shown in Figure 4. No experimental points have been included since the curves represent interpolated values obtained from Figures 2 and 3. The behavior is similar to that encountered in other binary systems containing CO_2 (*11, 16, 17, 20*). Some of the properties at the unique states of the *n*-decane-CO_2 system are presented as a function of composition in Table II.

In order to illustrate still further the nature of the phase behavior of this sytem, there is shown in Figure 5 the product of the pressure and equilibrium ratio for both *n*-decane and CO_2 as a function of pressure for eight temperatures between 40° and 460° F.

A large number of other diagrams, particularly those pertaining to the volumetric behavior of this system, could be presented. However, the behavior is similar to that encountered in other binary systems with CO_2 and a hydrocarbon as components.

ACKNOWLEDGMENT

This work is a contribution of the American Petroleum Institute Research Project 37 at the California Institute of Technology. Virginia Berry and Virginia Moore contributed materially to the reduction of the experimental data to a form suitable for publication. B. Lawson Miller assisted in the preparation of the manuscript.

LITERATURE CITED

(1) Am. Petroleum Inst. Research Project 44, Petroleum Research Laboratory, Carnegie Institute of Technology, "Selected Values of Properties of Hydrocarbons and Related Compounds."
(2) Bridgeman, O.C., *J. Am. Chem. Soc.* **49**, 1174 (1927).
(3) Couch, H.T., Kozicki, William, Sage, B.H., J. CHEM. ENG. DATA **8**, 346 (1963).
(4) Kendall, B.J., Sage, B.H., *Petroleum (London)* **14**, 184 (1951).
(5) Kuenen, J.P., *Phil. Mag.* **44**, 174 (1897).
(6) Kuenen, J.P., *Z. physik. Chem.* **24**, 667 (1897).
(7) Kuenen, J.P., Robson, W.G., *Phil. Mag.* **4**, 116 (1902).
(8) Meyer, C.H., Van Dusen, M.S., *Bur. Standards J. Research* **10**, 381 (1933).
(9) Michels, A., Blaisse, B., Michels, C., *Proc. Roy. Soc.* (London) **A160**, 358 (1937).
(10) Michels, A., Michels, C., *Ibid.*, **A153**, 201 (1935).
(11) Olds, R.H., Reamer, H.H., Sage, B.H., Lacey, W.N., *Ind. Eng. Chem.* **41**, 475 (1949).
(12) Olds, R.H., Sage, B.H., Lacey, W.N., Fundamental Research on Occurrence and Recovery of Petroleum 1943, American Petroleum Institute, 1944, pp. 44-61.
(13) Poettmann, F.H., Katz, D.L., *Ind. Eng. Chem.* **37**, 847 (1945).
(14) Reamer, H.H., Fiskin, J.M., Sage, B.H., *Ibid.*, **41**, 2871 (1949).
(15) Reamer, H.H., Olds, R.H., Sage, B.H., Lacey, W.N., *Ibid.*, **34**, 1526 (1942).
(16) *Ibid.*, **36**, 88 (1944).
(17) *Ibid.*. **37**, 688 (1945).
(18) Reamer, H.H., Sage, B.H., *Am. Doc. Inst.*, Washington, D. C., Doc. No. 7685 (1963).
(19) Reamer, H.H., Sage, B.H., *Rev. Sci. Instr.* **26**, 592 (1955).
(20) Reamer, H.H., Sage, B.H., Lacey, W.N., *Ind. Eng. Chem.* **43**, 2515 (1951).
(21) Sage, B.H., Lacey, W.N., *Trans. Am. Inst. Mining Met. Engrs.* **136**, 136 (1940).

RECEIVED for review April 4, 1963. Accepted July 8, 1963. A more detailed form of this paper (or extended version, or material supplementary to this article) has been deposited as Document No. 7685 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress Washington 25, D. C. A copy may be secured by citing the document number and by remitting $3.75 for photoprints or $2.00 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to Chief, Photoduplication Service, Libary of Congress.

Vapor Liquid Equilibrium in the Methane-*n*-Decane-Nitrogen System

A. AZARNOOSH[1] and J. J. McKETTA
The University of Texas, Austin, Tex.

Experimental data on the compositions of the conjugate phases are presented. These data are presented in the form of isotherms at 100, 160, 220, 280° F. At each of these isotherms equilibrium data were obtained at 1000, 2000, 3000, 4000, and 5000 p.s.i.a., with the nitrogen concentration varying from 0% to 100% in the vapor phase.

SINCE NITROGEN occurs extensively in petroleum fluids, a knowledge of its equilibrium data is of importance in the petroleum industry. *K* values for nitrogen are reported in the N.G.A.A. data book (*3*) up to a convergence pressure of 5000 p.s.i.a. Jacoby (*5*) in his review of the *K* values of an earlier edition of this book, with reference to the nonhydrocarbon *K* value, emphasizes the need for more experimental data on the effect of nitrogen on the hydrocarbon *K* values.

In this work the methane-*n*-decane-nitrogen system was investigated at temperatures of 100, 160, 220, and 280° F. At each of the isotherms, equilibrium data were obtained at 1000, 2000, 3000, 4000 and 5000 p.s.i.a. with the nitrogen concentration varying from 0% to 100% in the vapor phase.

[1] Present address: National Iranian Oil Company, Teheran, Iran.

Table I. Experimental Ternary Data

Vapor Phase			Liquid Phase		
C_1	n-C_{10}	N_2	C_1	n-C_{10}	N_2
		100° F.			
		1000 p.s.i.a.			
0.9058	0.00060	0.0936	0.2430	0.7460	0.0110
0.8196	0.00100	0.1793	0.2070	0.7600	0.0330
0.7277	0.00063	0.2717	0.1721	0.7878	0.0401
0.6477	0.00047	0.3518	0.1798	0.7870	0.0332
0.6167	0.00038	0.3829	0.1472	0.7990	0.0538
0.5519	0.00034	0.4478	0.1352	0.8165	0.0483
0.4616	0.00033	0.5380	0.1177	0.8212	0.0611
0.3603	0.00031	0.6394	0.0964	0.8350	0.0686
0.2563	0.00032	0.7433	0.0517	0.8656	0.0837
0.1456	0.00030	0.8541	0.0256	0.8880	0.0864
		2000 p.s.i.a.			
0.9275	0.00120	0.0713	0.3950	0.0840	0.0210
0.8370	0.00128	0.1617	0.3500	0.6080	0.0420
0.6494	0.00073	0.3499	0.2778	0.6510	0.0712
0.5520	0.00050	0.4475	0.2250	0.6775	0.0975
0.3910	0.00041	0.6086	0.1600	0.7160	0.1240
0.1234	0.00042	0.8762	0.0505	0.7810	0.1685
0.0794	0.00034	0.9203	0.0256	0.7992	0.1752
		3000 p.s.i.a.			
0.8320	0.00300	0.1650	0.4790	0.4763	0.0447
0.7563	0.00200	0.2417	0.4180	0.5120	0.0700
0.6440	0.00180	0.3542	0.3630	0.5420	0.0950
0.5555	0.00114	0.4433	0.3147	0.5625	0.1228
0.3855	0.00117	0.6133	0.2220	0.6190	0.1590
0.2706	0.00089	0.7285	0.1550	0.6670	0.1780
0.1563	0.00080	0.8430	0.0950	0.6940	0.2110
		4000 p.s.i.a.			
0.8515	0.00682	0.1417	0.5840	0.3700	0.0460
0.7534	0.00472	0.2418	0.5120	0.4000	0.0880
0.6198	0.00375	0.3765	0.4150	0.4640	0.1210
0.4878	0.00353	0.5087	0.3400	0.5050	0.1550
0.3670	0.00300	0.6300	0.2470	0.5650	0.1880
0.2349	0.00176	0.7634	0.1790	0.5930	0.2280
0.1418	0.00160	0.8566	0.1177	0.6280	0.2543
0.0649	0.00129	0.9338	0.0438	0.6698	0.2864
		5000 p.s.i.a.			
0.8634	0.00712	0.1295	0.6370	0.2945	0.0685
0.7741	0.00685	0.2190	0.5850	0.3210	0.0940
0.6972	0.00373	0.2991	0.5230	0.3560	0.1210
0.6140	0.00500	0.3810	0.4590	0.3840	0.1570
0.5620	0.00430	0.4337	0.4360	0.3870	0.1770
0.4669	0.00554	0.5276	0.3610	0.4410	0.1980
0.3730	0.00600	0.6210	0.2760	0.4970	0.2270
0.3360	0.00500	0.6590	0.2420	0.5200	0.2380
0.2500	0.00450	0.7455	0.1785	0.5440	0.2775
0.1510	0.00460	0.8444	0.1248	0.5840	0.2912
0.0655	0.0030	0.9315	0.0520	0.6180	0.3300
0.0625	0.00500	0.9325	0.0408	0.6270	0.3322
		160° F.			
		1000 p.s.i.a.			
0.8746	0.00164	0.1238	0.2160	0.7690	0.0150
0.7739	0.00126	0.2248	0.1620	0.8050	0.0330
0.8076	0.00161	0.1908	0.1960	0.7800	0.0240
0.5464	0.00111	0.4525	0.1405	0.8105	0.0490
0.3666	0.00092	0.6325	0.1074	0.8345	0.0581
0.2745	0.00087	0.7246	0.0775	0.8520	0.0705
0.1818	0.00085	0.8173	0.0387	0.8774	0.0839
		2000 p.s.i.a.			
0.9014	0.00309	0.0956	0.3754	0.5950	0.0296
0.7151	0.00240	0.2825	0.3030	0.6505	0.0465
0.5923	0.00200	0.4057	0.2507	0.6690	0.0803
0.3490	0.0012	0.6498	0.1480	0.7284	0.1236
0.3349	0.00140	0.6637	0.1545	0.7270	0.1185
0.2270	0.0011	0.7719	0.1052	0.7522	0.1426
0.1715	0.0014	0.8271	0.0753	0.7660	0.1587
0.0935	0.00106	0.9055	0.0308	0.7950	0.1742
0.0919	0.00094	0.9072	0.0419	0.7880	0.1701
		3000 p.s.i.a.			
0.8958	0.00442	0.0998	0.4940	0.4741	0.0319
0.7702	0.00357	0.2263	0.4316	0.5132	0.0552
0.6123	0.00240	0.3853	0.3466	0.5544	0.0990
0.4544	0.00250	0.5431	0.2649	0.6060	0.1291
0.3849	0.00197	0.6131	0.2221	0.6335	0.1444
0.2738	0.00220	0.7240	0.1631	0.6575	0.1794
		160° F. (*Cont.*)			
		3000 p.s.i.a. (*Cont.*)			
0.1700	0.00254	0.8275	0.1006	0.6880	0.2114
0.0848	0.00168	0.9135	0.0429	0.7209	0.2362
		4000 p.s.i.a.			
0.8382	0.00890	0.1529	0.5600	0.3840	0.0560
0.7384	0.00543	0.2562	0.4800	0.4280	0.0920
0.5886	0.00402	0.4074	0.3810	0.4775	0.1415
0.4216	0.00470	0.5737	0.2870	0.5260	0.1870
0.2590	0.00300	0.7380	0.1825	0.5876	0.2299
0.1602	0.0027	0.8371	0.1160	0.6250	0.2590
0.0895	0.00258	0.9079	0.0631	0.6590	0.2779
		5000 p.s.i.a.			
0.8830	0.03307	0.0839	0.7290	0.2240	0.0470
0.8764	0.01478	0.1088	0.6750	0.2620	0.0630
0.8275	0.01250	0.1600	0.6360	0.2850	0.0790
0.7685	0.00953	0.2220	0.5830	0.3060	0.1110
0.6905	0.00850	0.3010	0.5110	0.3580	0.1310
0.5520	0.00760	0.4404	0.4150	0.4060	0.1790
0.4453	0.00842	0.5463	0.3420	0.4350	0.2230
0.3550	0.00645	0.6386	0.2600	0.4800	0.2600
0.2445	0.00550	0.7500	0.1800	0.5233	0.2967
0.1481	0.00520	0.8467	0.1058	0.5630	0.3312
		220° F.			
		1000 p.s.i.a.			
0.9310	0.00510	0.0639	0.2198	0.7706	0.0096
0.7738	0.00460	0.2216	0.1946	0.7768	0.0286
0.6276	0.00388	0.3685	0.1604	0.8085	0.0311
0.5140	0.00340	0.4826	0.1167	0.8310	0.0523
0.3606	0.00340	0.6360	0.0805	0.8475	0.0720
0.2770	0.00323	0.7198	0.0633	0.8525	0.0842
0.1977	0.00270	0.7996	0.0430	0.8700	0.0870
0.0775	0.00310	0.9194	0.0174	0.8830	0.0996
		2000 p.s.i.a.			
0.9232	0.00745	0.0693	0.3730	0.6090	0.0180
0.8617	0.00790	0.1304	0.3570	0.6130	0.0300
0.7600	0.00430	0.2357	0.3070	0.6450	0.0480
0.6170	0.00555	0.3774	0.2420	0.6818	0.0762
0.4630	0.00510	0.5319	0.1958	0.6910	0.1132
0.4200	0.0050	0.5750	0.1780	0.7060	0.1160
0.2372	0.0055	0.7573	0.0882	0.7610	0.1508
0.1212	0.00416	0.8747	0.0564	0.7778	0.1658
0.0516	0.0036	0.9448	0.0202	0.7950	0.1848
		3000 p.s.i.a.			
0.9633	0.01018	0.0265	0.5350	0.446	0.0190
0.9608	0.01313	0.0261	0.5160	0.470	0.0140
0.8550	0.0107	0.1343	0.457	0.492	0.0510
0.6638	0.0094	0.3268	0.3500	0.5570	0.0930
0.5268	0.00884	0.4644	0.2908	0.5820	0.1272
0.3438	0.0044	0.6518	0.1780	0.6520	0.1700
0.2665	0.0050	0.7285	0.1280	0.6680	0.2040
0.1295	0.0050	0.8655	0.0660	0.7070	0.2270
		4000 p.s.i.a.			
0.9172	0.01680	0.0660	0.6250	0.3480	0.0270
0.7751	0.01565	0.2093	0.5125	0.4080	0.0795
0.6712	0.01400	0.3148	0.4270	0.4500	0.1230
0.5175	0.00892	0.4736	0.3310	0.4970	0.1720
0.3502	0.00587	0.6439	0.2180	0.5640	0.2180
0.2525	0.01034	0.7372	0.1650	0.5920	0.2430
0.1354	0.00740	0.8572	0.0804	0.6400	0.2796
		5000 p.s.i.a.			
0.8243	0.0706	0.1051	0.7365	0.2050	0.0585
0.8210	0.0604	0.1186	0.6660	0.2485	0.0855
0.8088	0.0523	0.1389	0.6620	0.2510	0.0870
0.7989	0.04325	0.1579	0.6400	0.2625	0.0975
0.7922	0.04423	0.1636	0.6230	0.2670	0.1100
0.7885	0.0325	0.1790	0.6000	0.2870	0.1130
0.7608	0.0242	0.2150	0.5809	0.3017	0.1174
0.6815	0.0111	0.3074	0.5140	0.3380	0.1480
0.6127	0.0132	0.3741	0.4480	0.3680	0.1840
0.4730	0.0128	0.5142	0.3459	0.4375	0.2166
0.3752	0.0100	0.6148	0.2780	0.4580	0.2640
0.2800	0.0111	0.7089	0.1940	0.5060	0.3000
0.1800	0.0102	0.8098	0.1350	0.5444	0.3210

Table I. Experimental Ternary Data *(Continued)*

Vapor Phase			Liquid Phase		
C_1	n-C_{10}	N_2	C_1	n-C_{10}	N_2
		280°			
		1000 p.s.i.a.			
0.9657	0.01250	0.0218	0.2205	0.7762	0.0033
0.9175	0.01080	0.0717	0.2018	0.7880	0.0112
0.8270	0.00900	0.1640	0.1815	0.8010	0.0175
0.6920	0.00814	0.2999	0.1530	0.8140	0.0333
0.5532	0.00684	0.4400	0.1200	0.8295	0.0505
0.3737	0.00774	0.6186	0.0839	0.8445	0.0716
0.2504	0.00710	0.7425	0.0532	0.8665	0.0803
0.1013	0.00670	0.8920	0.0216	0.8845	0.0939
		2000 p.s.i.a.			
0.9114	0.0120	0.0766	0.3600	0.6260	0.0140
0.8391	0.00445	0.1565	0.3260	0.637	0.037
0.7178	0.0098	0.2724	0.2820	0.662	0.056
0.6163	0.00903	0.3747	0.2250	0.6850	0.090
0.4844	0.0096	0.5060	0.1943	0.701	0.1047
0.3598	0.0107	0.6295	0.148	0.728	0.124
0.2726	0.0080	0.7194	0.1022	0.7430	0.1548
0.2025	0.0068	0.7907	0.0740	0.7620	0.1640
0.0966	0.0081	0.8953	0.0350	0.783	0.182
		3000 p.s.i.a.			
0.9207	0.01530	0.0640	0.5050	0.4730	0.0220
0.8364	0.01033	0.1533	0.4250	0.5220	0.0530
0.7750	0.01020	0.2148	0.3850	0.5360	0.0790
0.6527	0.01120	0.3361	0.3300	0.5600	0.1100
0.4650	0.00878	0.5262	0.2330	0.5940	0.1730
		280° F. *(Cont.)*			
		3000 p.s.i.a. *(Cont.)*			
0.3290	0.00724	0.6638	0.1605	0.6303	0.2092
0.3032	0.0086	0.6882	0.1550	0.6515	0.1935
0.1605	0.00789	0.8316	0.0807	0.690	0.2293
0.1175	0.0108	0.8717	0.0592	0.7020	0.2388
		4000 p.s.i.a.			
0.9030	0.03800	0.0590	0.6300	0.3400	0.0300
0.8060	0.0185	0.1755	0.5379	0.3892	0.0729
0.720	0.0160	0.2640	0.4637	0.4213	0.1150
0.6550	0.0144	0.3306	0.3934	0.4590	0.1476
0.4676	0.0152	0.5172	0.2875	0.5200	0.1925
0.3310	0.0157	0.6533	0.1960	0.5640	0.2400
0.2530	0.0090	0.7380	0.1565	0.5880	0.2555
0.1795	0.0099	0.8106	0.1015	0.6080	0.2905
0.0560	0.0096	0.9344	0.0327	0.6560	0.3113
		5000 p.s.i.a.			
0.7706	0.0876	0.1418	0.6560	0.2580	0.0860
0.7622	0.0800	0.1578	0.6320	0.2530	0.1150
0.7390	0.0703	0.1907	0.5860	0.2850	0.1290
0.6867	0.0639	0.2494	0.4820	0.3370	0.1810
0.6128	0.0377	0.3495	0.4240	0.3690	0.2070
0.5059	0.0438	0.4503	0.3130	0.0426	0.2610
0.3667	0.0329	0.6004	0.2210	0.4980	0.2810
0.2464	0.0157	0.7379	0.1410	0.5250	0.3340
0.1021	0.0168	0.8811	0.0670	0.5600	0.3730

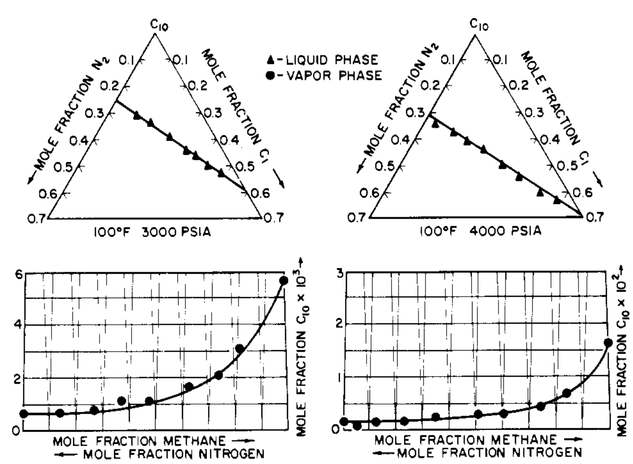
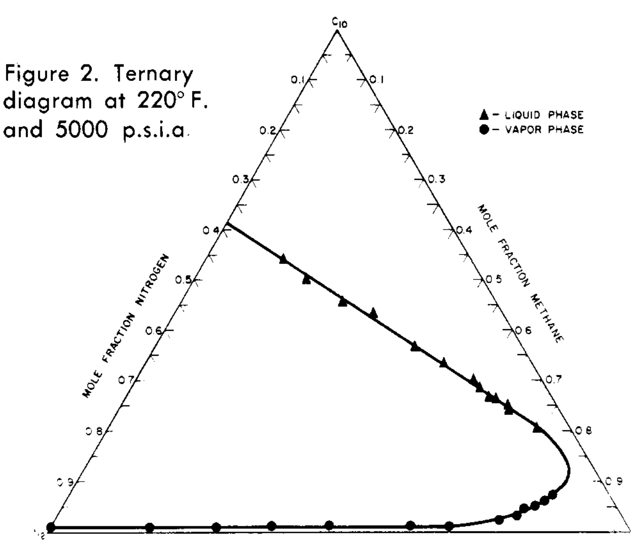


Figure 1. Ternary diagram

Figure 2. Ternary diagram at 220° F. and 5000 p.s.i.a.



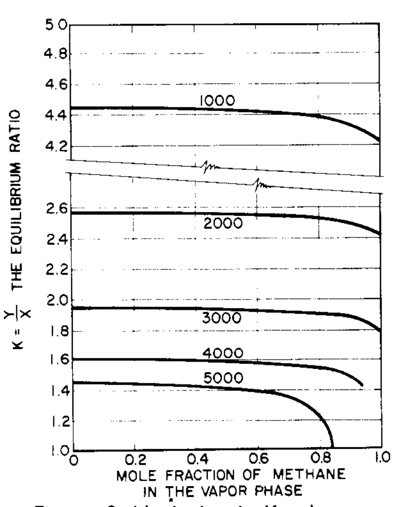


Figure 3. Variation in K value for methane at 220° F.

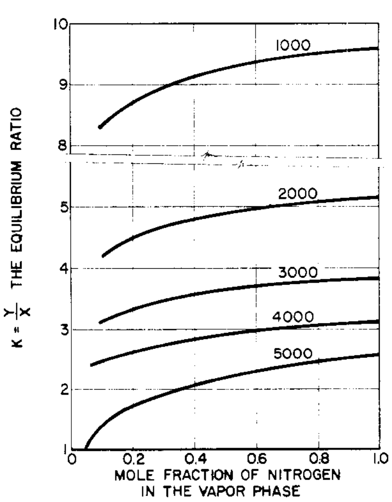


Figure 4. Variation in K value for nitrogen at 220° F.

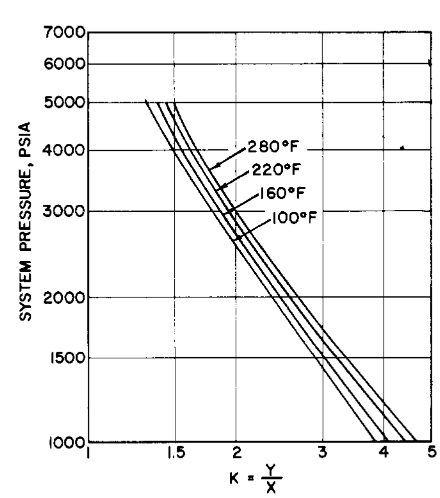


Figure 5. Experimental K values for methane

Table II. Smoothed Ternary Data

Methane			Nitrogen			n-Decane		
Y	X	K	Y	X	K	Y	X	$K \times 10^3$
				100° F.				
				1000 p.s.i.a.				
0.900	0.2392	3.758	0.0994	0.0122	8.20	0.00058	0.7486	0.775
0.800	0.2108	3.775	0.1995	0.0235	8.50	0.00048	0.7657	0.625
0.700	0.1847	3.788	0.2996	0.0340	8.83	0.00042	0.7813	0.537
0.600	0.1580	3.797	0.3996	0.0440	9.08	0.00037	0.7980	0.463
0.500	0.1312	3.803	0.4997	0.0537	9.30	0.00034	0.8151	0.417
0.400	0.1050	3.808	0.5997	0.0626	9.57	0.00032	0.8324	0.384
0.300	0.0788	3.812	0.6997	0.0715	9.80	0.00031	0.8497	0.365
0.200	0.0524	3.815	0.7997	0.0746	10.70	0.00030	0.8730	0.344
0.100	0.0262	3.817	0.8997	0.0870	10.32	0.00030	0.8868	0.338
				2000 p.s.i.a.				
0.900	0.3900	2.304	0.0988	0.0228	4.40	0.00116	0.5872	1.98
0.800	0.3462	2.310	0.1991	0.0433	4.60	0.00090	0.6207	1.45
0.700	0.2950	2.330	0.2993	0.0625	4.79	0.00075	0.6425	1.165
0.600	0.2560	2.345	0.3994	0.0820	4.88	0.00064	0.6620	0.967
0.500	0.2122	2.355	0.4995	0.1010	4.95	0.00050	0.6868	0.726
0.400	0.1695	2.360	0.5995	0.1183	5.07	0.00045	0.7122	0.633
0.300	0.1270	2.365	0.6996	0.1360	5.15	0.00040	0.7370	0.542
0.200	0.0844	2.370	0.7997	0.1520	5.26	0.00035	0.7636	0.458
0.100	0.0422	2.373	0.8997	0.1700	5.30	0.00033	0.7878	0.418
				3000 p.s.i.a.				
0.900	0.5160	1.742	0.0963	0.0290	3.41	0.00368	0.4550	8.10
0.800	0.4540	1.760	0.1976	0.0559	3.53	0.00240	0.4901	4.90
0.700	0.3950	1.770	0.2982	0.0828	3.62	0.00180	0.5222	3.45
0.600	0.3370	1.777	0.3986	0.1080	3.70	0.00145	0.5550	2.61
0.500	0.2810	1.782	0.4987	0.1330	3.76	0.0013	0.5860	2.05
0.400	0.2240	1.785	0.5989	0.1570	3.82	0.0011	0.6190	1.78
0.300	0.1680	1.787	0.6991	0.1810	3.87	0.00095	0.6510	1.46
0.200	0.1118	1.788	0.7992	0.2050	3.92	0.00085	0.6832	1.246
0.100	0.0558	1.790	0.8993	0.2270	3.96	0.00075	0.7172	1.045
				4000 p.s.i.a.				
0.900	0.6180	1.454	0.0910	0.0338	2.96	0.0090	0.3482	25.84
0.800	0.5420	1.467	0.1942	0.0658	3.04	0.0058	0.3922	14.80
0.700	0.4700	1.475	0.2957	0.0975	3.07	0.0043	0.4325	9.94
0.600	0.4060	1.479	0.3966	0.1280	3.12	0.0034	0.4660	7.30
0.500	0.3370	1.483	0.4973	0.1580	3.16	0.0027	0.5050	5.34
0.400	0.2690	1.485	0.5978	0.1870	3.20	0.0022	0.5440	4.05
0.300	0.2020	1.486	0.6982	0.2170	3.22	0.0018	0.5810	3.10
0.200	0.1345	1.488	0.7985	0.2470	3.24	0.00155	0.6185	2.50
0.100	0.0667	1.489	0.8986	0.2750	3.265	0.00140	0.6583	2.125
				5000 p.s.i.a.				
0.900	0.7250	1.24	0.0865	0.0348	2.49	0.0135	0.2402	56.2
0.800	0.6320	1.27	0.1910	0.0750	2.542	0.0090	0.2930	30.7
0.700	0.5460	1.29	0.2925	0.1130	2.59	0.0075	0.3410	22.0
0.600	0.4600	1.304	0.3935	0.1500	2.62	0.0065	0.3900	16.65
0.500	0.3820	1.310	0.4945	0.1860	2.655	0.0055	0.4320	12.72
0.400	0.3030	1.317	0.5950	0.2210	2.69	0.0050	0.4760	10.50
0.300	0.2280	1.318	0.6955	0.2560	2.72	0.0045	0.5260	8.55
0.200	0.1515	1.320	0.7985	0.2882	2.76	0.00425	0.5603	7.60
0.100	0.0757	1.320	0.8960	0.3200	2.79	0.0040	0.6043	6.63
				160° F.				
				1000 p.s.i.a.				
0.900	0.2232	4.028	0.0983	0.0120	8.33	0.00170	0.7648	2.22
0.800	0.1971	4.055	0.1985	0.0228	8.76	0.00146	0.7801	1.87
0.700	0.1720	4.070	0.2987	0.0330	9.08	0.00126	0.7950	1.585
0.600	0.1471	4.08	0.3989	0.0430	9.28	0.0011	0.8099	1.36
0.500	0.1225	4.081	0.4990	0.0528	9.46	0.00097	0.8247	1.18
0.400	0.0980	4.083	0.5991	0.0620	9.68	0.0009	0.8400	1.07
0.300	0.0734	4.090	0.6992	0.0710	9.85	0.00085	0.8556	0.99
0.200	0.0488	4.092	0.7992	0.0796	10.05	0.00082	0.8716	0.94
0.100	0.0244	4.096	0.8992	0.0877	10.25	0.0008	0.8879	0.90
				2000 p.s.i.a.				
0.900	0.3750	2.400	0.0970	0.0230	4.35	0.0030	0.6020	5.00
0.800	0.3310	2.415	0.1977	0.0423	4.72	0.00234	0.6267	3.73
0.700	0.2880	2.426	0.2980	0.0614	4.88	0.0020	0.6506	3.08
0.600	0.2460	2.435	0.3982	0.0800	5.00	0.00178	0.6732	2.64
0.500	0.2044	2.442	0.4985	0.0982	5.10	0.00152	0.6984	2.16
0.400	0.1635	2.447	0.5988	0.1155	5.16	0.0012	0.7210	1.66
0.300	0.1225	2.451	0.6989	0.1330	5.26	0.00112	0.7445	1.51
0.200	0.0815	2.454	0.7989	0.1510	5.30	0.00107	0.7675	1.39
0.100	0.0407	2.458	0.8989	0.1670	5.38	0.00105	0.7923	1.33

Table II. Smoothed Ternary Data (Continued)

Methane			Nitrogen			n-Decane		
Y	X	K	Y	X	K	Y	X	$K \times 10^3$
				3000 p.s.i.a.				
0.900	0.4960	1.812	0.0955	0.0289	3.30	0.0045	0.4751	9.45
0.800	0.4370	1.830	0.1965	0.0555	3.54	0.0035	0.5075	6.90
0.700	0.3800	1.841	0.2968	0.0814	3.65	0.0032	0.5386	5.95
0.600	0.3244	1.849	0.3973	0.1065	3.73	0.00275	0.5691	4.85
0.500	0.2690	1.856	0.4975	0.1312	3.79	0.0025	0.5998	4.17
0.400	0.2150	1.860	0.5976	0.1550	3.85	0.0024	0.6300	3.81
0.300	0.1610	1.864	0.6980	0.1805	3.87	0.0020	0.6585	3.04
0.200	0.1071	1.867	0.7981	0.2055	3.88	0.0019	0.6874	2.76
0.100	0.0534	1.870	0.8983	0.2318	3.89	0.0017	0.7148	2.38
				4000 p.s.i.a.				
0.900	0.608	1.478	0.0886	0.0323	2.68	0.0114	0.3397	33.6
0.800	0.5315	1.505	0.1928	0.0675	2.855	0.0072	0.4010	17.9
0.700	0.4585	1.525	0.2950	0.1020	2.89	0.0050	0.4395	11.38
0.600	0.3892	1.54	0.3960	0.1320	2.995	0.0040	0.4788	8.35
0.500	0.3230	1.549	0.4965	0.1640	3.03	0.0035	0.5130	6.7
0.400	0.2572	1.555	0.5970	0.1940	3.077	0.0030	0.5488	5.46
0.300	0.1928	1.557	0.6972	0.2252	3.10	0.0028	0.5820	4.82
0.200	0.1280	1.558	0.7974	0.2560	3.11	0.0026	0.6160	4.22
0.100	0.0642	1.56	0.8976	0.2858	3.14	0.0024	0.6500	3.69
				5000 p.s.i.a.				
0.900	0.7360	1.22	0.0700	0.0370	1.89	0.0300	0.227	132.0
0.800	0.6100	1.311	0.1885	0.0920	2.06	0.0115	0.298	38.6
0.700	0.5170	1.354	0.2910	0.1340	2.17	0.0090	0.349	25.8
0.600	0.4370	1.372	0.3925	0.1730	2.27	0.0075	0.390	19.2
0.500	0.3625	1.377	0.4930	0.2085	2.37	0.0070	0.4290	16.3
0.400	0.2895	1.380	0.5939	0.2435	2.44	0.0061	0.4670	13.0
0.300	0.2170	1.383	0.6945	0.2777	2.505	0.0055	0.506	10.86
0.200	0.1444	1.385	0.7948	0.3120	2.545	0.0052	0.5436	9.6
0.100	0.0721	1.387	0.8950	0.3470	2.58	0.0050	0.5809	8.6
				220° F.				
				1000 p.s.i.a.				
0.900	0.2075	4.33	0.0958	0.0117	8.20	0.0042	0.7808	0.54
0.800	0.1826	4.38	0.1959	0.0230	8.68	0.0041	0.7944	0.52
0.700	0.1590	4.40	0.2961	0.0335	8.95	0.0039	0.8075	0.48
0.600	0.1367	4.42	0.3964	0.0440	9.10	0.0036	0.8193	0.43
0.500	0.1126	4.43	0.4965	0.0540	9.25	0.0035	0.8334	0.42
0.400	0.0903	4.44	0.5966	0.0642	9.35	0.0034	0.8455	0.40
0.300	0.0676	4.45	0.6967	0.0743	9.42	0.0033	0.8581	0.38
0.200	0.0450	4.45	0.7968	0.0843	9.50	0.0032	0.8707	0.37
0.100	0.0225	4.45	0.8969	0.0944	9.55	0.0031	0.8831	0.35
				2000 p.s.i.a.				
0.900	0.3620	2.49	0.0933	0.0224	4.16	0.0067	0.6156	1.09
0.800	0.3175	2.52	0.1935	0.0430	4.50	0.0065	0.6395	1.02
0.700	0.2755	2.54	0.2941	0.0631	4.67	0.0059	0.6614	0.89
0.600	0.2350	2.55	0.3947	0.0825	4.78	0.0053	0.6825	0.78
0.500	0.1955	2.557	0.4950	0.1014	4.88	0.0050	0.7031	0.71
0.400	0.1561	2.561	0.5955	0.1200	4.96	0.0045	0.7139	0.63
0.300	0.1168	2.563	0.6960	0.1390	5.01	0.0040	0.7442	0.54
0.200	0.0780	2.565	0.7961	0.1573	5.06	0.0039	0.7647	0.51
0.100	0.0390	2.567	0.8963	0.1755	5.10	0.0037	0.7855	0.48
				3000 p.s.i.a.				
0.900	0.4810	1.873	0.0890	0.0298	2.99	0.0110	0.4892	2.25
0.800	0.4210	1.903	0.1910	0.0572	3.34	0.0090	0.5218	1.73
0.700	0.3650	1.917	0.2922	0.0850	3.44	0.0078	0.5500	1.42
0.600	0.3115	1.926	0.3930	0.1100	3.57	0.0070	0.5785	1.21
0.500	0.2585	1.933	0.4936	0.1356	3.64	0.0064	0.6059	1.05
0.400	0.2065	1.937	0.5940	0.1605	3.70	0.0060	0.6330	0.95
0.300	0.1545	1.94	0.6945	0.1850	3.75	0.0055	0.6605	0.83
0.200	0.1030	1.942	0.7948	0.2100	3.78	0.0052	0.6870	0.76
0.100	0.0514	1.943	0.8950	0.2350	3.80	0.0050	0.7136	0.70
				4000 p.s.i.a.				
0.900	0.6040	1.49	0.0800	0.0332	2.41	0.0200	0.3628	5.52
0.800	0.5210	1.537	0.1860	0.0720	2.58	0.0140	0.4070	3.42
0.700	0.4475	1.565	0.2886	0.1070	2.70	0.0114	0.4455	2.56
0.600	0.3795	1.580	0.3905	0.1385	2.82	0.0095	0.4820	1.97
0.500	0.3135	1.595	0.4916	0.1700	2.88	0.0084	0.5165	1.63
0.400	0.2500	1.60	0.5925	0.2010	2.95	0.0075	0.5490	1.37
0.300	0.1870	1.605	0.6932	0.2310	3.00	0.0068	0.5820	1.17
0.200	0.1245	1.608	0.7936	0.2600	3.05	0.0064	0.6155	1.04
0.100	0.0621	1.61	0.8940	0.2900	3.075	0.0060	0.6479	0.93
				5000 p.s.i.a.				
0.837	0.8370	1.00	0.0430	0.0430	1.00	0.1200	0.1200	100.00
0.800	0.6500	1.23	0.1525	0.0960	1.59	0.0475	0.2540	18.70
0.700	0.5220	1.34	0.2780	0.1500	1.86	0.0220	0.3280	6.70
0.600	0.4330	1.385	0.3830	0.1900	2.02	0.0170	0.3770	4.50

(Continued on page 518)

Table II. Smoothed Ternary Data *(Continued)*

Methane			Nitrogen			n-Decane		
Y	X	K	Y	X	K	Y	X	$K \times 10^3$
0.500	0.3550	1.410	0.4855	0.2270	2.14	0.0145	0.4180	3.46
0.400	0.2810	1.425	0.5875	0.2590	2.27	0.0125	0.4600	2.72
0.300	0.2090	1.435	0.6890	0.2920	2.36	0.0110	0.4990	2.20
0.200	0.1390	1.44	0.7900	0.3230	2.45	0.0100	0.5380	1.86
0.100	0.0692	1.445	0.8910	0.3540	2.52	0.0090	0.5768	1.56
				280° F.				
				1000 p.s.i.a.				
0.900	0.2010	4.470	0.0895	0.0120	7.45	0.0105	0.7870	1.334
0.800	0.0763	4.540	0.1911	0.0240	7.98	0.0089	0.7997	1.112
0.700	0.1525	4.590	0.2018	0.0351	8.30	0.0082	0.8124	1.007
0.600	0.1300	4.617	0.3922	0.0458	8.55	0.0078	0.8242	0.947
0.500	0.1080	4.630	0.4925	0.0563	8.75	0.0075	0.8357	0.897
0.400	0.0863	4.637	0.5931	0.0666	8.90	0.0069	0.8471	0.814
0.300	0.0662	4.640	0.6933	0.0770	9.06	0.0067	0.8608	0.778
0.200	0.0432	4.645	0.7935	0.0861	9.20	0.0065	0.8708	0.746
0.100	0.0216	4.646	0.8937	0.0960	9.30	0.0063	0.8824	0.714
				2000 p.s.i.a.				
0.900	0.3540	2.540	0.0877	0.0240	3.65	0.0123	0.6220	1.860
0.800	0.3075	2.600	0.1894	0.0460	4.12	0.0106	0.6465	1.640
0.700	0.2662	2.630	0.2904	0.0660	4.40	0.0096	0.6678	1.440
0.600	0.2262	2.650	0.3911	0.0850	4.60	0.0089	0.6888	1.292
0.500	0.1880	2.660	0.4916	0.1030	4.77	0.0084	0.7090	1.183
0.400	0.1498	2.670	0.5920	0.1230	4.82	0.0080	0.7272	1.102
0.300	0.1120	2.675	0.6922	0.1410	4.91	0.0078	0.7470	1.044
0.200	0.0747	2.678	0.7925	0.1600	4.95	0.0075	0.7653	0.980
0.100	0.0373	2.679	0.8927	0.1780	5.07	0.0073	0.7847	0.931
				3000 p.s.i.a.				
0.900	0.4860	1.850	0.0866	0.0303	2.86	0.0134	0.4837	2.770
0.800	0.4160	1.920	0.1894	0.0622	3.05	0.0106	0.5218	2.025
0.700	0.3570	1.960	0.2905	0.0906	3.20	0.0095	0.5500	1.725
0.600	0.3030	1.980	0.3912	0.1180	3.32	0.0088	0.5790	1.520
0.500	0.2510	1.992	0.4915	0.1450	3.39	0.0085	0.6040	1.405
0.400	0.2000	2.000	0.5918	0.1700	3.48	0.0082	0.6300	1.300
0.300	0.1462	2.050	0.6920	0.1960	3.53	0.0080	0.6578	1.218
0.200	0.0968	2.070	0.7921	0.2220	3.57	0.0079	0.6812	1.162
0.100	0.0478	2.090	0.8921	0.2470	3.61	0.0079	0.7052	1.120
				4000 p.s.i.a.				
0.900	0.6270	1.435	0.0690	0.0335	2.06	0.0310	0.3410	9.100
0.800	0.5260	1.520	0.1818	0.0800	2.27	0.0182	0.3940	4.620
0.700	0.4460	1.570	0.2845	0.1190	2.37	0.0155	0.4350	3.560
0.600	0.3750	1.600	0.3865	0.1540	2.51	0.0135	0.4710	2.870
0.500	0.3090	1.617	0.4880	0.1860	2.63	0.0120	0.5050	2.375
0.400	0.2450	1.630	0.5890	0.2160	2.72	0.0110	0.5390	2.040
0.300	0.1830	1.640	0.6900	0.2470	2.79	0.0100	0.5700	1.755
0.200	0.1210	1.650	0.7902	0.2770	2.86	0.0098	0.6020	1.630
0.100	0.0604	1.655	0.8905	0.3045	2.92	0.0095	0.6351	1.495
				5000 p.s.i.a.				
0.790	0.7900	1.000	0.0600	0.0600	1.00	0.1500	0.1500	100.00
0.750	0.6040	1.240	0.1780	0.1220	1.46	0.0720	0.2740	26.30
0.700	0.5180	1.350	0.2480	0.1610	1.54	0.0520	0.3210	16.20
0.600	0.4150	1.445	0.3640	0.2070	1.76	0.0360	0.3780	9.55
0.500	0.3350	1.490	0.4715	0.2460	1.92	0.0285	0.4190	6.80
0.400	0.2650	1.510	0.5770	0.2770	2.08	0.0230	0.4580	5.02
0.300	0.1975	1.520	0.6810	0.3080	2.21	0.0190	0.4945	3.83
0.200	0.1311	1.525	0.7840	0.3400	2.30	0.0160	0.5289	3.02
0.100	0.0656	1.525	0.8855	0.3700	2.39	0.0145	0.5644	2.57

EXPERIMENTAL

A variable volume equilibrium cell, Sloan-type, with an internal stirring motor was used (*1*). During the analysis of the sample, in a GC-2 Beckman chromatograph, two different kinds of columns were used. A portion of the sample introduced to a column was placed in a temperature programmer in order to separate the decane from methane and nitrogen. Another portion of the same sample was introduced to another column to separate the methane from nitrogen. A complete description of this technique along with the calibrations of the two columns and calculations of the results are available (*1*).

RESULTS

The ternary data obtained for each isotherm are tabulated, in mole fractions, in Table I and were plotted on triangular diagrams similar to that of Figures 1 and 2. These data were smoothed by plotting the best curve through the data points on the *Y–X* diagram for each component in the system. The proper adjustment for each point was made so that it was consistent with all three *Y–X* curves as well as with the vapor and liquid composition lines on the triangular diagram. Smoothed data obtained in this manner are tabulated in Table II. Diagrams similar to Figures 3 and 4 were prepared to show the

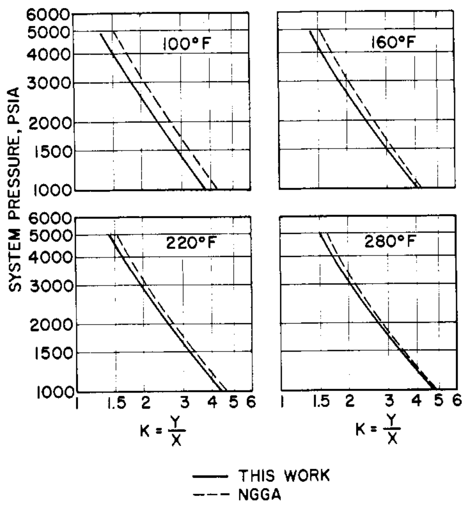


Figure 6. Experimental K values of methane compared to N.G.A.A. charts

variation in K values for nitrogen and methane as a function of the mole fraction of nitrogen and methane respectively in the vapor phase.

The K values for methane at 0% methane in the vapor phase were obtained from the K charts similar to Figure 3. These values have no physical meaning in the ternary system, but they are the K values for methane at a convergence pressure equal to the critical pressure of the normal decane-nitrogen system at the corresponding temperature. For each isotherm these K values were plotted against the pressure on a log-log paper as shown in Figure 5. At temperatures of 100, 160, 220, and 280° F. critical pressures for the binary system of n-decane-nitrogen were estimated by the method suggested by Grieves and Thodos (*4*). These values are 22,000, 20,000, 19,000, and 18,000 respectively.

The K-values for methane at these convergence pressures were evaluated from N.G.A.A. data book and are plotted in Figure 6 along with individual curves of Figure 5 at the corresponding temperature.

MATERIAL USED

The methane and normal decane were Phillips Petroleum Co. research grade chemicals with a minimum purity as follows: methane, 99% (the principal impurity was nitrogen); n-decane, 99.43%. The nitrogen used was OP grade with a minimum purity of 99.9%.

ACKNOWLEDGMENT

This work was carried out under a National Science Foundation Grant. The authors are grateful for this assistance.

LITERATURE CITED

(1) Azarnoosh, A., "Phase Equilibrium in Nitrogen-Methane-Decane System" Ph. D. Dissertation, University of Texas, Austin, Tex. (June, 1963).
(2) Azarnoosh, A., McKetta, J.J. J. CHEM. ENG. DATA, 8, 321 (1963).
(3) Equilibrium Ratio Data Book, Natural Gasoline Association of America, Tulsa, Oklahoma (1960).
(4) Grieves, R.B., Thodos, G. *J. Soc. Petr. Eng.*, 197–202 (Sept., 1962).
(5) Jacoby, R.H., "Discussion of Equilibrium Ratio Data Book With Particular Reference to Non-Hydrocarbon K Values." N.G.A.A. Proc., 34th Annual Convention, Dallas, (1955), p. 70–72.

RECEIVED for review April 8, 1963. Accepted July 19, 1963.

Adsorption Rates in a Vapor-Solid System

JOHN F. HAMAN and KARL KAMMERMEYER
Department of Chemical Engineering, University of Iowa, Iowa City, Iowa.

The adsorption rates of carbon dioxide and seven light hydrocarbons on microporous glass have been measured. The pressure and temperature dependence of the rates was studied, and comparison of the equilibrium adsorption values with those of other investigators is made. An equation is presented which allows straight-line correlation of the rate data over practically the entire time range.

TO STUDY the general behavior of the adsorption rates of hydrocarbons on porous solids the investigation of the following items was considered essential: sorption rate curves for CO_2 and seven light hydrocarbon vapors on microporous glass, the generalized effect of pressure and temperature on these curves, approximate equilibrium times for this series of adsorbates, comparison of equilibrium adsorption values obtained with those of other investigators using similar conditions and adsorbent, correlation of the rate data by an equation which would allow straight-line plotting of the data over practically the entire time range, and suggestion of the possible mechanistic scheme of adsorption.

EXPERIMENTAL

Adsorbent. The adsorbent used throughout the investigation was microporous Vycor glass No. 7930, an intermediate in the manufacture of 96% silica glass by the Corning Glass Works, Corning, N. Y. The adsorbent was in the form of disks 5 mm. thick and 50 mm. in diameter, each weighing approximately 15 grams. From one to five glass disks were used in the adsorbent chamber depending on the adsorbate and the temperature of the experiment. The properties of No. 7930 Vycor glass are given in detail by Nordberg (*10*). Some properties of Vycor disks very similar to the ones used are presented by Egger (*4*).