from Figure 4. The dependence of the equilibrium constant on composition is clearly shown in Figure 5. If the equilibrium constants were independent of composition, the constant pressure lines would have been horizontal. With decreasing pressure, this condition is approached. However, even the lowest pressure of 700 p.s.i.a. exhibited a marked slope. The maximum deviations obviously occur in the critical region.

Cross plots of Figure 5 and similar plots using constant composition parameters produced Figure 6. This figure presents the equilibrium constant as a function of pressure for constant composition parameters at 100° F. The extrapolated portions of Figure 6 represent regions in which the data were extrapolated to limiting compositions of zero mole fraction for propane and *n*-butane. For propane the extrapolation was made in a region where the ratio of propane to *n*-butane is small, and for *n*-butane, this extrapolation covers a range having a small *n*-butane to propane ratio. Consequently, even large errors in these extrapolated equilibrium constants will have a very small effect on the resulting vapor and liquid compositions.

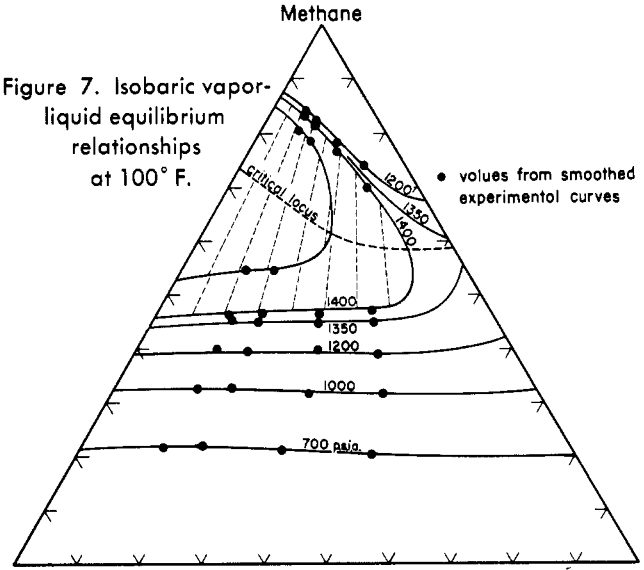

Figure 7. Isobaric vapor-liquid equilibrium relationships at 100° F.

Figure 6 was used to calculate the composition of the coexisting phases at constant pressures and varying composition parameters. Figure 7 presents on a triangular plot the phase behavior of the methane-propane-*n*-butane system at different pressures. The solid lines represent the results from the equilibrium constants of Figure 6, whereas the dots represent points obtained from the smoothed curves such as presented in Figure 1. These calculated values and smoothed experimental data are in good agreement and offer a good proof of satisfactory internal consistency and manipulation of the data.

ACKNOWLEDGMENT

The authors extend their thanks to the National Science Foundation for the financial assistance that has made this work possible.

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CORRECTION

In "Vapor-Liquid Equilibria: Microsampling Technique Applied to a New Variable Volume Cell" [T. J. Rigas, D. F. Mason, and George Thodos, *Ind. Eng. Chem.* **50**, 1297 (1958)] all pressures concerned with the experimental investigation should be increased by 15 p.s.i.a. This change brings the data of this study and those of Sage, Hicks and Lacey within the designated experimental error.

Partial Volumetric Behavior in Hydrocarbon Systems

Methane-Cyclohexane System in the Liquid Phase

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The concept of partial thermodynamic properties was perhaps first originated by Lewis (*4*), and it has been found that, in the course of many engineering operations, a knowledge of the partial volumetric behavior of the components of binary and multicomponent systems is useful for the prediction of the behavior of fluid systems of industrial interest (*12,13*). This is particularly true in connection with the evaluation of diffusion coefficients from experimental data (*8*) and the application of such coefficients to the prediction of material transport (*7*) under conditions involving a concentration gradient.

As a part of a study of the transport of methane in the liquid phase of the methane-cyclohexane system, measurements of the volumetric behavior of four mixtures of methane and cyclohexane were made (*10*). In addition, adequate volumetric data concerning the behavior of methane (*2,3,5,6*) and of cyclohexane (*9*) were available. These measurements were used as the basis for the evaluation of the partial volumetric behavior of methane and cyclohexane in the liquid phase of the methane-cyclohexane system.

METHODS AND PROCEDURE

The calculations were carried out using the method of graphical intercepts proposed by Roozeboom (*11*). By application of this method, curves of variation in molal volume with respect to mole fraction for isobaric, isothermal conditions were prepared for each of the several temperatures of interest. The intercept of a tangent to this curve at each of the several compositions of interest was determined, thus yielding directly the partial molal volume (hereafter referred to as partial volume) of the components. In this instance, the partial volume of each of the components may be established from

$$\overline{\underset{\cdot}{V}_k} = \underset{\cdot}{V} + (1 - \underset{\cdot}{n}_k)\left(\frac{\partial \underset{\cdot}{V}}{\partial \underset{\cdot}{n}_k}\right)_{T,P} \qquad (1)$$

In the application of this method the uncertainties in the evaluation of the partial volumes increase rapidly as the mole fraction of the component decreases.

It is possible, however, to check the consistency of the volumetric data by application of a relationship originally presented by Gibbs (*1*), and called the Gibbs-Duhem equation,

$$n_k \left(\frac{\partial \bar{V}_k}{\partial n_k}\right)_{T,P} = n_j \left(\frac{\partial \bar{V}_j}{\partial n_j}\right)_{T,P} \tag{2}$$

Equation 2 can be combined with the following integral expression to yield rather useful relationships:

$$\bar{V}_k = V_k^\circ + \int_1^{n_k} \left(\frac{\partial \bar{V}}{\partial n_k}\right)_{T,P} dn_k \tag{3}$$

$$\bar{V}_k = V_k^\circ - \int_0^{1-n_k} \left(\frac{n_j}{n_k}\right)\left(\frac{\partial \bar{V}_j}{\partial n_j}\right)_{T,P} dn_j \tag{4}$$

Likewise,

$$\bar{V}_j = V_j^\circ - \int_0^{1-n_j} \left(\frac{n_k}{n_j}\right)\left(\frac{\partial \bar{V}_k}{\partial n_k}\right)_{T,P} dn_k \tag{5}$$

Equations 4 and 5 show that the partial volume of one component can be readily evaluated from the partial volume of the other component.

The original experimental data (*10*), together with the experimental information for methane (*2,3,5,6*) and cyclohexane (*9*), were originally smoothed carefully with respect to pressure, temperature, and composition. Smoothed values of the molal volume were made available (*10*) as a function of even values of pressure, temperature, and composition. From these large-scale plots concerning the volumetric behavior of the liquid phase, the appropriate values of the partial volumes of methane and of cyclohexane were determined by application of Equation 1 for situations in which the mole fraction of the component in question was at least 0.4. By use of Equations 4 and 5, the values of the corresponding partial volume for other states containing smaller quantities of each of the components were determined.

As an example, the influence of composition upon the molal volume of the methane-cyclohexane system (*10*) is shown in Figure 1 for a temperature of 220° F. A marked decrease in molal volume occurs with an increase in the mole fraction of methane under isobaric, isothermal conditions at mole fractions of methane less than 0.6 and at pressures below 8000 p.s.i.

The partial volumes of methane in the liquid phase are recorded in Table I as a function of even values of the mole fraction of methane, the pressure, and the temperature. These data have been carried to one more significant figure than is probably justified by the absolute accuracy of the data. This has been done in the interest of providing somewhat higher precision in obtaining differences for adjacent states, which will not be dependent upon absolute accuracy. Values of the bubble-point pressure for each composition and temperature are included in the table.

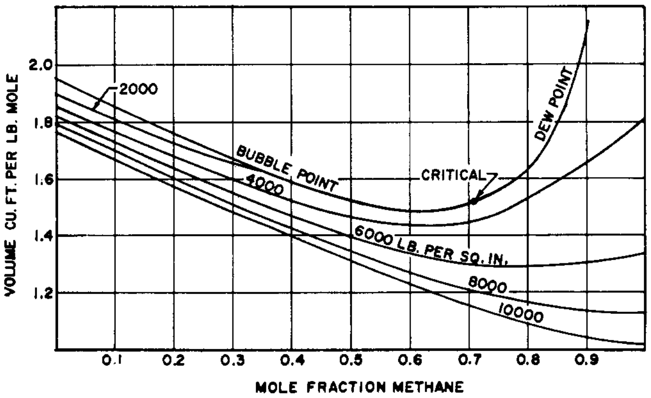

Figure 1. Influence of composition on molal volume of methane-cyclohexane system at 220° F.

Similar information for cyclohexane is presented in Table II. The same values of pressure and temperature were employed. Again the bubble-point pressures are included as a matter of convenience. The values of the partial volumes recorded in Tables I and II describe the experimentally determined volumetric behavior of the methane-cyclohexane system in the liquid phase with an uncertainty of approximately 1%. This measure of uncertainty was established by comparison of the specific volumes calculated from the partial volumetric data with those determined by experiment (*10*). The data satisfy the requirements of Equation 3 because they were obtained by an equivalent graphical operation. In addition, they have been interrelated through Equations 4 and 5 between 0.4 and 0.6 mole fraction of methane. The deviation between the two methods of evaluation in this limited composition interval was not greater than 0.5% in the value of the partial volume. In order to check the thermodynamic consistency of the data of Tables I and II in other parts of the composition range, Equations 4 and 5 have been applied. This procedure permits the partial volume of methane to be established from the change in the partial volume of cyclohexane with composition and, similarly, the partial volume of cyclohexane from the corresponding partial behavior of methane. Table III records for methane and for cyclohexane at 160° F. the difference between the partial volume as established from Equations 4 and 5, respectively, and the values presented in Tables I and II. This difference represents the divergence of the data in the tables from thermodynamic consistency with the Gibbs-Duhem equation. Figure 2

(*Text continued on page 210*)

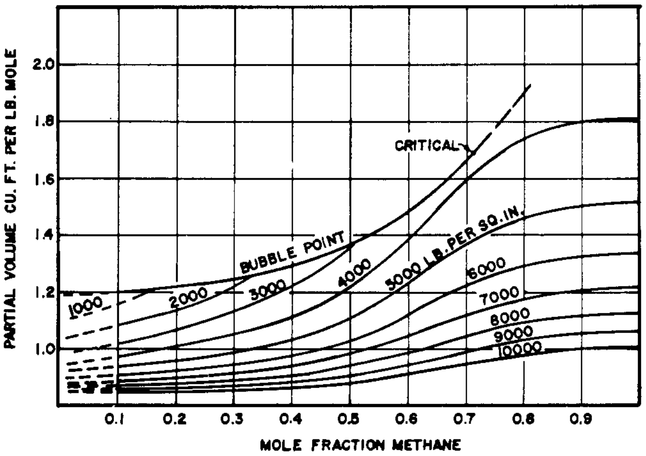

Figure 2. Effect of composition on partial molal volume of methane at 220° F.

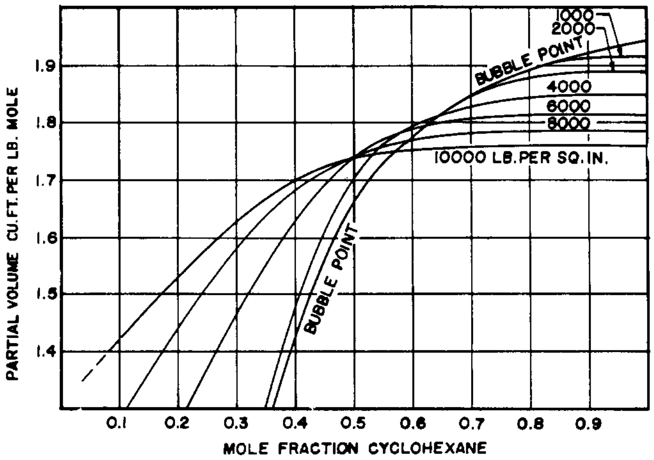

Figure 3. Effect of composition on partial molal volume of cyclohexane at 220° F.

Table I. Partial Volume of Methane in the Methane-Cyclohexane 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
70° F.									
	(458)[a]	(958)	(1488)	(2058)	(2645)	(3260)	(3810)	(4080)[b]	(3825)[b]
Bubble point	0.83[c]	0.86	0.88	0.917	0.956	0.999	1.054	1.150	1.319
600	0.82	...	...	...	...	...	...	...	...
800	0.82	...	...	...	...	...	...	...	...
1,000	0.82	0.85	...	...	...	...	...	...	...
1,250	0.81	0.84	...	...	...	...	...	...	...
1,500	0.81	0.84	0.88	...	...	...	...	...	...
1,750	0.80	0.83	0.87	...	...	...	...	...	...
2,000	0.80	0.82	0.86	...	...	...	...	...	...
2,250	0.79	0.82	0.85	0.908	...	...	...	...	...
2,500	0.79	0.81	0.85	0.898	...	...	...	...	...
2,750	0.78	0.80	0.84	0.888	0.951	...	...	...	...
3,000	0.78	0.80	0.83	0.878	0.938	...	...	...	...
3,500	0.77	0.79	0.82	0.859	0.914	0.984	...	...	...
4,000	0.76	0.78	0.80	0.841	0.893	0.955	1.037	...	...
4,500	0.76	0.77	0.79	0.825	0.873	0.929	1.000	1.090	1.148
5,000	0.75	0.76	0.78	0.810	0.854	0.907	0.971	1.034	1.078
6,000	0.74	0.75	0.76	0.786	0.821	0.870	0.925	0.970	0.994
7,000	0.72	0.73	0.75	0.766	0.796	0.840	0.888	0.924	0.939
8,000	0.72	0.72	0.73	0.750	0.775	0.814	0.856	0.883	0.895
9,000	0.71	0.72	0.72	0.736	0.756	0.790	0.826	0.849	0.861
10,000	0.70	0.71	0.71	0.724	0.743	0.767	0.796	0.820	0.832
100° F.									
	(494)[a]	(1013)	(1575)	(2170)	(2778)	(3378)	(3890)	(4028)[b]	(3750)[b]
Bubble point	0.90[c]	0.93	0.95	0.985	1.020	1.070	1.149	1.269	1.393
600	0.90	...	...	...	...	...	...	...	...
800	0.89	...	...	...	...	...	...	...	...
1,000	0.89	...	...	...	...	...	...	...	...
1,250	0.88	0.92	...	...	...	...	...	...	...
1,500	0.87	0.90	...	...	...	...	...	...	...
1,750	0.86	0.90	0.94	...	...	...	...	...	...
2,000	0.86	0.88	0.93	...	...	...	...	...	...
2,250	0.85	0.88	0.92	0.978	...	...	...	...	...
2,500	0.84	0.87	0.90	0.959	...	...	...	...	...
2,750	0.83	0.86	0.89	0.941	...	...	...	...	...
3,000	0.83	0.85	0.88	0.925	1.004	...	...	...	...
3,500	0.81	0.83	0.86	0.899	0.969	1.058	...	...	...
4,000	0.80	0.82	0.84	0.879	0.940	1.018	1.138	...	1.339
4,500	0.79	0.81	0.83	0.862	0.915	0.986	1.090	1.182	1.243
5,000	0.78	0.80	0.81	0.846	0.892	0.957	1.047	1.116	1.162
6,000	0.77	0.78	0.79	0.818	0.856	0.908	0.978	1.034	1.060
7,000	0.75	0.76	0.78	0.797	0.826	0.874	0.928	0.974	0.990
8,000	0.74	0.75	0.76	0.779	0.803	0.847	0.891	0.924	0.938
9,000	0.74	0.74	0.75	0.764	0.783	0.822	0.859	0.884	0.896
10,000	0.74	0.74	0.74	0.753	0.768	0.799	0.828	0.847	0.862
160° F.									
	(540)[a]	(1108)	(1693)	(2309)	(2898)	(3470)	(3830)	(3845)	(3500)[b]
Bubble point	1.02	1.05	1.08	1.120	1.171	1.250	1.366	1.541	1.845
600	1.02[c]	...	...	...	...	...	...	...	...
800	1.01	...	...	...	...	...	...	...	...
1,000	1.00	...	...	...	...	...	...	...	...
1,250	0.99	1.04	...	...	...	...	...	...	...
1,500	0.98	1.03	...	...	...	...	...	...	...
1,750	0.97	1.01	1.08	...	...	...	...	...	...
2,000	0.96	1.00	1.06	...	...	...	...	...	...
2,250	0.95	0.99	1.04	...	...	...	...	...	...
2,500	0.94	0.97	1.02	1.097	...	...	...	...	...
2,750	0.93	0.96	1.00	1.072	...	...	...	...	...
3,000	0.92	0.95	0.99	1.047	1.157	...	...	...	...
3,500	0.90	0.93	0.96	1.006	1.097	1.245	...	...	...
4,000	0.89	0.91	0.94	0.978	1.055	1.177	1.341	1.496	1.576
4,500	0.87	0.89	0.92	0.951	1.022	1.124	1.270	1.372	1.436
5,000	0.86	0.87	0.90	0.929	0.990	1.081	1.204	1.283	1.329
6,000	0.83	0.85	0.86	0.891	0.938	1.013	1.097	1.162	1.194
7,000	0.82	0.83	0.84	0.862	0.898	0.960	1.023	1.074	1.098
8,000	0.80	0.81	0.82	0.838	0.869	0.915	0.966	1.006	1.028
9,000	0.80	0.80	0.81	0.822	0.843	0.876	0.914	0.951	0.975
10,000	0.79	0.80	0.80	0.809	0.822	0.844	0.868	0.905	0.932

Table I. (Continued)

	Mole Fraction Methane								
Pressure, P.S.I.A.	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
					220° F.				
	(587)[a]	(1170)	(1772)	(2390)	(2958)	(3450)	(3685)	(3587)[b]	(2950)[b]
Bubble point	1.20[c]	1.22	1.25	1.295	1.365	1.483	1.667	1.894	...
600	...	...	...	...	...	...	...	...	...
800	1.18	...	...	...	...	...	...	...	...
1,000	1.16	...	...	...	...	...	...	...	...
1,250	1.14	1.21	...	...	...	...	...	...	...
1,500	1.12	1.19	...	...	...	...	...	...	...
1,750	1.11	1.16	...	...	...	...	...	...	...
2,000	1.09	1.14	1.22	...	...	...	...	...	...
2,250	1.07	1.12	1.20	...	...	...	...	...	...
2,500	1.06	1.10	1.17	1.282	...	...	...	...	...
2,750	1.04	1.08	1.15	1.252	...	...	...	...	...
3,000	1.02	1.06	1.13	1.223	1.357	...	...	...	...
3,500	1.00	1.03	1.09	1.165	1.288	1.473	...	...	...
4,000	0.97	1.01	1.05	1.114	1.223	1.383	1.591	1.732	1.798
4,500	0.95	0.98	1.02	1.073	1.164	1.303	1.472	1.570	1.629
5,000	0.94	0.96	0.99	1.034	1.110	1.232	1.367	1.453	1.503
6,000	0.91	0.92	0.95	0.979	1.036	1.126	1.220	1.289	1.329
7,000	0.88	0.90	0.92	0.939	0.985	1.048	1.118	1.178	1.207
8,000	0.87	0.88	0.89	0.908	0.942	0.989	1.047	1.094	1.120
9,000	0.86	0.86	0.87	0.855	0.905	0.947	0.990	1.031	1.052
10,000	0.85	0.85	0.85	0.865	0.878	0.911	0.944	0.976	1.000
					280° F.				
	(627)[a]	(1219)	(1821)	(2430)	(2932)	(3283)	(3341)[b]	(3114)[b]	...
Bubble point	1.40[c]	1.43	1.48	1.561	1.701	1.885	2.146	2.443	...
600	...	...	...	...	...	...	...	...	...
800	1.37	...	...	...	...	...	...	...	...
1,000	1.34	...	...	...	...	...	...	...	...
1,250	1.30	1.42	...	...	...	...	...	...	...
1,500	1.27	1.38	...	...	...	...	...	...	...
1,750	1.24	1.35	...	...	...	...	...	...	...
2,000	1.21	1.32	1.45	...	...	...	...	...	...
2,250	1.18	1.28	1.41	...	...	...	...	...	...
2,500	1.16	1.26	1.37	1.548	...	...	...	...	...
2,750	1.14	1.23	1.34	1.504	...	...	...	...	...
3,000	1.12	1.21	1.31	1.460	1.682	...	...	...	...
3,500	1.09	1.16	1.25	1.380	1.545	1.785	2.068	2.212	2.262
4,000	1.07	1.13	1.20	1.308	1.438	1.615	1.852	1.966	2.016
4,500	1.05	1.09	1.15	1.241	1.340	1.497	1.675	1.776	1.828
5,000	1.03	1.06	1.11	1.180	1.270	1.406	1.541	1.634	1.678
6,000	0.99	1.02	1.05	1.099	1.165	1.261	1.352	1.429	1.468
7,000	0.96	0.98	1.00	1.037	1.090	1.157	1.230	1.292	1.322
8,000	0.94	0.95	0.97	0.993	1.030	1.074	1.136	1.190	1.217
9,000	0.92	0.93	0.94	0.957	0.982	1.016	1.070	1.117	1.139
10,000	0.90	0.91	0.91	0.926	0.942	0.973	1.014	1.055	1.078
					340° F.				
	(668)[a]	(1255)	(1858)	(2410)	(2790)	(2910)	(2753)[b]	(2065)[b]	...
Bubble point	1.81[c]	1.82	1.84	1.919	2.133	2.508	2.996	...	...
600	...	...	...	...	...	...	...	...	...
800	1.77	...	...	...	...	...	...	...	...
1,000	1.70	...	...	...	...	...	...	...	...
1,250	1.63	...	...	...	...	...	...	...	...
1,500	1.57	1.74	...	...	...	...	...	...	...
1,750	1.52	1.67	...	...	...	...	...	...	...
2,000	1.47	1.60	1.80	...	...	...	...	...	...
2,250	1.42	1.55	1.74	...	...	...	...	...	...
2,500	1.39	1.50	1.68	1.894	...	...	...	...	...
2,750	1.35	1.46	1.62	1.823	...	...	...	...	...
3,000	1.32	1.43	1.57	1.761	2.047	2.450	2.765	2.856	...
3,500	1.26	1.36	1.48	1.646	1.852	2.148	2.384	2.486	2.510
4,000	1.22	1.30	1.40	1.544	1.707	1.903	2.108	2.200	2.225
4,500	1.17	1.26	1.34	1.451	1.571	1.728	1.906	1.990	2.016
5,000	1.13	1.21	1.28	1.374	1.470	1.597	1.745	1.823	1.854
6,000	1.07	1.13	1.19	1.246	1.312	1.412	1.509	1.575	1.605
7,000	1.04	1.08	1.12	1.159	1.208	1.275	1.355	1.409	1.434
8,000	1.01	1.04	1.06	1.094	1.130	1.172	1.240	1.294	1.315
9,000	0.98	1.00	1.02	1.039	1.065	1.102	1.160	1.209	1.227
10,000	0.95	0.96	0.97	0.990	1.015	1.055	1.100	1.139	1.153

[a] Values in parentheses represent bubble point pressures, p.s.i. [b] Retrograde dew point. [c] Partial molal volume, cu. ft./lb. mole.

Table II. Partial Volume of Cyclohexane in the Methane-Cyclohexane System

Pressure, P.S.I.A.	Mole Fraction Cyclohexane 0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
					70° F.				
	(3825)^{a,b}	(4080)^{b}	(3810)	(3260)	(2645)	(2058)	(1488)	(958)	(458)
Bubble point	...	0.98	1.34	1.497	1.589	1.656	1.693	1.715	1.727
600	...	...	...	...	...	...	...	...	1.725
800	...	...	...	...	...	...	...	...	1.722
1,000	...	...	...	...	...	...	...	1.714	1.719
1,250	...	...	...	...	...	...	...	1.711	1.715
1,500	...	...	...	...	...	...	1.693	1.708	1.711
1,750	...	...	...	...	...	...	1.689	1.705	1.707
2,000	...	...	...	...	...	...	1.686	1.702	1.704
2,250	...	...	...	...	...	1.653	1.683	1.699	1.701
2,500	...	...	...	...	...	1.650	1.680	1.696	1.698
2,750	...	...	...	...	1.591	1.646	1.678	1.693	1.695
3,000	...	...	...	...	1.592	1.645	1.676	1.691	1.692
3,500	...	...	...	1.503	1.600	1.647	1.674	1.687	1.687
4,000	...	...	1.35	1.515	1.605	1.649	1.672	1.683	1.683
4,500	0.77^{c}	1.11	1.38	1.527	1.611	1.652	1.671	1.679	1.679
5,000	1.00	1.21	1.40	1.538	1.614	1.652	1.669	1.675	1.675
6,000	1.17	1.31	1.45	1.557	1.621	1.651	1.664	1.668	1.668
7,000	1.27	1.38	1.48	1.571	1.624	1.649	1.657	1.660	1.660
8,000	1.34	1.42	1.50	1.579	1.623	1.645	1.651	1.652	1.652
9,000	1.39	1.46	1.53	1.585	1.622	1.639	1.644	1.646	1.646
10,000	1.42	1.49	1.55	1.588	1.617	1.634	1.639	1.640	1.640
					100° F.				
	(3750)^{a,b}	(4028)^{b}	(3890)	(3378)	(2778)	(2170)	(1575)	(1013)	(494)
Bubble point	...	0.89	1.26	1.484	1.609	1.677	1.719	1.748	1.763
600	...	...	...	...	...	...	...	...	1.761
800	...	...	...	...	...	...	...	...	1.758
1,000	...	...	...	...	...	...	...	...	1.755
1,250	...	...	...	...	...	...	...	1.745	1.751
1,500	...	...	...	...	...	...	...	1.742	1.747
1.750	...	...	...	...	...	...	1.718	1.739	1.743
2,000	...	...	...	...	...	...	1.717	1.736	1.740
2,250	...	...	...	...	...	1.678	1.715	1.733	1.736
2,500	...	...	...	...	...	1.679	1.714	1.730	1.733
2,750	...	...	...	...	...	1.681	1.712	1.727	1.730
3,000	...	...	...	...	1.614	1.682	1.711	1.724	1.727
3,500	...	...	...	1.489	1.625	1.684	1.708	1.719	1.720
4,000	...	...	1.28	1.510	1.634	1.684	1.705	1.714	1.715
4,500	0.66^{c}	1.03	1.33	1.529	1.641	1.685	1.703	1.710	1.710
5,000	0.91	1.16	1.38	1.546	1.646	1.683	1.700	1.705	1.705
6,000	1.14	1.30	1.45	1.573	1.650	1.681	1.693	1.694	1.695
7,000	1.24	1.37	1.49	1.590	1.650	1.675	1.685	1.685	1.686
8,000	1.32	1.43	1.52	1.599	1.647	1.669	1.677	1.677	1.678
9,000	1.38	1.46	1.54	1.604	1.647	1.662	1.666	1.669	1.670
10,000	1.43	1.50	1.56	1.608	1.642	1.655	1.658	1.661	1.663
					160° F.				
	(3500)^{a,b}	(3845)	(3830)	(3470)	(2898)	(2309)	(1693)	(1108)	(540)
Bubble point	...	0.66	1.13	1.465	1.647	1.726	1.780	1.818	1.837
600	...	...	...	...	...	...	...	...	1.836
800	...	...	...	...	...	...	...	...	1.833
1,000	...	...	...	...	...	...	...	...	1.830
1,250	...	...	...	...	...	...	...	1.816	1.826
1,500	...	...	...	...	...	...	...	1.813	1.822
1,750	...	...	...	...	...	...	1.780	1.809	1.818
2,000	...	...	...	...	...	...	1.778	1.806	1.814
2,250	...	...	...	...	...	...	1.778	1.803	1.810
2,500	...	...	...	...	...	1.732	1.778	1.799	1.806
2,750	...	...	...	...	...	1.737	1.778	1.796	1.801
3,000	...	...	...	...	1.651	1.742	1.778	1.792	1.796
3,500	...	...	...	1.467	1.667	1.748	1.774	1.785	1.787
4,000	...	0.72	1.16	1.498	1.681	1.748	1.770	1.779	1.780
4,500	0.52^{c}	0.91	1.26	1.527	1.690	1.746	1.766	1.772	1.773
5,000	0.81	1.08	1.34	1.553	1.696	1.744	1.762	1.767	1.767
6,000	1.11	1.27	1.44	1.597	1.700	1.738	1.751	1.755	1.755
7,000	1.22	1.37	1.50	1.624	1.700	1.732	1.742	1.743	1.744
8,000	1.29	1.43	1.55	1.642	1.699	1.721	1.729	1.731	1.733
9,000	1.35	1.47	1.58	1.656	1.697	1.710	1.719	1.720	1.721
10,000	1.39	1.51	1.61	1.668	1.694	1.702	1.708	1.710	1.710

Table II. (Continued)

	Mole Fraction Cyclohexane								
Pressure, P.S.I.A.	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
					220° F.				
	(2950)[a,b]	(3587)[b]	(3685)	(3450)	(2958)	(2390)	(1772)	(1170)	(587)
Bubble point	...	...	1.02	1.425	1.674	1.776	1.849	1.893	1.922
600	...	...	...	...	...	...	...	...	...
800	...	...	...	...	...	...	...	...	1.917
1,000	...	...	...	...	...	...	...	...	1.913
1,250	...	...	...	...	...	...	...	1.892	1.907
1,500	...	...	...	...	...	...	...	1.888	1.902
1,750	...	...	...	...	...	...	...	1.883	1.897
2,000	...	...	...	...	...	...	1.845	1.897	1.891
2,250	...	...	...	...	...	...	1.843	1.874	1.886
2,500	...	...	...	...	...	1.777	1.840	1.870	1.880
2,750	...	...	...	...	...	1.779	1.837	1.866	1.874
3,000	...	...	...	...	1.676	1.781	1.834	1.861	1.869
3,500	...	...	...	1.430	1.692	1.787	1.830	1.853	1.858
4,000	...	0.69	1.10	1.477	1.707	1.794	1.827	1.845	1.848
4,500	0.51[c]	0.87	1.22	1.524	1.720	1.796	1.824	1.837	1.839
5,000	0.77	1.05	1.33	1.566	1.730	1.794	1.818	1.829	1.831
6,000	1.03	1.26	1.47	1.629	1.742	1.791	1.808	1.813	1.815
7,000	1.18	1.36	1.54	1.667	1.745	1.784	1.797	1.798	1.800
8,000	1.28	1.44	1.58	1.685	1.742	1.770	1.783	1.786	1.788
9,000	1.35	1.49	1.61	1.693	1.741	1.760	1.769	1.773	1.774
10,000	1.42	1.53	1.63	1.700	1.740	1.752	1.758	1.760	1.760
					280° F.				
	...	(3114)[a,b]	(3341)[b]	(3283)	(2932)	(2430)	(1821)	(1219)	(627)
Bubble point	...	...	0.87	1.348	1.672	1.819	1.913	1.972	2.017
600	...	...	...	...	...	...	...	...	...
800	...	...	...	...	...	...	...	...	2.012
1,000	...	...	...	...	...	...	...	...	2.006
1,250	...	...	...	...	...	...	...	...	1.998
1,500	...	...	...	...	...	...	...	1.965	1.990
1,750	...	...	...	...	...	...	...	1.960	1.982
2,000	...	...	...	...	...	...	1.908	1.954	1.975
2,250	...	...	...	...	...	...	1.902	1.948	1.967
2,500	...	...	...	...	...	1.818	1.900	1.942	1.959
2,750	...	...	...	...	...	1.814	1.897	1.937	1.951
3,000	...	...	...	...	1.676	1.812	1.893	1.931	1.944
3,500	...	0.48	0.93	1.385	1.699	1.815	1.889	1.920	1.930
4,000	...	0.69	1.10	1.466	1.720	1.825	1.881	1.908	1.917
4,500	0.53[c]	0.89	1.24	1.534	1.738	1.829	1.877	1.896	1.905
5,000	0.76	1.05	1.34	1.588	1.754	1.832	1.871	1.886	1.894
6,000	1.03	1.25	1.47	1.669	1.777	1.834	1.860	1.870	1.875
7,000	1.18	1.37	1.55	1.710	1.786	1.824	1.843	1.853	1.856
8,000	1.28	1.45	1.61	1.730	1.786	1.816	1.828	1.836	1.840
9,000	1.34	1.50	1.65	1.741	1.786	1.810	1.818	1.823	1.826
10,000	1.39	1.55	1.68	1.749	1.786	1.803	1.808	1.810	1.811
					340° F.				
	...	(2065)[a,b]	(2753)	(2910)	(2790)	(2410)	(1858)	(1255)	(668)
Bubble point	...	...	0.65	1.147	1.583	1.848	1.975	2.064	2.129
600	...	...	...	...	...	...	...	...	...
800	...	...	...	...	...	...	...	...	2.121
1,000	...	...	...	...	...	...	...	...	2.108
1,250	...	...	...	...	...	...	...	...	2.096
1,500	...	...	...	...	...	...	...	2.053	2.084
1,750	...	...	...	...	...	...	...	2.040	2.073
2,000	...	...	...	...	...	...	1.971	2.029	2.061
2,250	...	...	...	...	...	...	1.963	2.019	2.049
2,500	...	...	...	...	...	1.847	1.955	2.008	2.038
2,750	...	...	...	...	...	1.845	1.948	1.996	2.027
3,000	...	...	0.80	1.220	1.617	1.844	1.941	1.985	2.016
3,500	...	0.71	1.04	1.386	1.680	1.841	1.927	1.967	1.998
4,000	...	0.86	1.18	1.483	1.723	1.841	1.915	1.952	1.982
4,500	0.67[c]	0.98	1.28	1.557	1.749	1.846	1.908	1.939	1.966
5,000	0.79	1.09	1.37	1.615	1.770	1.854	1.901	1.930	1.950
6,000	0.99	1.25	1.50	1.698	1.798	1.861	1.893	1.915	1.928
7,000	1.15	1.37	1.59	1.749	1.820	1.861	1.883	1.901	1.910
8,000	1.28	1.47	1.65	1.770	1.830	1.861	1.875	1.886	1.893
9,000	1.37	1.53	1.68	1.783	1.833	1.856	1.867	1.874	1.878
10,000	1.45	1.57	1.69	1.784	1.833	1.855	1.860	1.860	1.862

[a] Values in parentheses represent bubble-point pressures, p.s.i. [b] Retrograde dew point. [c] Partial molal volume, cu.ft./lb. mole.

Table III. Divergence of Tabulated Partial Volumes from Gibbs-Duhem Equation at 160° F.

Mole Fraction Methane	Difference,[a] Cu. Ft./Lb. Mole	Mole Fraction Cyclohexane	Difference,[b] Cu. Ft./Lb. Mole
	Pressure 5000 p.s.i.		
1.0	0	1.0	0
0.9	-0.002	0.9	0.000
0.8	-0.004	0.8	0.000
0.7	-0.003	0.7	0.000
0.6	-0.004	0.6	0.001
0.5	-0.002	0.5	0.002
0.4	-0.003	0.4	-0.006
0.3	0.002	0.3	0.001
0.2	-0.003	0.2	0.003
0.1	-0.003	0.1	-0.029
Average	-0.003		-0.003
	Pressure 10,000 p.s.i.		
1.0	0	1.0	0
0.9	0.002	0.9	0.000
0.8	0.000	0.8	0.000
0.7	-0.001	0.7	0.000
0.6	0.002	0.6	-0.005
0.5	0.001	0.5	-0.004
0.4	0.002	0.4	0.000
0.3	0.004	0.3	0.012
0.2	0.003	0.2	0.008
0.1	0.002	0.1	0.006
Average	0.002		0.002

[a] Difference = $(\bar{V}_k)_{\text{exp}} - (\bar{V}_k)_{\text{Eq. 4}}$.

[b] Difference = $(\bar{V}_j)_{\text{exp}} - (\bar{V}_j)_{\text{Eq. 5}}$.

shows the partial volume of methane as a function of composition for a temperature of 220° F. In reporting the partial volumetric behavior of methane no attempt was made to carry the evaluation to pressures below those for which experimental measurements in the liquid phase were available.

Figure 3 depicts the partial volume of cyclohexane in the methane-cyclohexane system at a temperature of 220° F. These data again are presented as a function of composition and, in this case, there is a marked decrease in the partial volume of cyclohexane as the mole fraction of methane is increased. In order to illustrate the effect of pressure upon the partial volume of methane, there is shown in Figure 4 the partial volume of this component as a function of pressure for a composition corresponding to 0.8 mole fraction of methane. In this instance the partial volume of methane for a pressure of 10,000 p.s.i. at 340° F. is only about one third of that at 3000 p.s.i. In a similar fashion, the influence of pressure upon the partial volume of cyclohexane for a composition of 0.8 mole fraction of cyclohexane is shown in Figure 5. There is a small influence of pressure upon partial volume, particularly for values below 3000 p.s.i. at the higher temperatures.

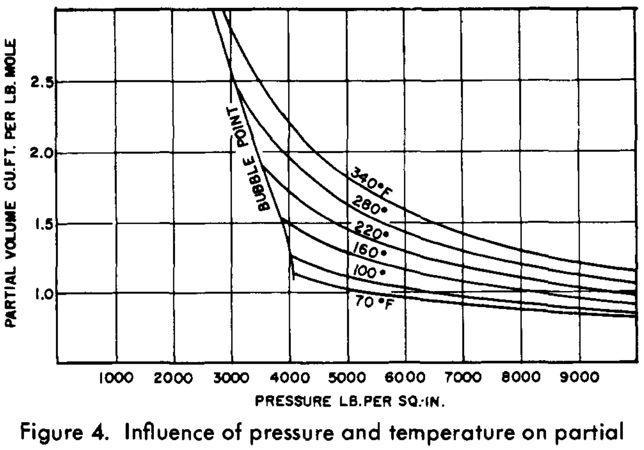

Figure 4. Influence of pressure and temperature on partial molal volume of methane for a mixture containing 0.8 mole fraction of methane

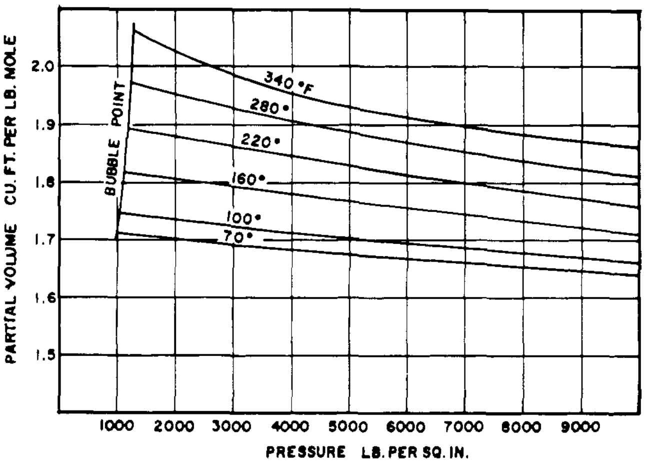

Figure 5. Influence of pressure and temperature on partial molal volume of cyclohexane for a mixture containing 0.8 mole fraction of cyclohexane

NOMENCLATURE

n = mole fraction of a component
V = volume, cu. ft./lb. mole
$\bar{V}$ = partial volume of a component, cu. ft./lb. mole
∂ = partial differential operator

Subscripts

j = cyclohexane
k = methane
P = pressure, p.s.i.
T = thermodynamic temperature, °R.

Superscript

° = pure component

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