	2.11	2.21	2.36	2.464	2.512	2.531	2.538	2.544	2.541
460° F.									
Bubble	...	...	...	...	...	(1192)[a]	(1058)	(822)	(541)
Point	...	...	...	...	...	...	2.280	2.831	3.387
200	...	...	...	...	...	...	...	...	...
400	...	...	...	...	...	...	...	...	...
600	...	...	...	...	...	...	...	...	3.367
800	...	...	...	...	...	...	...	...	3.323
1,000	...	...	...	...	...	...	...	2.902	3.258
1,250	...	...	...	...	...	1.724	2.430	2.974	3.232
1,500	...	...	...	...	...	1.952	2.599	3.018	3.187
1,750	...	...	...	...	...	2.164	2.708	3.033	3.146
2,000	...	...	...	...	1.755	2.344	2.784	3.030	3.109
2,250	...	...	...	1.420	1.955	2.476	2.832	3.012	3.078
2,500	...	...	...	1.660	2.120	2.563	2.863	3.003	3.044
2,750	...	...	...	1.854	2.249	2.621	2.976	2.984	3.012
3,000	...	...	1.69	2.000	2.342	2.656	2.874	2.962	2.983
3,500	...	...	1.89	2.180	2.449	2.699	2.854	2.926	2.936
4,000	1.48[b]	1.76	2.04	2.298	2.526	2.721	2.831	2.882	2.892
4,500	1.63	1.90	2.15	2.375	2.577	2.730	2.808	2.848	2.857
5,000	1.75	2.00	2.22	2.432	2.607	2.731	2.788	2.820	2.823
6,000	1.90	2.11	2.31	2.483	2.622	2.711	2.750	2.765	2.765
7,000	1.99	2.17	2.34	2.508	2.613	2.678	2.710	2.723	2.724
8,000	2.06	2.21	2.37	2.511	2.599	2.649	2.670	2.679	2.679
9,000	2.10	2.24	2.38	2.509	2.584	2.627	2.638	2.644	2.640
10,000	2.14	2.27	2.39	2.502	2.573	2.598	2.605	2.610	2.607

[a] Bubble point pressure expressed in pounds per square inch.
[b] Partial volume expressed in cubic feet per pound mole.

280°F. for a series of pressures. The increase in uncertainty as the mole fraction of methane decreases is indicated by the dashed ends of the curves near the left side of the diagram. Figure 2 depicts the effect of pressure upon the partial volume of methane for the same range of states as is covered in Figure 1. It is apparent that the partial volume is more strongly influenced by pressure at compositions rich in methane than for systems containing only small mole fractions of this component. The values corresponding to bubble point were obtained by extrapolation of the data in the homogeneous region to the boundary of the liquid-phase region.

The influence of the mole fraction of *n*-heptane upon the partial volume of this component is shown in Figure 3 for a temperature of 280°F. Again the uncertainties at compositions approaching infinite dilution have been indicated by the dashed ends of the curves near the left side of the diagram. The decrease in the partial volume with the decreasing mole fraction *n*-heptane is typical of the behavior encountered for other binary hydrocarbon systems.

Figure 4 indicates the effect of pressure upon the partial volume of *n*-heptane at a temperature of 280°F. At the higher mole fractions of *n*-heptane the behavior is similar to that found for the volumetric behavior of the pure component. However, at the lower mole fractions of *n*-heptane there is an increase in the partial volume as the pressure is

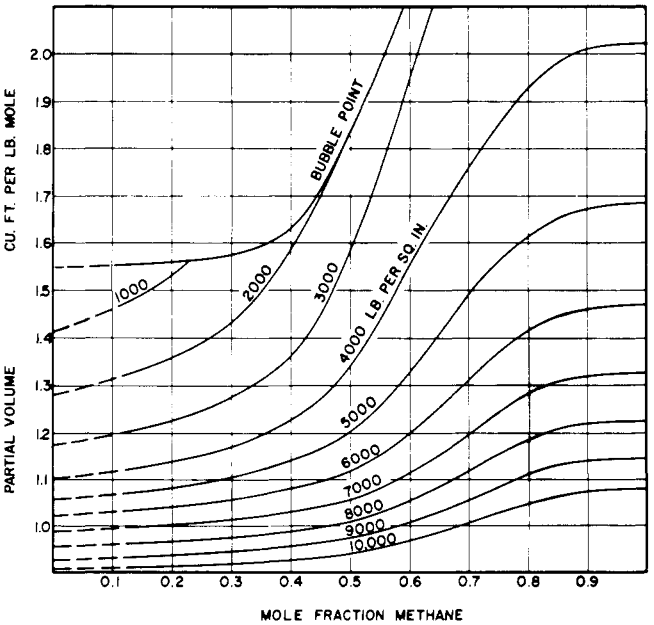

Figure 1. Influence of composition upon partial volume of methane at 280° F.

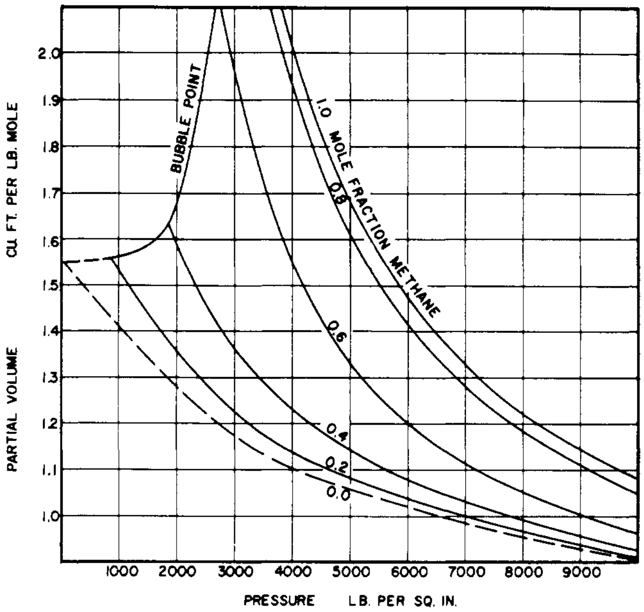

Figure 2. Effect of pressure upon partial volume of methane at 280° F.

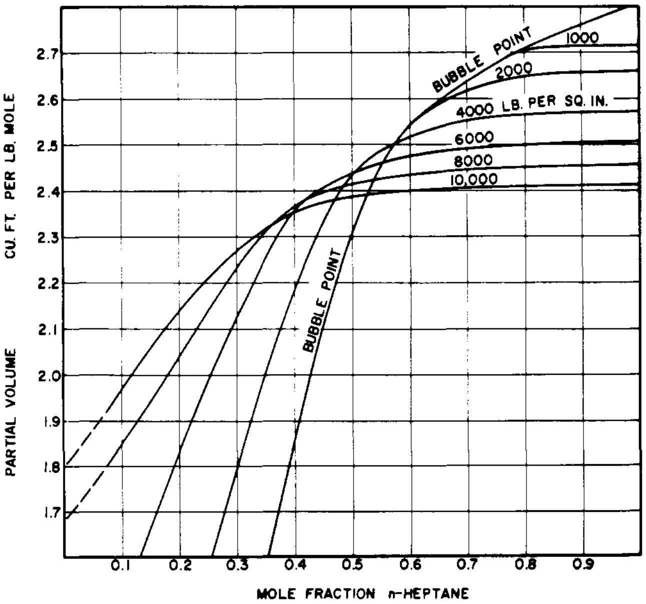

Figure 3. Influence of composition upon partial volume of *n*-heptane at 280° F.

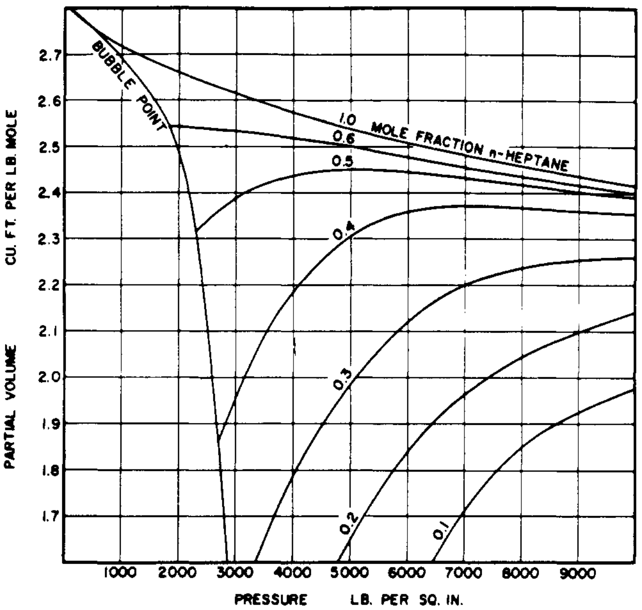

Figure 4. Effect of pressure upon partial volume of n-heptane at 280° F.

increased, at constant temperature. Such behavior is typical of that encountered for the partial volume of the less volatile component in binary hydrocarbon systems containing large mole fractions of methane. In a part of the single-phase region, negative partial volumes for the less volatile component may be encountered at the lower pressures for compositions rich in methane.

The influence of temperature, pressure, and composition upon the partial volumetric behavior appears to conform with that normally expected in such binary systems.

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NOMENCLATURE

$\underset{\cdot}{m}_k$ = lb. moles of component k
$\underset{\cdot}{n}_k$ = mole fraction of component k
$\underset{\cdot}{V}$ = molal volume, cu. ft./lb. mole
$\bar{\underset{\cdot}{V}}$ = partial molal volume, partial volume, cu. ft./lb. mole
$\underline{V}$ = total volume, cu. feet
$\bar{\partial}$ = partial differential operator

SUBSCRIPTS

j, k = components j and k
m_i = change in state during which quantity of all components other than k remains constant
m_j = change in state during which quantity of component j remains constant
P = pressure, p.s.i.
T = thermodynamic temperature, °R.

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Vapor-Liquid Equilibria in Binary Systems Containing Fluorocarbons and Chlorofluorocarbons

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Binary solutions of the five-carbon-atom perfluorocarbons have been reported (*8*) to form ideal solutions. Solutions of perfluorocarbons with hydrocarbons form solutions which have large positive deviations from ideal behavior (*4*), to such a degree that they are usually only partially miscible at temperatures on the order of the boiling points of the compounds in the system. Molecules containing carbon, fluorine, and chlorine (called chlorofluorocarbons in this article) seem to be an intermediate class of compounds, in that they are completely miscible with hydrocarbons and with perfluorocarbons boiling in the same range. Data presented here show that chlorofluorocarbons do not form ideal solutions with either perfluorocarbons or with hydrocarbons, however. Vapor-liquid equilibria for five binary systems at 1-atm. pressure are given: perfluoroheptane (C_7F_{16}) with a perfluorocyclic oxide ($C_8F_{16}O$); 1,2-dichlorohexafluorocyclopentene ($C_5Cl_2F_6$) with 2,2,3-trichloroheptafluorobutane ($C_4Cl_3F_7$); $C_5Cl_2F_6$ with $C_8F_{16}O$; $C_4Cl_3F_7$ with $C_8F_{16}O$; and $C_4Cl_3F_7$ with normal heptane (n-C_7H_{16}).

In addition to their thermodynamic interest, some of these systems are useful as mixtures for testing the performance of distillation columns operating with the different classes of compounds (*16*). In terms of the height of packing equivalent to a theoretical plate the efficiency of a laboratory column distilling perfluorocarbons is about half that obtained when the same column is distilling hydrocarbons.

APPARATUS

Equilibrium Still. A vapor recirculating still designed by Hipkin and Myers (*7*) was adapted for the small quantities of pure compounds available. In the apparatus used by the authors the capacity of the vaporizer was only about 7 ml., while that of the contactor was 1.5 ml. The authors inserted a small collector of 0.5-ml. capacity in the vapor condensate return line, in place of the three-way valve of Hipkin and Myers. In this way a sample of the vapor may be removed without significantly disturbing the continuous recycle of condensed vapor to the vaporizer.