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## Partial Volumetric Behavior in Hydrocarbon Systems. n-Decane and Carbon Dioxide in the Liquid Phase of the n-Decane-Carbon Dioxide System

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Partial molal volumes were evaluated for *n*-decane and carbon dioxide from experimental volumetric data for the *n*-decane-carbon dioxide system and corresponding information for the pure components. The evaluation extended to pressures of 10,000 p.s.i.a. in the temperature interval between 40° and 460° F. The internal inconsistency in terms of the standard error of estimate was 0.005 cubic foot per pound-mole. The partial volumes are presented in graphical and tabular form.

INFORMATION concerning the partial volumetric behavior of the components of binary and multicomponent systems helps to determine the heat and work associated with changes in state of these systems. In particular, such partial quantities are of importance in the evaluation of the molecular transport in systems where the concentration of each of the components is significant.

The volumetric and phase behavior of the *n*-decane-carbon dioxide system has been investigated at pressures up to 10,000 p.s.i.a. in the temperature interval between 40° and 460° F. (9). The volumetric behavior of carbon dioxide has been reported by several investigators (2, 5, 6, 7). In addition, the volumetric behavior of *n*-decane has been studied in some detail (8). The related volumetric and phase behavior of other binary systems containing carbon dioxide and a paraffin hydrocarbon has recently been reviewed (9).

The partial molal volume (hereafter referred to as partial volume) has been defined (3) as

$$\nabla_k = \left( \frac{\partial V}{\partial m_k} \right)_{T, P, m_i} \quad (1)$$

From the smooth volumetric data of the *n*-decane-carbon dioxide system (9) in the homogeneous region, large-scale diagrams of the isobaric, isothermal change in the molal volume with composition were prepared. The partial volumes of each of the components were reached by graphical application of the following expression (4):

$$\nabla_k = V + (1 - n_k) \left( \frac{\partial V}{\partial n_k} \right)_{T, P} \quad (2)$$

It was not feasible to employ Equation 2 at small mole fractions of the component in question because of the significant loss of precision which resulted from attempting to utilize graphical operations in these regions. Therefore, in the regions of small mole fractions, the partial volumes were established from

$$\nabla_k = \frac{V - n_j \nabla_j}{n_k} \quad (3)$$

In a number of cases, the partial volumes of each of the components were established by carrying out graphically the integration indicated in the following expression:

$$\nabla_k = V_k - \int_0^{1 - n_k} \left( \frac{n_j}{n_k} \right) \left( \frac{\partial \nabla_j}{\partial n_j} \right)_{T, P} dn_j \quad (4)$$

The foregoing expression is based upon the Gibbs-Duhem equation (1).

Equations 3 and 4 permit a direct check upon the internal consistency of the calculations. Equation 4 was employed to ascertain the over-all uncertainties in the calculations. The internal consistency of the partial volumetric data is presented in Table I, where the directly calculated values established from Equation 2 are compared with the integrated values obtained from Equation 4. A reasonable sample of the conditions covered in these calculations is set forth in the table. The average standard error of estimate for all the calculations carried out was 0.005 cubic foot per pound-mole. The information presented in Table I is typical of that found throughout the range of conditions for which experimental data are reported.

The average deviation without regard to sign in the partial volumes for the states in Table I was 0.003 cubic foot per pound-mole for carbon dioxide and 0.004 cubic foot per pound-mole for *n*-decane. The partial volumes of carbon dioxide and *n*-decane are reported in Tables II and III, respectively. These tabulations represent smooth values for even mole fractions of carbon dioxide and *n*-decane. At the smaller mole fractions of each of the components, the number of significant figures employed has been reduced as a result of the lower precision of the calculations in this region.

A large number of diagrams may be prepared from the data presented in Tables II and III. A few typical examples of the rather complicated behavior encountered with carbon dioxide and *n*-decane in this binary system have been included. Figure 1 presents the influence of composition upon the partial volume of carbon dioxide at a temperature of 220° F. The behavior is rather simple except for an unusual anomaly at pressures above 6000 p.s.i.a., where a small maximum in the values of the partial volume of carbon dioxide at a mole fraction of approximately 0.7 was found. Similar information for the same temperature is shown in Figure 2 for the partial volume of *n*-decane. The behavior depicted is similar to that found for other binary hydrocarbon systems containing carbon dioxide. The minimum in the partial volume of *n*-decane at approximately

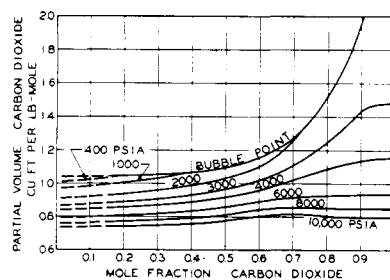


Figure 1. Influence of composition on partial molal volume of carbon dioxide at 220° F.

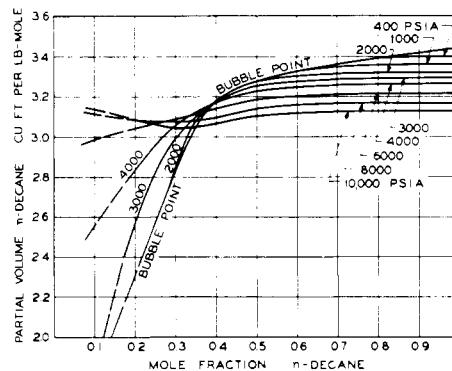


Figure 2. Influence of composition on partial molal volume of *n*-decane at 220° F.

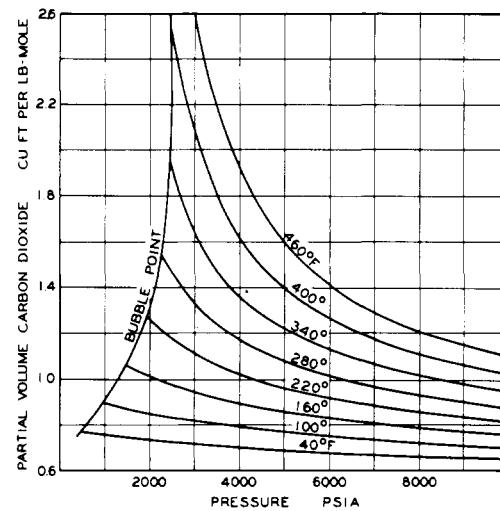


Figure 3. Effect of pressure on partial molal volume of carbon dioxide at 0.7 mole fraction carbon dioxide

Table I. Internal Consistency of Partial Volumetric Data<sup>a</sup>

Composition, Mole Fraction Carbon Dioxide	Carbon Dioxide		<i>n</i> -Decane		Carbon Dioxide		<i>n</i> -Decane	
	Graphical	Integrated	Graphical	Integrated	Graphical	Integrated	Graphical	Integrated
5000 P.S.I.A., 160° F.								
0.1	0.757	0.757	3.142	3.143	0.687	0.686	3.058	3.059
0.2	0.764	0.765	3.141	3.141	0.691	0.689	3.057	3.058
0.3	0.773	0.774	3.138	3.138	0.695	0.694	3.056	3.057
0.4	0.785	0.784	3.133	3.132	0.703	0.700	3.053	3.053
0.5	0.801	0.803	3.119	3.116	0.716	0.714	3.040	3.042
0.6	0.837	0.835	3.076	3.076	0.739	0.739	3.009	3.010
0.7	0.859	0.858	3.028	3.036	0.758	0.754	2.978	2.984
0.8	0.864	0.862	3.016	3.025	0.744	0.743	3.028	3.029
0.9	0.862	0.861	3.019	3.028	0.730	0.729	3.090	3.095
$\sigma^b$	0.001		0.005		0.002		0.003	
5000 P.S.I.A., 400° F.								
0.1	1.046	1.056	3.543	3.548	0.840	0.839	3.366	3.370
0.2	1.076	1.086	3.538	3.544	0.867	0.869	3.362	3.366
0.3	1.108	1.114	3.532	3.534	0.894	0.897	3.351	3.356
0.4	1.142	1.148	3.517	3.516	0.922	0.925	3.338	3.341
0.5	1.194	1.199	3.474	3.473	0.955	0.960	3.307	3.313
0.6	1.276	1.281	3.369	3.368	1.000	1.002	3.250	3.257
0.7	1.394	1.403	3.133	3.139	1.024	1.028	3.205	3.213
0.8	1.519	1.527	2.782	2.774	1.031	1.033	3.190	3.198
0.9	1.607	1.602	2.348	2.346	1.032	1.031	3.204	3.214
$\sigma^b$	0.007		0.004		0.003		0.006	

<sup>a</sup>Partial molal volume, cu.ft./lb.-mole.

<sup>b</sup>Standard error of estimate, cu.ft./lb.-mole,  $\sigma = \left[ \left\{ \sum_1^N (\nabla_{k,gr} - \nabla_{k,int})^2 \right\} / N \right]^{1/2}$

**Table II. Partial Molal Volume of Carbon Dioxide in Cubic Feet per Pound-Mole  
in the *n*-Decane-Carbon Dioxide System**

Pressure, P.S.I.A.	Mole Fraction Carbon Dioxide								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
40° F.									
Bubble Point <sup>a</sup>	(93)	(183)	(271)	(347)	(415)	(465)	(497)	(523)	(547)
200	0.83	0.79	0.759	0.734	0.736	0.752	0.765	0.774	0.779
400	0.83	0.79	0.759	0.734	...	...	...	...	...
600	0.83	0.79	0.758	0.733	0.735	0.750	0.763	0.772	0.777
800	0.83	0.79	0.757	0.732	0.733	0.746	0.758	0.766	0.771
1,000	0.83	0.79	0.755	0.730	0.731	0.742	0.753	0.760	0.765
1,250	0.82	0.79	0.753	0.728	0.729	0.738	0.747	0.754	0.758
1,500	0.82	0.78	0.751	0.726	0.726	0.734	0.742	0.747	0.751
1,750	0.82	0.78	0.749	0.724	0.723	0.730	0.737	0.741	0.744
2,000	0.82	0.78	0.746	0.721	0.720	0.726	0.732	0.735	0.737
2,250	0.81	0.78	0.743	0.718	0.717	0.723	0.727	0.729	0.731
2,500	0.80	0.77	0.740	0.716	0.715	0.720	0.723	0.724	0.725
2,750	0.80	0.77	0.737	0.714	0.713	0.718	0.719	0.719	0.718
3,000	0.80	0.76	0.733	0.711	0.711	0.716	0.714	0.713	0.712
3,500	0.78	0.75	0.725	0.705	0.707	0.711	0.706	0.703	0.701
4,000	0.77	0.74	0.716	0.698	0.702	0.706	0.698	0.693	0.690
4,500	0.76	0.73	0.707	0.691	0.697	0.700	0.691	0.684	0.680
5,000	0.75	0.72	0.698	0.684	0.692	0.695	0.685	0.677	0.672
6,000	0.72	0.70	0.680	0.669	0.681	0.686	0.675	0.666	0.659
7,000	0.70	0.68	0.664	0.656	0.670	0.677	0.668	0.658	0.649
8,000	0.68	0.66	0.650	0.644	0.659	0.669	0.662	0.650	0.640
9,000	0.66	0.65	0.637	0.634	0.650	0.664	0.658	0.643	0.632
10,000	0.64	0.63	0.626	0.626	0.644	0.660	0.655	0.638	0.625
100° F.									
Bubble Point <sup>a</sup>	(138)	(281)	(427)	(570)	(705)	(837)	(956)	(1048)	(1125)
200	0.85	0.82	0.813	0.814	0.824	0.848	0.896	0.968	1.100
400	0.84	0.82	...	...	...	...	...	...	...
600	0.84	0.81	0.808	0.811	...	...	...	...	...
800	0.83	0.81	0.803	0.803	0.821	...	...	...	...
1,000	0.82	0.80	0.797	0.796	0.813	0.841	0.893	...	...
1,250	0.81	0.80	0.791	0.788	0.805	0.832	0.876	0.940	1.047
1,500	0.81	0.79	0.785	0.781	0.797	0.823	0.864	0.916	0.978
1,750	0.80	0.79	0.780	0.775	0.791	0.816	0.853	0.898	0.933
2,000	0.79	0.78	0.774	0.770	0.784	0.810	0.845	0.883	0.900
2,250	0.78	0.78	0.770	0.766	0.779	0.805	0.837	0.868	0.875
2,500	0.78	0.77	0.765	0.762	0.774	0.801	0.830	0.854	0.855
2,750	0.77	0.77	0.760	0.759	0.769	0.797	0.823	0.841	0.838
3,000	0.76	0.76	0.756	0.756	0.766	0.793	0.816	0.829	0.824
3,500	0.75	0.75	0.748	0.749	0.759	0.784	0.804	0.805	0.799
4,000	0.74	0.74	0.740	0.742	0.752	0.775	0.792	0.785	0.780
4,500	0.73	0.73	0.732	0.734	0.744	0.766	0.781	0.770	0.765
5,000	0.72	0.72	0.724	0.726	0.737	0.757	0.770	0.758	0.752
6,000	0.70	0.70	0.707	0.711	0.721	0.739	0.750	0.736	0.729
7,000	0.69	0.69	0.692	0.697	0.707	0.723	0.733	0.718	0.713
8,000	0.67	0.68	0.680	0.685	0.694	0.709	0.721	0.704	0.699
9,000	0.66	0.67	0.669	0.674	0.682	0.696	0.711	0.694	0.686
10,000	0.65	0.66	0.658	0.664	0.673	0.685	0.701	0.687	0.675
160° F.									
Bubble Point <sup>a</sup>	(178)	(374)	(583)	(802)	(1027)	(1250)	(1471)	(1692)	(1844)
200	0.91	0.91	0.913	0.922	0.944	0.982	1.060	1.220	1.498
400	0.90	0.91	...	...	...	...	...	...	...
600	0.89	0.90	0.912	...	...	...	...	...	...
800	0.88	0.89	0.900	...	...	...	...	...	...
1,000	0.87	0.88	0.890	0.910	...	...	...	...	...
1,250	0.86	0.87	0.878	0.896	0.930	0.982	...	...	...
1,500	0.85	0.86	0.868	0.884	0.915	0.966	1.057	...	...
1,750	0.84	0.85	0.858	0.873	0.902	0.951	1.033	1.203	...
2,000	0.83	0.84	0.850	0.864	0.890	0.937	1.012	1.146	1.400
2,250	0.82	0.83	0.842	0.856	0.881	0.924	0.992	1.105	1.271
2,500	0.82	0.82	0.834	0.848	0.872	0.912	0.974	1.069	1.185
2,750	0.81	0.82	0.827	0.841	0.864	0.902	0.958	1.036	1.108
3,000	0.80	0.81	0.820	0.834	0.857	0.893	0.943	1.006	1.050
3,500	0.79	0.80	0.807	0.820	0.841	0.876	0.918	0.957	0.972
4,000	0.78	0.79	0.795	0.807	0.827	0.863	0.897	0.917	0.923
4,500	0.77	0.78	0.783	0.795	0.813	0.849	0.878	0.887	0.889
5,000	0.76	0.76	0.773	0.785	0.801	0.837	0.859	0.864	0.862
6,000	0.74	0.74	0.754	0.765	0.781	0.814	0.828	0.824	0.821
7,000	0.72	0.73	0.738	0.748	0.763	0.793	0.803	0.795	0.790
8,000	0.71	0.72	0.723	0.732	0.745	0.774	0.785	0.774	0.766
9,000	0.70	0.70	0.709	0.716	0.729	0.756	0.770	0.758	0.746
10,000	0.69	0.69	0.695	0.703	0.716	0.739	0.758	0.744	0.730

**Table II. Partial Molal Volume of Carbon Dioxide in Cubic Feet per Pound-Mole  
in the *n*-Decane-Carbon Dioxide System (Continued)**

Pressure, P.S.I.A.	Mole Fraction Carbon Dioxide								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
	220° F.								
Bubble Point <sup>a</sup>	(217)	(458)	(725)	(1010)	(1311)	(1625)	(1945)	(2258)	(2391)
200	1.04	1.05	1.054	1.068	1.095	1.154	1.270	1.512	1.950
400	1.02	...	...	...	...	...	...	...	...
600	1.01	1.04	...	...	...	...	...	...	...
800	1.00	1.02	1.048	...	...	...	...	...	...
1,000	0.98	1.00	1.032	...	...	...	...	...	...
1,250	0.96	0.99	1.013	1.048	...	...	...	...	...
1,500	0.95	0.97	0.995	1.027	1.077	...	...	...	...
1,750	0.94	0.95	0.978	1.008	1.055	1.134	...	...	...
2,000	0.92	0.94	0.960	0.988	1.033	1.100	1.258	...	...
2,250	0.91	0.92	0.945	0.970	1.014	1.074	1.213	...	...
2,500	0.90	0.91	0.932	0.955	0.996	1.053	1.174	1.382	1.750
2,750	0.89	0.90	0.918	0.941	0.980	1.036	1.140	1.303	1.566
3,000	0.88	0.89	0.905	0.928	0.964	1.020	1.110	1.245	1.430
3,500	0.86	0.87	0.885	0.905	0.937	0.988	1.060	1.156	1.246
4,000	0.85	0.86	0.869	0.886	0.913	0.960	1.020	1.090	1.133
4,500	0.84	0.84	0.855	0.871	0.895	0.938	0.989	1.034	1.059
5,000	0.82	0.83	0.842	0.858	0.879	0.920	0.964	0.990	1.007
6,000	0.80	0.81	0.818	0.832	0.854	0.892	0.918	0.929	0.932
7,000	0.78	0.79	0.796	0.808	0.830	0.867	0.880	0.883	0.884
8,000	0.76	0.77	0.780	0.788	0.809	0.842	0.852	0.850	0.847
9,000	0.75	0.76	0.762	0.770	0.790	0.819	0.832	0.824	0.817
10,000	0.74	0.74	0.747	0.754	0.774	0.802	0.816	0.803	0.793
	280° F.								
Bubble Point <sup>a</sup>	(252)	(529)	(840)	(1184)	(1544)	(1903)	(2267)	(2616)	(2662) <sup>b</sup>
200	1.24	1.25	1.257	1.273	1.307	1.386	1.541	1.880	2.49 <sup>c</sup>
400	1.21	...	...	...	...	...	...	...	...
600	1.18	1.24	...	...	...	...	...	...	...
800	1.15	1.20	...	...	...	...	...	...	...
1,000	1.12	1.17	1.229	...	...	...	...	...	...
1,250	1.10	1.14	1.190	1.260	...	...	...	...	...
1,500	1.07	1.11	1.156	1.215	...	...	...	...	...
1,750	1.05	1.08	1.126	1.177	1.253	...	...	...	...
2,000	1.03	1.06	1.099	1.143	1.208	...	...	...	...
2,250	1.01	1.04	1.075	1.114	1.173	1.355	...	...	...
2,500	1.00	1.02	1.054	1.089	1.142	1.293	1.457	...	...
2,750	0.98	1.01	1.035	1.066	1.116	1.245	1.382	1.715	2.036
3,000	0.97	0.99	1.018	1.045	1.092	1.206	1.321	1.551	1.830
3,500	0.95	0.96	0.986	1.009	1.049	1.173	1.233	1.400	1.567
4,000	0.93	0.94	0.959	0.979	1.015	1.118	1.169	1.292	1.400
4,500	0.91	0.92	0.936	0.956	0.989	1.078	1.119	1.209	1.280
5,000	0.89	0.90	0.917	0.936	0.969	1.045	1.079	1.144	1.193
6,000	0.86	0.87	0.884	0.904	0.935	1.020	1.015	1.050	1.072
7,000	0.83	0.84	0.856	0.875	0.908	0.978	0.964	0.984	0.996
8,000	0.82	0.82	0.835	0.852	0.881	0.944	0.931	0.939	0.941
9,000	0.80	0.81	0.818	0.831	0.857	0.916	0.903	0.902	0.899
10,000	0.79	0.80	0.803	0.812	0.834	0.868	0.878	0.870	0.865
	340° F.								
Bubble Point <sup>a</sup>	(292)	(596)	(931)	(1304)	(1690)	(2079)	(2445)	(2711)	(2636) <sup>b</sup>
200	1.49	1.50	1.513	1.541	1.589	1.705	1.945	2.388	3.1 <sup>c</sup>
400	1.44	...	...	...	...	...	...	...	...
600	1.37	1.50	...	...	...	...	...	...	...
800	1.32	1.42	...	...	...	...	...	...	...
1,000	1.28	1.37	1.491	...	...	...	...	...	...
1,250	1.24	1.32	1.419	...	...	...	...	...	...
1,500	1.21	1.28	1.359	1.466	...	...	...	...	...
1,750	1.18	1.24	1.310	1.396	1.554	...	...	...	...
2,000	1.16	1.21	1.270	1.344	1.456	...	...	...	...
2,250	1.13	1.18	1.234	1.300	1.391	1.618	...	...	...
2,500	1.11	1.15	1.203	1.263	1.340	1.519	1.900	...	...
2,750	1.09	1.13	1.175	1.231	1.298	1.442	1.734	2.195	2.487
3,000	1.08	1.11	1.150	1.201	1.260	1.379	1.614	1.941	2.228
3,500	1.05	1.07	1.103	1.144	1.196	1.285	1.459	1.695	1.893
4,000	1.02	1.04	1.064	1.098	1.147	1.221	1.358	1.535	1.676
4,500	0.99	1.01	1.030	1.060	1.108	1.173	1.281	1.416	1.526
5,000	0.97	0.98	1.000	1.030	1.076	1.135	1.222	1.322	1.405
6,000	0.92	0.94	0.953	0.983	1.025	1.075	1.135	1.190	1.229
7,000	0.89	0.90	0.918	0.947	0.988	1.032	1.067	1.097	1.116
8,000	0.86	0.88	0.893	0.921	0.956	0.995	1.019	1.033	1.042
9,000	0.84	0.86	0.872	0.895	0.926	0.962	0.979	0.983	0.987
10,000	0.83	0.84	0.852	0.869	0.895	0.933	0.950	0.948	0.948

**Table II. Partial Molal Volume of Carbon Dioxide in Cubic Feet per Pound-Mole  
in the *n*-Decane-Carbon Dioxide System (Continued)**

Pressure, P.S.I.A.	Mole Fraction Carbon Dioxide								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
400° F.									
Bubble Point <sup>a</sup>	(327)	(646)	(1002)	(1383)	(1769)	(2150)	(2457)	(2586)	(2230) <sup>b</sup>
200	1.85	1.88	1.912	1.960	2.036	2.220	2.535	3.10	3.9 <sup>c</sup>
400	1.79	...	...	...	...	...	...	...	...
600	1.66	...	...	...	...	...	...	...	...
800	1.57	1.79	...	...	...	...	...	...	...
1,000	1.50	1.70	...	...	...	...	...	...	...
1,250	1.43	1.61	1.802	...	...	...	...	...	...
1,500	1.37	1.53	1.703	1.900	...	...	...	...	...
1,750	1.33	1.47	1.615	1.776	...	...	...	...	...
2,000	1.30	1.41	1.540	1.677	1.868	...	...	...	...
2,250	1.27	1.37	1.473	1.591	1.745	2.120	...	...	...
2,500	1.24	1.33	1.418	1.518	1.643	1.933	2.484	...	...
2,750	1.22	1.29	1.370	1.456	1.560	1.792	2.220	2.690	2.914
3,000	1.20	1.26	1.328	1.402	1.491	1.682	2.030	2.401	2.624
3,500	1.15	1.20	1.257	1.312	1.383	1.519	1.780	2.053	2.240
4,000	1.12	1.16	1.200	1.243	1.305	1.414	1.615	1.822	1.962
4,500	1.08	1.11	1.150	1.188	1.243	1.339	1.488	1.648	1.767
5,000	1.05	1.08	1.108	1.142	1.194	1.276	1.394	1.519	1.607
6,000	0.98	1.01	1.038	1.070	1.124	1.193	1.267	1.337	1.382
7,000	0.94	0.96	0.987	1.022	1.070	1.127	1.176	1.220	1.246
8,000	0.90	0.93	0.954	0.985	1.028	1.074	1.110	1.138	1.152
9,000	0.87	0.90	0.923	0.952	0.989	1.033	1.060	1.077	1.083
10,000	0.84	0.87	0.894	0.922	0.955	1.000	1.024	1.033	1.032
460° F									
Bubble Point <sup>a</sup>	(369)	(690)	(1049)	(1420)	(1792)	(2066)	(2210)	(2157) <sup>b</sup>	
200	2.43	2.52	2.625	2.740	2.900	3.250	3.99	...	
400	2.40	...	...	...	...	...	...	...	...
600	2.20	...	...	...	...	...	...	...	...
800	2.03	2.42	...	...	...	...	...	...	...
1,000	1.89	2.25	...	...	...	...	...	...	...
1,250	1.75	2.08	2.444	...	...	...	...	...	...
1,500	1.64	1.94	2.244	2.642	...	...	...	...	...
1,750	1.55	1.82	2.076	2.372	...	...	...	...	...
2,000	1.48	1.72	1.938	2.164	2.550	...	...	...	...
2,250	1.42	1.63	1.819	2.003	2.266	2.788	3.84	4.08	4.09
2,500	1.37	1.56	1.723	1.873	2.058	2.442	3.247	3.10	3.64
2,750	1.33	1.49	1.643	1.768	1.904	2.225	2.861	3.201	3.28
3,000	1.30	1.44	1.574	1.680	1.787	2.060	2.580	2.898	3.000
3,500	1.24	1.35	1.459	1.539	1.617	1.814	2.177	2.444	2.556
4,000	1.19	1.28	1.368	1.431	1.500	1.645	1.916	2.128	2.236
4,500	1.16	1.22	1.293	1.348	1.408	1.523	1.731	1.900	1.994
5,000	1.12	1.18	1.231	1.282	1.338	1.435	1.594	1.730	1.806
6,000	1.05	1.09	1.130	1.178	1.230	1.316	1.410	1.498	1.549
7,000	0.99	1.02	1.055	1.101	1.158	1.229	1.292	1.344	1.381
8,000	0.94	0.97	1.002	1.044	1.100	1.161	1.207	1.241	1.264
9,000	0.89	0.93	0.962	1.000	1.056	1.112	1.147	1.167	1.179
10,000	0.84	0.88	0.924	0.965	1.018	1.076	1.104	1.116	1.114

<sup>a</sup> Values in parentheses represent bubble-point pressures in p.s.i. <sup>b</sup> Retrograde dew point. <sup>c</sup> Estimated.

0.3 mole fraction *n*-decane for the higher pressures is somewhat unusual and, it apparently is limited to binary hydrocarbon systems containing carbon dioxide.

Figure 3 shows the rather simple behavior typical of the effect of temperature and pressure upon the partial volume of carbon dioxide at 0.7 mole fraction carbon dioxide. The data have only been extended to bubble point but cover the range of temperatures between 40° and 460° F. Similar information for *n*-decane is shown in Figure 4. Again, relatively simple behavior was encountered.

Much more complicated behavior is encountered near the phase boundaries. For example, Figure 5 shows the partial volume of carbon dioxide as a function of pressure at bubble point for temperatures between 40° and 460° F. The composition of the bubble-point liquid and the tem-

perature are shown as parametric variables upon this diagram. There is a larger uncertainty in the evaluation of the partial volumetric behavior of the components at bubble point than in the single-phase portions of the system. For this reason, the partial molal volumes at bubble point have not been recorded in tabular form. A similar diagram is presented in Figure 6 for the partial molal volume of *n*-decane at bubble point. The rather unusual behavior indicated by the curve corresponding to a mole fraction of 0.6 *n*-decane results from the nature of the projection near the maximum in the partial volume of *n*-decane at a pressure of about 1400 p.s.i.a.

The figures included represent only a few of the many examples that could be drawn portraying the interrelation of the numerous variables involved.

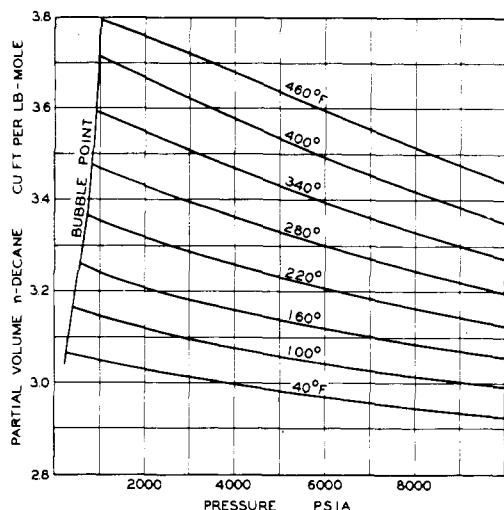


Figure 4. Effect of pressure on partial molal volume of *n*-decane at 0.7 mole fraction *n*-decane

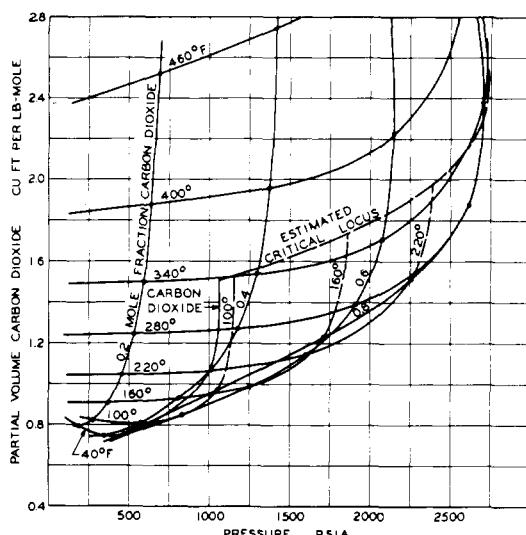


Figure 5. Partial molal volume of carbon dioxide at bubble point

Table III. Partial Molal Volume of *n*-Decane in Cubic Feet per Pound-Mole in the *n*-Decane-Carbon Dioxide System

Pressure, P.S.I.A.	Mole Fraction <i>n</i> -Decane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
40° F.									
Bubble Point <sup>a</sup>	(547) <sup>a</sup>	(523)	(497)	(465)	(415)	(347)	(271)	(183)	(93)
200	2.94	2.98	3.018	3.046	3.062	3.066	3.066	3.065	3.060
400	...	...	...	...	...	...	...	3.063	3.055
600	2.94	2.98	3.020	3.048	3.063	3.063	3.058	3.049	3.046
800	2.95	2.99	3.022	3.049	3.061	3.059	3.053	3.045	3.042
1,000	2.96	2.99	3.024	3.048	3.058	3.055	3.048	3.041	3.038
1,250	2.97	3.00	3.025	3.046	3.054	3.051	3.043	3.037	3.033
1,500	2.98	3.01	3.026	3.043	3.050	3.047	3.039	3.032	3.029
1,750	2.99	3.01	3.026	3.040	3.046	3.042	3.034	3.027	3.024
2,000	3.00	3.01	3.026	3.036	3.042	3.038	3.030	3.023	3.020
2,250	3.00	3.02	3.025	3.033	3.038	3.034	3.026	3.019	3.015
2,500	3.01	3.02	3.024	3.029	3.034	3.029	3.022	3.015	3.011
2,750	3.02	3.02	3.022	3.025	3.029	3.025	3.018	3.011	3.006
3,000	3.02	3.02	3.020	3.021	3.025	3.021	3.014	3.007	3.003
3,500	3.03	3.02	3.013	3.008	3.014	3.013	3.006	2.999	2.995
4,000	3.04	3.02	3.005	2.996	3.002	3.005	2.999	2.992	2.988
4,500	3.04	3.02	2.997	2.986	2.992	2.996	2.991	2.984	2.980
5,000	3.04	3.02	2.990	2.978	2.982	2.987	2.983	2.977	2.974
6,000	3.03	3.01	2.976	2.961	2.965	2.970	2.967	2.963	2.961
7,000	3.02	2.99	2.962	2.947	2.950	2.956	2.954	2.951	2.950
8,000	3.02	2.98	2.948	2.932	2.937	2.944	2.943	2.940	2.939
9,000	3.02	2.97	2.931	2.919	2.926	2.934	2.933	2.931	2.930
10,000	3.01	2.96	2.916	2.907	2.916	2.924	2.924	2.923	2.923
100° F.									
Bubble Point <sup>a</sup>	(1125) <sup>a</sup>	(1048)	(956)	(837)	(705)	(570)	(427)	(281)	(138)
200	2.36	2.84	3.019	3.090	3.131	3.152	3.164	3.169	3.169
400	...	...	...	...	...	...	...	...	3.165
600	...	...	...	...	...	3.151	3.159	3.156	3.151
800	...	...	...	...	...	3.147	3.152	3.148	3.145
1,000	...	...	3.018	3.088	3.128	3.142	3.146	3.141	3.138
1,250	2.41	2.85	3.015	3.084	3.125	3.136	3.137	3.134	3.131
1,500	2.52	2.86	3.011	3.081	3.121	3.131	3.130	3.126	3.124
1,750	2.62	2.88	3.008	3.077	3.117	3.125	3.123	3.120	3.118
2,000	2.71	2.89	3.005	3.072	3.112	3.119	3.116	3.113	3.112
2,250	2.79	2.90	3.002	3.067	3.106	3.114	3.110	3.108	3.107
2,500	2.85	2.92	2.999	3.062	3.100	3.108	3.104	3.103	3.102
2,750	2.90	2.93	2.997	3.056	3.094	3.103	3.099	3.097	3.096
3,000	2.94	2.95	2.995	3.050	3.086	3.097	3.094	3.093	3.092
3,500	3.00	2.97	2.992	3.038	3.072	3.084	3.083	3.083	3.082
4,000	3.04	3.00	2.989	3.025	3.060	3.072	3.072	3.073	3.073
4,500	3.05	3.02	2.987	3.017	3.050	3.063	3.064	3.065	3.065
5,000	3.06	3.03	2.984	3.010	3.041	3.054	3.055	3.056	3.056
6,000	3.06	3.03	2.981	3.001	3.027	3.038	3.040	3.041	3.042
7,000	3.06	3.02	2.970	2.991	3.015	3.023	3.025	3.027	3.028
8,000	3.04	3.00	2.955	2.979	3.002	3.010	3.012	3.014	3.015
9,000	3.03	2.98	2.938	2.967	2.988	2.998	3.000	3.001	3.002
10,000	3.02	2.97	2.924	2.955	2.977	2.987	2.989	2.990	2.991

Table III. Partial Molal Volume of *n*-Decane in Cubic Feet per Pound-Mole in the *n*-Decane-Carbon Dioxide System (Continued)

Pressure, P.S.I.A.	Mole Fraction <i>n</i> -Decane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
	160° F.								
Bubble Point <sup>a</sup>	(1844)	(1692)	(1471)	(1250)	(1027)	(802)	(583)	(374)	(178)
200	1.01	2.48	2.950	3.125	3.199	3.237	3.259	3.275	3.289
400	...	...	...	...	...	...	...	...	3.288
600	...	...	...	...	...	...	3.257	3.261	3.264
800	...	...	...	...	...	...	3.248	3.252	3.254
1,000	...	...	...	...	...	3.232	3.240	3.244	3.246
1,250	...	...	...	3.125	3.198	3.225	3.231	3.234	3.237
1,500	...	...	2.951	3.123	3.196	3.218	3.223	3.226	3.228
1,750	...	2.49	2.959	3.120	3.193	3.211	3.215	3.219	3.221
2,000	1.31	2.55	2.966	3.117	3.188	3.204	3.208	3.212	3.214
2,250	1.87	2.61	2.974	3.114	3.182	3.197	3.202	3.205	3.207
2,500	2.10	2.68	2.981	3.110	3.176	3.190	3.195	3.198	3.200
2,750	2.34	2.74	2.988	3.107	3.168	3.183	3.188	3.191	3.194
3,000	2.56	2.79	2.995	3.103	3.161	3.176	3.182	3.185	3.187
3,500	2.79	2.88	3.008	3.095	3.148	3.164	3.170	3.173	3.175
4,000	2.90	2.95	3.019	3.088	3.137	3.152	3.159	3.162	3.163
4,500	2.97	2.99	3.025	3.082	3.128	3.142	3.148	3.151	3.152
5,000	3.02	3.02	3.028	3.076	3.119	3.133	3.138	3.141	3.142
6,000	3.06	3.04	3.028	3.064	3.103	3.115	3.119	3.121	3.122
7,000	3.08	3.05	3.020	3.050	3.087	3.097	3.101	3.104	3.105
8,000	3.08	3.04	3.009	3.036	3.071	3.081	3.084	3.087	3.088
9,000	3.09	3.03	2.995	3.023	3.055	3.067	3.069	3.071	3.072
10,000	3.09	3.03	2.978	3.009	3.040	3.053	3.056	3.057	3.058
220° F.									
Bubble Point <sup>a</sup>	(2391)	(2258)	(1945)	(1625)	(1311)	(1010)	(725)	(458)	(217)
200	...	1.97	2.837	3.164	3.271	3.329	3.365	3.390	3.414
400	...	...	...	...	...	...	...	...	3.399
600	...	...	...	...	...	...	3.381	3.384	3.384
800	...	...	...	...	...	...	3.361	3.369	3.372
1,000	...	...	...	...	...	...	3.353	3.359	3.362
1,250	...	...	...	...	...	3.329	3.343	3.348	3.351
1,500	...	...	...	3.167	3.274	3.320	3.334	3.337	3.341
1,750	...	...	...	3.167	3.277	3.315	3.325	3.328	3.331
2,000	...	...	2.847	3.170	3.277	3.306	3.316	3.319	3.322
2,250	...	2.886	3.172	3.273	3.299	3.309	3.311	3.314	3.314
2,500	...	2.28	2.924	3.173	3.268	3.291	3.301	3.303	3.306
2,750	1.23	2.45	2.957	3.173	3.262	3.284	3.294	3.296	3.299
3,000	1.78	2.56	2.994	3.172	3.256	3.276	3.287	3.289	3.292
3,500	2.31	2.73	3.031	3.169	3.242	3.263	3.273	3.275	3.278
4,000	2.56	2.84	3.061	3.165	3.227	3.249	3.258	3.260	3.263
4,500	2.72	2.92	3.075	3.160	3.214	3.235	3.245	3.248	3.250
5,000	2.84	2.98	3.080	3.152	3.203	3.222	3.232	3.235	3.237
6,000	2.98	3.04	3.082	3.132	3.182	3.198	3.206	3.211	3.213
7,000	3.08	3.08	3.080	3.112	3.158	3.176	3.184	3.189	3.191
8,000	3.11	3.08	3.072	3.096	3.137	3.156	3.162	3.166	3.167
9,000	3.13	3.09	3.059	3.081	3.120	3.137	3.142	3.146	3.147
10,000	3.14	3.09	3.043	3.066	3.102	3.121	3.124	3.126	3.127
280° F.									
Bubble Point <sup>a</sup>	(2662) <sup>b</sup>	(2616)	(2267)	(1903)	(1544)	(1184)	(840)	(529)	(252)
200	...	1.40	2.680	3.144	3.339	3.416	3.474	3.517	3.550
400	...	...	...	...	...	...	...	...	3.535
600	...	...	...	...	...	...	...	3.510	3.517
800	...	...	...	...	...	...	3.494	3.502	3.502
1,000	...	...	...	...	...	...	3.467	3.481	3.490
1,250	...	...	...	...	...	3.417	3.457	3.467	3.476
1,500	...	...	...	...	...	3.418	3.447	3.456	3.463
1,750	...	...	...	3.160	3.351	3.417	3.438	3.446	3.451
2,000	...	...	...	3.160	3.360	3.413	3.429	3.436	3.440
2,250	...	...	...	3.189	3.361	3.407	3.420	3.427	3.430
2,500	...	2.791	3.207	3.359	3.401	3.411	3.417	3.420	3.420
2,750	...	1.88	2.883	3.223	3.355	3.394	3.403	3.408	3.411
3,000	0.78	2.29	2.948	3.228	3.250	3.386	3.394	3.399	3.402
3,500	1.69	2.53	3.022	3.238	3.339	3.371	3.379	3.382	3.385
4,000	2.12	2.70	3.067	3.240	3.325	3.354	3.363	3.366	3.368
4,500	2.36	2.83	3.099	3.237	3.310	3.336	3.346	3.349	3.351
5,000	2.56	2.92	3.119	3.228	3.293	3.319	3.330	3.332	3.334
6,000	2.86	3.03	3.138	3.204	3.263	3.287	3.299	3.303	3.305
7,000	3.04	3.10	3.139	3.181	3.230	3.256	3.270	3.274	3.276
8,000	3.11	3.12	3.131	3.159	3.205	3.232	3.245	3.248	3.250
9,000	3.14	3.13	3.120	3.141	3.187	3.211	3.220	3.222	3.224
10,000	3.16	3.14	3.106	3.126	3.170	3.192	3.196	3.198	3.200

(Continued on page 56)

Table III. Partial Molal Volume of *n*-Decane in Cubic Feet per Pound-Mole in the *n*-Decane-Carbon Dioxide System (Continued)

Pressure, P.S.I.A.	Mole Fraction <i>n</i> -Decane								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
340° F.									
Bubble Point <sup>a</sup>	(2636) <sup>b</sup>	(2711)	(2445)	(2079)	(1690)	(1304)	(931)	(596)	(292)
200	...	0.84	2.488	3.093	3.375	3.506	3.592	3.660	3.709
400	...	...	...	...	...	...	...	...	3.698
600	...	...	...	...	...	...	...	3.659	3.678
800	...	...	...	...	...	...	...	3.642	3.659
1,000	...	...	...	...	...	...	3.589	3.626	3.641
1,250	...	...	...	...	...	...	3.578	3.608	3.621
1,500	...	...	...	...	...	3.511	3.568	3.591	3.603
1,750	...	...	...	...	3.394	3.516	3.558	3.576	3.586
2,000	...	...	...	...	3.430	3.516	3.548	3.562	3.571
2,250	...	...	...	3.150	3.443	3.514	3.539	3.550	3.558
2,500	...	...	2.532	3.199	3.448	3.510	3.529	3.538	3.546
2,750	...	1.48	2.734	3.230	3.449	3.503	3.520	3.527	3.534
3,000	0.34	1.99	2.850	3.256	3.448	3.495	3.510	3.517	3.523
3,500	1.34	2.33	2.980	3.292	3.439	3.476	3.490	3.496	3.501
4,000	1.86	2.56	3.052	3.309	3.421	3.455	3.471	3.476	3.480
4,500	2.17	2.73	3.099	3.309	3.403	3.436	3.450	3.455	3.459
5,000	2.43	2.85	3.133	3.301	3.384	3.417	3.430	3.435	3.438
6,000	2.80	3.01	3.174	3.277	3.843	3.378	3.393	3.397	3.400
7,000	2.98	3.10	3.183	3.247	3.306	3.342	3.359	3.362	3.364
8,000	3.08	3.13	3.178	3.224	3.280	3.313	3.328	3.332	3.334
9,000	3.14	3.15	3.170	3.206	3.258	3.288	3.300	3.304	3.306
10,000	3.18	3.17	3.157	3.190	3.239	3.264	3.272	3.278	3.280
400° F.									
Bubble Point <sup>a</sup>	(2230) <sup>b</sup>	(2586)	(2457)	(2150)	(1769)	(1383)	(1002)	(646)	(327)
200	...	0.26	2.128	2.965	3.382	3.576	3.716	3.820	3.899
400	...	...	...	...	...	...	...	...	3.889
600	...	...	...	...	...	...	...	...	3.862
800	...	...	...	...	...	...	...	3.800	3.838
1,000	...	...	...	...	...	...	...	3.779	3.816
1,250	...	...	...	...	...	...	3.701	3.756	3.790
1,500	...	...	...	...	...	3.583	3.688	3.736	3.766
1,750	...	...	...	...	...	3.596	3.675	3.717	3.743
2,000	...	...	...	...	3.458	3.604	3.663	3.700	3.722
2,250	...	...	...	3.010	3.493	3.607	3.653	3.683	3.703
2,500	...	...	2.184	3.113	3.514	3.606	3.642	3.668	3.684
2,750	...	1.30	2.494	3.195	3.527	3.603	3.632	3.653	3.667
3,000	0.56	1.70	2.687	3.254	3.533	3.597	3.622	3.639	3.650
3,500	1.17	2.13	2.897	3.324	3.530	3.581	3.601	3.612	3.620
4,000	1.69	2.41	3.005	3.357	3.515	3.560	3.579	3.586	3.592
4,500	2.07	2.62	3.078	3.365	3.496	3.539	3.555	3.561	3.566
5,000	2.35	2.78	3.133	3.369	3.474	3.517	3.532	3.538	3.543
6,000	2.74	2.99	3.194	3.340	3.428	3.472	3.490	3.496	3.500
7,000	2.91	3.08	3.217	3.316	3.388	3.432	3.453	3.459	3.464
8,000	3.02	3.13	3.219	3.292	3.358	3.398	3.416	3.424	3.428
9,000	3.12	3.17	3.213	3.271	3.331	3.366	3.382	3.391	3.395
10,000	3.20	3.19	3.205	3.250	3.307	3.338	3.351	3.362	3.366
460° F.									
Bubble Point <sup>a</sup>	(2157) <sup>b</sup>	(2210)	(2066)	(1792)	(1420)	(1049)	(690)	(369)	
200	...	...	1.000	2.485	3.124	3.543	3.795	3.977	4.115
400	...	...	...	...	...	...	...	...	4.110
600	...	...	...	...	...	...	...	...	4.078
800	...	...	...	...	...	...	...	3.960	4.046
1,000	...	...	...	...	...	...	...	3.933	4.015
1,250	...	...	...	...	...	...	3.789	3.904	3.979
1,500	...	...	...	...	3.565	3.780	3.879	3.944	
1,750	...	...	...	...	3.614	3.772	3.856	3.912	
2,000	...	...	...	3.820	3.639	3.763	3.836	3.884	
2,250	...	...	1.187	2.840	3.442	3.655	3.753	3.817	3.858
2,500	...	0.86	1.696	3.030	3.514	3.662	3.744	3.800	3.834
2,750	...	1.14	2.034	3.140	3.558	3.666	3.734	3.783	3.812
3,000	0.89	1.41	2.300	3.215	3.581	3.667	3.723	3.767	3.791
3,500	1.17	1.91	2.696	3.322	3.597	3.664	3.703	3.731	3.751
4,000	1.59	2.26	2.893	3.382	3.596	3.654	3.680	3.700	3.716
4,500	2.00	2.52	3.022	3.411	3.584	3.636	3.657	3.671	3.686
5,000	2.31	2.71	3.110	3.420	3.564	3.615	3.635	3.647	3.659
6,000	2.69	2.95	3.210	3.404	3.524	3.571	3.595	3.604	3.612
7,000	2.88	3.09	3.249	3.379	3.476	3.528	3.552	3.561	3.567
8,000	3.02	3.16	3.260	3.354	3.438	3.489	3.510	3.522	3.526
9,000	3.12	3.19	3.256	3.330	3.404	3.455	3.472	3.485	3.489
10,000	3.20	3.21	3.248	3.304	3.374	3.420	3.438	3.452	3.456

<sup>a</sup>Values in parentheses represent bubble-point pressures in p.s.i. <sup>b</sup>Retrograde dew point.

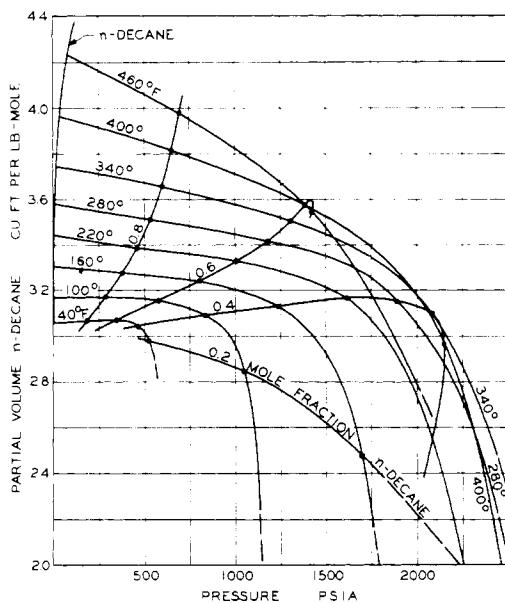


Figure 6. Partial molal volume of *n*-decane at bubble point

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#### NOMENCLATURE

$d$  = differential operator  
 $m_k$  = lb.-moles of component  $k$

$N$	= number of points
$n_k$	= mole fraction of component $k$
$V$	= molal volume, cu. ft./lb.-mole
$\nabla$	= partial molal volume, partial volume, cu. ft./lb.-mole
$V$	= total volume, cu. ft.
$\sum$	= summation
$\sigma$	= standard error of estimate, cu. ft./lb.-mole
$\partial$	= partial differential operator

#### Subscripts

$gr$	= graphical
$int$	= integrated
$j, k$	= components $j$ and $k$
$m_i$	= change in state during which the weight of all components other than $k$ remains constant
$P$	= pressure, p.s.i.a.
$T$	= thermodynamic temperature, °R.

#### Superscript

$^{\circ}$  = pure component

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## Viscosity of Hydrocarbons. Methane

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Confirmatory measurements of the viscosity of methane in the gas phase were carried out at pressures up to 5000 p.s.i.a in the temperature interval between 40° and 400° F. These measurements corroborate and extend the results reported in earlier, more extensive investigations which were carried out with entirely different types of instruments. A comparison of the current measurements with those obtained by other investigators has been included along with an analytical expression describing the effect of temperature and specific weight upon the viscosity of methane.

THE VISCOSITY of methane has been investigated extensively. However, the agreement among the several investigators leaves something to be desired. Ross and Brown (1) reported measurements at temperatures between 32° and 77° F., while Barua, Ross, and Afzal (2) extended these measurements to temperatures above 300° F. Measurements are reported with a rolling-ball viscometer (16) at temperatures from 100° to 220° F. Bicher and Katz (3) reported measurements at temperatures between 77°

and 437° F., while Carr (7) made an investigation at temperatures up to 200° F. Comings, Mayland, and Egly (8) reported data from 86° to 203° F.; Baron, Roof, and Wells (1) reported measurements at temperatures between 125° and 275° F.; while Kestin and Leidenfrost (10) made measurements in the vicinity of 70° F.

The significant dispersion among these several investigators indicated the need for further confirmatory measurements with an entirely different type of instrument. For