Diffusion Coefficients in Hydrocarbon Systems. Methane in the Liquid Phase of the Methane-Propane System

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Limited experimental work concerning the molecular transport of the lighter paraffins in hydrocarbon liquids is available. The early measurements of Pomeroy (*12*) and Lacey (*1,4,5,9*) have been supplemented by data upon the molecular transport of methane in the liquid phase of several binary hydrocarbon systems (*13–17*) at elevated pressures. Drickamer contributed to the knowledge of molecular transport in liquid and gas phases at elevated pressures and discussions of the transport of carbon dioxide and carbon disulfide (*6,8*) are given as examples. Kirkwood presented some of the basic ideas in molecular transport (*7*), and the application of these ideas to situations of industrial interest is available (*11*).

Interest has been shown in the possibility of a resistance at liquid-gas interfaces (*3,24*). The theoretical discussion of Schrage (*23*) indicated that such resistances should be important only when the mean free path of the diffusing molecule is of the order of the thickness of the interface. Investigations with hydrocarbons involving transfer from a liquid to a gas phase indicated that such resistances are small (*22*) for pressures above that of the atmosphere. Because the pertinent literature relating to material transport has been reviewed (*15*) no further consideration of the large experimental background in this field is included.

Experimental measurements of the Fick diffusion coefficient for methane in the liquid phase of the methane-propane system were made at pressures up to within 500 pounds per square inch of the critical state at the temperature in question and in the temperature interval between 40° and 160° F. This study and earlier investigations (*13–17*) furnish a reasonable background of data regarding the molecular transport of methane in binary paraffin hydrocarbon liquids.

METHODS AND APPARATUS

A transient method involving the introduction of methane into an isochoric chamber containing a heterogeneous mixture of methane and propane was used in this study. A nest of parallel-vertical tubes was employed to decrease the convection resulting from vibration of the liquid phase. As the surface rapidly came to equilibrium with the gas phase, the extended surface area resulting from the presence of the tubes did not appreciably influence the diffusion measurements. The heterogeneous system was brought to equilibrium at the desired initial state. The pressure was suddenly raised to a predetermined terminal value, and the quantity of methane required to maintain isobaric conditions thereafter was determined as a function of time. The equipment has been described (*15*).

Isobaric conditions were maintained with an uncertainty of 0.10 pound per square inch and the value of the pressure was known within 0.05%. Temperatures were measured by means of a strain-free platinum resistance thermometer (*10*) which was compared to the indication of a similar instrument calibrated by the National Bureau of Standards. Experimental evidence indicates that the temperature of the isochoric vessel was related to the international platinum scale within 0.02° F. The standard error of estimate of the total weight of methane introduced at any particular time was 0.3×10^{-6} pound.

The quantity of propane used in each measurement was determined by weighing bomb techniques (*21*). Care was excercised to avoid conditions for which the interface between the liquid and gas phases was above the upper end of the small vertical tubes.

Methods of analysis similar to those employed in earlier studies (*13–17*) were used in this investigation. The Fick diffusion coefficient was evaluated from the experimental measurements by application of the following expression:

$$D^*_{F,k} = \left[\frac{(1 + \bar{V}^*_{j,l}\sigma_{j,l} + \bar{V}^*_{k,l}\sigma_{k,l})^*}{(1 + \bar{V}_{j,l}\sigma_{j,l})^*\left(1 + \dfrac{\sigma_k}{\sigma_j}\right)^*}\right]\left[\frac{\pi m_k^2}{4\theta(\sigma_{k,i,e} - \sigma_{k,o})^2}\right]\left[\frac{\bar{V}^*_{k,g}}{\bar{V}^*_{k,g} - \bar{V}^*_{k,l}}\right]^2 \quad (1)$$

The asterisks in Equation 1 indicate average values of the partial specific volume over the range of compositions encountered during a particular measurement. Effects of hydrodynamic velocity (*11*) and the change in volume of the liquid phase in the experimental equipment were taken into account in the derivation of Equation 1, but no regard was taken of the resistance at the interface. Accuracy of the experimental measurements was not sufficient to justify an attempt to evaluate any small interfacial resistance which might exist under these conditions.

The analysis was based upon the assumption of local equilibrium (*7*) in each of the phases. Earlier equilibrium studies of the methane-propane system (*2,18,19*) were employed to establish the volumetric and phase behavior of the system. The magnitude of the first bracketed term of Equation 1, which is concerned with the hydrodynamic velocity, is shown in Figure 1 where it is designated as the volumetric correction factor. Figure 2 depicts the weight correction factor which accounts for the difference in weight of methane introduced into the isochoric chamber and that passing the interface. These two correction terms tend to compensate one another, since one is larger and the other smaller than unity.

MATERIALS

The propane was purchased as instrument grade from the Phillips Petroleum Co. and was reported to contain less than 0.005 mole fraction of impurities. This hydrocarbon was condensed under a low pressure at liquid nitrogen temperatures to remove any noncondensable gases and was then stored in a stainless steel container. The propane was introduced into the apparatus without further purification. The vapor pressure of this material varied by less

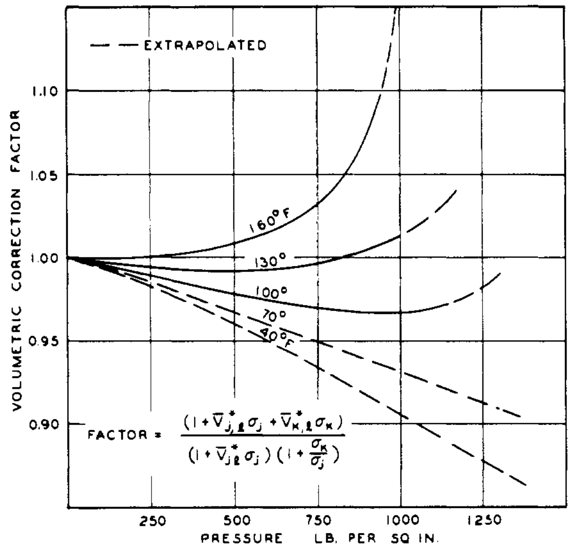

Figure 1. Volumetric correction factor for methane-propane system

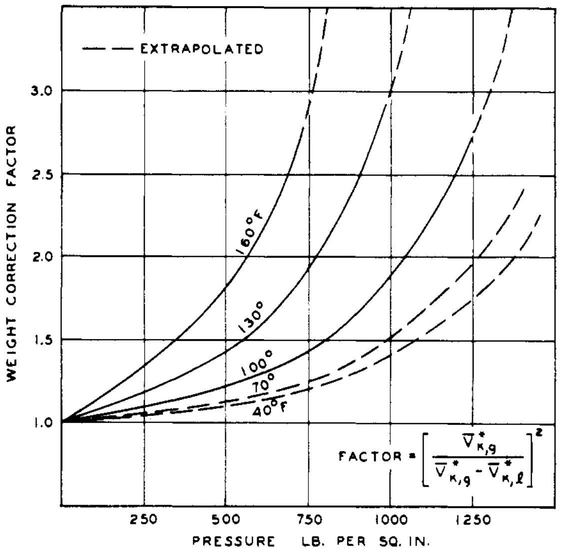

Figure 2. Weight correction factor for methane-propane system

than 0.1 pound per square inch upon change in quality, or weight fraction gas, from 0.6 to 0.02 and was in good agreement with critically chosen values (*20*).

Methane was obtained from a well in the San Joaquin Valley of California and contained approximately 0.003 mole fraction of carbon dioxide with traces of heavier hydrocarbons, and was in equilibrium with an aqueous phase. The gas was dried by passage over calcium chloride and anhydrous calcium sulfate. Heavier hydrocarbons were removed by contact with activated charcoal and alumina while the carbon dioxide was absorbed by potassium hydroxide and Ascarite. These operations were carried out at a pressure in excess of 500 pounds per square inch and the purified gas employed did not contain more than 0.001 mole fraction of material other than methane, as established by mass spectrographic analysis.

EXPERIMENTAL MEASUREMENTS

Measurements of the quantity of methane required as a function of time to maintain the isochoric, isothermal, heterogeneous system under isobaric conditions was established for a variety of compositions of the liquid phase at five temperatures between 40° and 160° F. The pressure differentials employed for these measurements were between 100 and 200 pounds per square inch. The quantity of methane added after isobaric conditions had been attained was nearly a linear function of the square root of time during the early part of each measurement. It is not possible to apply the simple analysis of Equation 1 (*12*) for conditions such that the quantity of diffusing component which has crossed the interface exceeds about half that required for equilibrium.

The experimental data obtained from this study are similar in form to those already available (*13–15*) and are not presented graphically. Table I records a sample set of data obtained for a specified combination of temperature, initial composition, and pressure difference. Agitation was initiated at a time of 11,290 seconds in order to bring the system to equilibrium and this accounts for the marked increase in the quantity of methane added near the end of the period covered by the data of Table I. Table II gives a detailed record similar to the example shown in Table I for all experimental data obtained in this investigation.

Table I. Sample of Detailed Experimental Measurements at 70° F.

Pressure, Lb./Square Inch Abs.	Weight Fraction Methane	Time, Sec.	Methane Added, Lb. × 10^{-6}
462.8[a]	0.057	0	
563.1[b]	0.066	460	...
		870	13.121
		2180	91.320
		2840	127.271
		3410	154.562
		4040	180.804
		4780	211.244
		5470	234.599
		5820	247.982
		7050	288.394
		7890	310.699
		8250	319.621
		8560	326.969
		9260	345.075
		9870	360.820
		10390	373.416
		11060	385.225
		11890	652.888
		12880	652.888

[a] Initial equilibrium pressure.
[b] Constant operating pressure during diffusion.

A summary of experimental results obtained in the study of the methane-propane system is recorded in Table III. The standard error of estimate for the experimental points from a straight line corresponding to a single value of $\Delta m_k/\theta^{1/2}$ was recorded for each set of measurements. In the evaluation of the standard error it was assumed that all the uncertainty was associated with the weight of methane and that no error in time was involved. The average standard deviation of the experimental points from a straight line with a slope of $\Delta m_k/\theta^{1/2}$ for each set of experimental conditions was 2.8×10^{-6} pound. The Fick diffusion coefficient was determined from the experimental measurements by use of Equation 1 with the correction factors set forth in Figures 1 and 2. The value of this coefficient uncorrected for hydrodynamic velocity is included in Table III for each set of measurements.

Table II. Experimental Measurements of Diffusion of Methane into Liquid Phase of Methane-Propane System

Time, Sec.	Methane Added,[a] Lb. × 10^{-6}	Time, Sec.	Methane Added,[a] Lb. × 10^{-6}	Time, Sec.	Methane Added,[a] Lb. × 10^{-6}
40° F.		40° F.		40° F.	
(319.1)[b]		(419.4)[b]		(520.8)[b]	
(419.4)[c]		(520.6)[c]		(621.1)[c]	
0	....	0	....	0	....
600	....	350	....	240	....
830	....	600	13.047	510	72.485
1240	42.584	880	33.824	960	105.088
2220	108.100	1480	82.145	1140	122.263
2610	129.874	2880	174.195	1650	163.891
3720	191.150	3610	210.194	1890	179.610
4100	205.024	4360	243.535	2210	199.114
4320	214.658	5240	282.916	3010	246.855
5250	236.239	5920	308.285	3260	260.537
6460	296.744	6440	326.888	4040	298.089
7490	337.017	7160	350.323	4420	313.518
8286	358.405	7730	369.410	4740	330.402
9080	382.492	8360	389.704	5850	373.776
9830	405.230	8970	407.825	6190	386.585
11,580	443.189	9990	437.783	6640	399.393
12,500	463.807	10,740	455.420	6750	402.886
15,860	465.734	11,220	468.709	7040	415.113
16,840	543.774	12,290	494.077	8070	448.298
17,900	561.887	13,010	513.405	9810	498.368
18,630	570.174	13,640	526.693	11,750	551.931
19,430	585.589	14,730	546.988	12,610	574.346
20,970	599.077	15,020	555.685	23,270	969.373
21,940	607.748	15,690	566.316	23,490	969.373
22,490	613.336	17,450	742.202		
23,500	623.742	18,450	754.041		
24,060	629.522	19,760	812.267		
25,260	641.855	20,340	833.770		
27,590	659.775	20,640	842.950		
28,220	664.785	21,020	848.266		
29,180	673.841	21,120	848.266		
29,580	674.420	21,170	848.266		
29,960	676.732				
30,430	681.549				
31,170	683.861				
32,170	689.642				
35,860	706.984				
36,490	739.742				
37,240	760.938				
39,400	760.938				
40° F.		70° F.		70°F.	
(621.1)[b]		(259.0)[b]		(362.9)[b]	
(721.5)[c]		(360.8)[c]		(463.2)[c]	
0	....	0	....	0	....
510	....	430	....	430	....
1170	....	1690	51.575	1780	56.857
2090	75.784	2490	97.877	2280	84.430
2540	182.290	2940	121.110	4240	182.112
3220	220.524	3580	151.923	4550	190.448
3850	250.905	4290	184.713	4950	207.121
4440	282.311	4920	205.475	6560	263.122
5220	314.058	5510	225.413	7060	276.802
5800	338.296	6040	243.867	8080	301.811
6270	358.436	6650	262.487	8680	320.407
6930	378.577	7140	277.482	9380	337.506
7490	399.059	7670	293.465	10,010	352.469
8370	427.734	8450	313.238	10,570	362.728
8730	443.437	9150	329.880	11,170	376.836
9350	461.529	10,080	350.971	11,780	388.592
9850	480.987	10,700	365.636	12,470	401.630
10,580	496.690	11,490	379.148	12,980	411.463
11,070	510.004	12,180	392.495	13,470	420.654
11,890	532.534	13,100	407.984	14,080	431.769
12,460	547.213	13,850	418.530	14,540	439.036
13,070	563.257	14,810	431.876	15,240	527.100
13,760	580.325	15,620	444.069	15,590	602.125
14,380	595.004	16,440	451.814	16,110	602.125
14,810	602.856	17,340	463.019		
15,410	615.828	18,360	472.575		
16,080	629.141	19,260	480.485		
16,660	640.748	20,110	489.383		
17,270	652.354	20,930	493.996		

Table II. (*Contd.*)

Time, Sec.	Methane Added[a] Lb. × 10^{-6}	Time, Sec.	Methane Added,[a] Lb. × 10^{-6}	Time, Sec.	Methane Added,[a] Lb. × 10^{-6}
40° F.		70° F.		70° F.	
(621.1)[b]		(259.0)[b]		(362.9)[b]	
(721.5)[c]		(360.8)[c]		(463.2)[c]	
18,590	677.274	21,940	501.741		
19,780	699.804	22,840	507.673		
21,000	721.310	23,700	511.957		
22,530	745.547	24,880	540.463		
25,520	1030.931	25,860	569.463		
26,410	1032.297	26,430	569.463		
27,930	1032.297				
70° F.		70° F.		70° F.	
(462.8)[b]		(564.4)[b]		(763.0)[b]	
(563.1)[c]		(664.8)[c]		(863.4)[c]	
0	....	0	....	0	....
460	....	360	....	440	....
870	13.121	930	50.993	1030	64.973
2180	91.320	1370	79.148	1850	120.427
2840	127.271	1950	117.940	2630	168.432
3410	154.562	2360	142.655	3740	225.128
4040	180.804	2730	159.548	4160	244.578
4780	211.244	3250	185.514	5550	298.791
5470	234.599	3670	205.222	6490	335.623
5820	247.982	4220	228.060	7110	358.798
7050	288.394	4710	248.394	7960	381.973
7890	310.699	5160	263.098	9220	419.632
8250	319.621	5620	279.365	9900	437.427
8560	326.969	6090	296.571	10,670	456.050
9260	345.075	6690	318.157	11,490	476.742
9870	360.820	7330	338.805	12,900	888.927
10,390	373.416	7820	352.882	13,990	888.927
11,060	385.225	8370	367.586	14,550	888.927
11,890	652.888	9040	385.418		
12,880	652.888	9620	518.061		
		10,660	736.110		
		11,150	736.110		
100° F.		100° F.		100° F.	
(403.6)[b]		(505.1)[b]		(606.2)[b]	
(503.9)[c]		(605.5)[c]		(706.6)[c]	
0	....	0	....	0	....
710	....	210	....	210	....
1110	....	827	10.767	560	34.383
1180	57.905	1280	39.100	990	57.083
2380	84.756	2130	88.401	1680	97.475
2800	101.100	2860	122.118	2820	156.560
4410	181.887	3520	147.618	3670	188.940
5620	224.148	4370	185.302	4550	223.991
6730	259.638	5140	211.369	5210	243.352
8080	302.132	5900	234.036	5810	263.048
9460	339.257	6440	253.019	6290	276.734
10,750	367.509	7300	277.103	7220	304.107
11,610	392.725	8250	305.153	7780	324.132
12,280	406.501	9690	338.870	8340	334.151
13,450	429.616	11,090	376.270	9499	364.528
13,950	458.802	12,420	401.204	10,380	387.561
15,610	468.842	13,650	426.704	10,960	397.576
16,840	486.354	14,852	450.504	11,530	411.596
17,590	501.764	16,320	479.405	12,290	430.624
		17,480	497.821	12,790	437.968
				13,790	462.335
				14,470	862.583
				15,830	863.250
				16,260	863.250
100° F.		100° F.		130° F.	
(706.8)[b]		(765.8)[b]		(434.3)[b]	
(807.1)[c]		(966.5)[c]		(484.4)[c]	
0	....	0	....	0	....
270	....	580	....	250	....
1000	61.580	1180	90.241	810	30.465
1880	107.765	1820	150.089	1030	34.049
2340	135.091	2300	190.300	1680	51.297
2810	153.950	2930	239.395	1870	57.122
3640	188.973	3500	283.346	2270	65.410

Table II. (Contd.)

Time, Sec.	Methane Added,[a] Lb. × 10^{-6}	Time, Sec.	Methane Added,[a] Lb. × 10^{-6}	Time, Sec.	Methane Added,[a] Lb. × 10^{-6}
100° F.		100° F.		130° F.	
(706.8)[b]		(765.8)[b]		(434.3)[b]	
(807.1)[c]		(966.5)[c]		(484.4)[c]	
4240	210.142	4090	326.362	2550	74.594
4800	230.925	4700	366.573	3260	87.587
5300	248.629	5330	406.317	3500	89.379
5760	263.639	6090	448.398	4450	108.419
6540	286.732	6860	492.817	4690	112.675
8640	340.229	8030	548.925	4950	117.379
10,310	394.496	8350	562.017	5290	123.204
12,150	422.592	8920	588.668	5570	125.892
14,240	463.389	9460	606.903	5970	129.476
16,180	498.028	10,150	632.619	6570	138.212
18,660	543.058	10,710	655.530	7020	143.588
		11,390	674.233	7430	148.068
		11,990	694.806	7870	152.100
		12,530	707.430	8300	156.133
		13,180	725.666	9150	162.853
		14,820	766.344	9510	165.541
		16,100	792.995	10,220	170.917
		16,770	803.749	10,650	174.053
		17,800	820.114	12,140	185.253
		18,420	828.998	14,160	194.214
		19,830	849.103	14,870	197.798
		20,720	861.728	16,300	203.174
		21,900	875.287	17,510	206.086
		22,610	881.833	18,000	227.591
		22,900	980.022	21,290	227.591
		23,400	988.906		
		24,990	988.906		
130° F.		130° F.		130° F.	
(539.6)[b]		(651.7)[b]		(751.8)[b]	
(592.1)[c]		(701.9)[c]		(801.9)[c]	
0	....	0	....	0	....
160	....	370	....	280	....
470	....	1340	....	470	4.588
1350	....	1730	9.282	1070	11.470
2080	27.946	2040	16.243	1870	22.942
2410	36.800	2630	30.165	2270	27.913
3120	54.232	3100	36.132	3020	41.296
3820	68.066	3670	48.066	3360	48.178
4870	77.750	4000	57.347	3950	58.120
5780	92.138	4280	58.673	4290	63.473
6480	103.759	4920	70.607	4890	72.268
7020	109.570	5910	85.535	5760	84.886
7600	116.487	6600	93.811	6470	94.445
8080	122.021	7210	98.783	7100	101.328
8470	126.448	7780	106.407	7500	105.916
9030	132.535	8460	112.705	8220	114.711
9990	142.773	8900	117.678	8480	121.593
10,420	147.200	10,080	125.965	10,920	136.123
10,820	151.627	10,380	128.617	11,230	138.417
11,310	154.117	10,710	131.600	11,620	141.859
11,670	157.991	11,050	134.583	12,090	146.447
12,060	162.140	11,540	138.893	12,510	150.271
13,030	167.675	12,600	176.351	12,810	152.947
14,540	197.558	13,280	190.273	13,620	190.037
15,090	210.562	13,590	200.549	14,090	210.685
15,400	220.523	13,780	205.853	14,300	218.715
16,150	220.523	13,830	205.853	14,500	225.597
				14,740	231.333
				14,890	231.333
130° F.		160° F.		160° F.	
(852.7)[b]		(525.3)[b]		(687.4)[b]	
(902.8)[c]		(575.5)[c]		(737.7)[c]	
0	....	0	....	0	....
250	....	120	....	150	....
1020	20.853	2060	82.260	3410	0.699
1620	31.714	3460	127.288	3590	2.796
1990	39.534	4160	134.946	3750	4.544
2650	47.788	4860	146.830	4080	8.389
3100	53.870	5290	151.848	4330	11.185
3760	62.124	6250	162.147	4940	15.030
4320	69.944	6500	163.995	5470	15.730

Table II. (Contd.)

Time, Sec.	Methane Added,[a] Lb. × 10^{-6}	Time, Sec.	Methane Added,[a] Lb. × 10^{-6}	Time, Sec.	Methane Added,[a] Lb. × 10^{-6}
130° F.		160° F.		160° F.	
(852.7)[b]		(525.3)[b]		(687.4)[b]	
(902.8)[c]		(575.5)[c]		(737.7)[c]	
4880	77.330	7200	168.220	5810	19.575
5370	83.846	8040	172.446	6230	23.070
5900	90.797	8540	175.087	6600	25.866
6300	96.010	9060	177.463	7050	29.012
6700	101.224	9880	181.161	7240	30.410
7500	106.871	11,300	186.178	7680	33.906
8400	117.298			8220	38.450
8830	121.642	(634.1)[b]		8510	40.547
9230	124.683	(687.3)[c]		8830	42.994
9840	129.462			9130	45.091
10,320	132.938	0	....	10,050	49.286
10,720	134.675	160	....	10,760	52.082
11,410	137.716	3830	7.306	11,120	54.180
11,720	143.798	4550	19.378	11,740	57.675
12,020	148.143	4760	22.237	12,590	62.219
14,610	218.956	5210	28.273	15,370	67.812
14,850	228.079	6090	38.438	16,110	76.550
15,090	236.333	6590	42.568	16,310	76.550
15,250	236.333	7180	47.650	16,480	76.550
		7910	51.780		
		9560	63.534		
		10,390	67.663		
		11,650	72.111		
		13,810	78.782		
		16,060	79.735		

[a] Weight added to heterogeneous isochoric system.

[b] Initial equilibrium pressure expressed in pounds per square inch absolute.

[c] Constant operating pressure during diffusion expressed in pounds per square inch absolute.

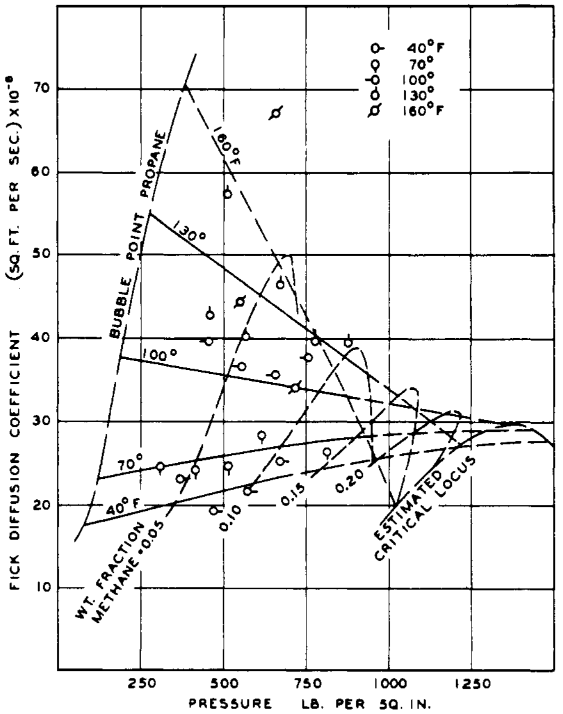

Figure 3. Effect of pressure upon Fick diffusion coefficient for methane

The variation of the Fick diffusion coefficient with state is shown in Figure 3, in which the experimental points recorded in Table III are depicted. Experimental points are shown at the average pressure associated with each transient measurement. A smooth set of curves was located so as to yield the minimum standard error of estimate for all the data. There was a somewhat smaller number of

Table III. Summary of Experimental Results

Pressure, Lb./Sq.Inch Abs.		Compn. Methane, Weight Fraction		Concn. Methane, Lb./Cu.Ft.		$\frac{(\Delta m_k)^2}{\theta}$,[a]	Standard Error of Estimate,	Volumetric Correction	Fick Diffusion Coefficient, Sq.Ft./Sec. × 10^{-8}	
Initial	Final	Initial	Final	Initial	Final	Lb.^{2}/Sec. × 10^{-12}	Lb. × 10^{-6}	Factor	Uncorrected	Corrected
						40° F.[b]				
319.1	419.4	0.043	0.063	1.339	1.909	33.524	3.0	0.9678	23.83	23.06
419.4	520.6	0.063	0.074	1.909	2.511	31.360	1.3	0.9583	20.48	19.63
520.8	621.1	0.074	0.106	2.511	3.100	32.604	5.4	0.9479	22.80	21.62
621.1	721.5	0.106	0.130	3.100	3.690	37.577	5.4	0.9370	27.01	25.31
						70° F.[b]				
259.0	360.8	0.022	0.039	0.650	1.148	26.420	2.2	0.9777	25.07	24.51
362.9	463.2	0.039	0.057	1.456	1.657	26.420	3.6	0.9709	24.96	24.23
462.8	563.1	0.057	0.066	1.654	2.147	25.402	2.4	0.9636	25.49	24.56
564.4	664.8	0.066	0.096	2.150	2.642	28.409	1.2	0.9558	29.76	28.44
763.0	863.4	0.117	0.141	3.138	3.656	28.302	5.0	0.9408	27.98	26.33
						100° F.				
403.6	503.9	0.034	0.050	0.934	1.352	26.832	5.4	0.9781	39.71	38.84
505.1	605.5	0.050	0.062	1.360	1.783	24.010	2.1	0.9747	36.64	35.72
606.2	706.6	0.066	0.085	1.782	2.213	22.657	1.7	0.9718	35.57	34.57
706.8	807.1	0.085	0.106	2.215	2.640	21.436	0.9	0.9690	37.66	36.50
765.8	966.5	0.097	0.142	2.460	3.329	69.556	6.6	0.9670	35.33	34.17
						130° F.[c]				
434.2	484.4	0.022	0.030	0.607	0.790	4.840	1.5	0.9922	43.08	42.74
539.6	592.1	0.039	0.047	0.993	1.188	4.622	2.6	0.9930	40.35	40.07
651.7	701.9	0.057	0.066	1.409	1.599	4.368	1.5	0.9956	46.70	46.49
751.8	801.9	0.075	0.084	1.788	1.979	3.168	2.8	0.9990	39.62	39.58
852.6	902.8	0.094	0.150	2.170	2.359	2.592	2.0	1.0038	39.26	39.41
						160° F.				
525.3	575.5	0.020	0.027	0.461	0.629	2.856	2.9	1.0125	43.71	44.25
634.1	687.3	0.036	0.045	0.817	0.991	3.764	1.2	1.0244	65.62	67.22
687.4	737.7	0.045	0.053	0.991	1.157	1.538	1.4	1.0310	33.05	34.08

[a] Effective cross-sectional area, 0.019262 square foot.
[b] Values of volumetric correction factor for 40° and 70° F. extrapolated from data at higher temperatures.
[c] Volumetric correction factors at 130° F. interpolated.

experimental points obtained at 160° F. than at the lower temperatures and the uncertainty of measurement was somewhat larger at this temperature than for other conditions of measurement.

Lines of constant composition were included in Figure 3 together with an estimate of the behavior at the critical state. The average relative standard deviation, exclusive of data obtained at 160° F., is approximately 8.5%, which is no larger than would be expected from the probable error in the over-all measurement. When data at 160° F. are included, the average relative standard deviation increases to 14.3%. The requirements for accuracy in the evaluation of the concentrations and partial volumes required in the solution of Equation 1 contribute materially to the digression of the experimental points shown in Figure 3 from the simple curves used in the smoothing operation. Proximity of the critical temperature of propane and relatively low critical pressures for the mixtures limited the range of conditions investigated and increased the experimental uncertainty.

Variation of the Fick diffusion coefficient with temperature is shown in Figure 4. At the lower temperatures an increase in pressure results in an increase in the Fick diffusion coefficient, while the reverse is true at the higher temperatures. Smoothed values of the Fick diffusion coefficient for the liquid phases are recorded in Table IV as a function of state. The composition and concentration of the liquid phase are indicated for the convenience of the reader. The relationship of these variables to the pressure and temperature was taken from an experimental study of the equilibrium behavior of the methane-propane system (*2,18,19*).

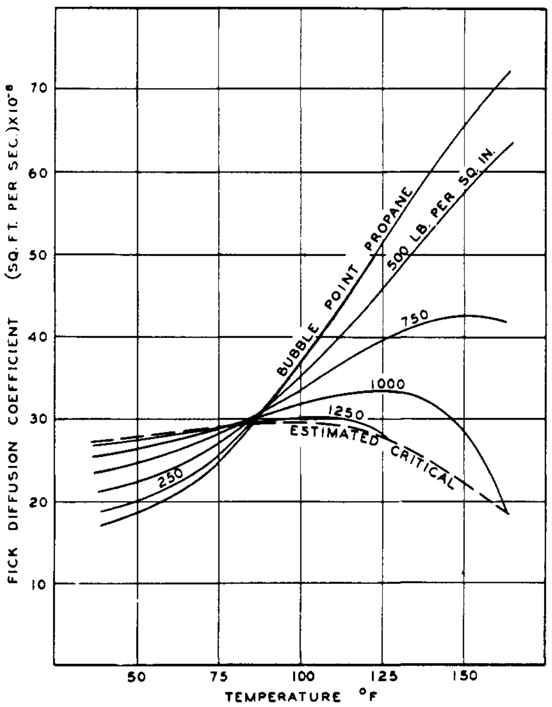

Figure 4. Influence of temperature upon Fick diffusion coefficient for methane

Table IV. Fick Diffusion Coefficient for Methane

Pressure, Lb./Sq.Inch Abs.	Compn. Methane, Weight Fraction	Concn. Methane, Lb./Cu.Ft.	Fick Diffusion Coefficient, Sq.Ft./Sec. × 10^{-8}
	40° F.		
250	0.031	0.949	19.1
500	0.080	2.389	21.5
750	0.139	3.856	23.8^a
1000	0.211	5.321	25.8^a
1250	0.308	6.669	27.1^a
	70° F.		
250	0.022	0.603	24.1
500	0.065	1.842	25.9
750	0.115	3.070	27.4
1000	0.176	4.350	28.4^a
1250	0.263	5.411	28.9^a
	100° F.		
250	0.009	0.268	37.1
500	0.049	1.335	35.4
750	0.094	2.396	33.7
1000	0.151	3.474	32.0^a
1250	0.231	4.385	30.3^a
	130° F.		
250	....	....	....
500	0.033	0.849	48
750	0.074	1.781	41
1000	0.129	2.705	33^a
1250	....	....	....
	160° F.		
250	....	....	....
500	0.016	0.388	62
750	0.055	1.197	42
1000	0.126	2.011	22^a
1250	....	....	....

^{a}Values obtained by extrapolation of experimental data at lower pressures.

The Fick diffusion coefficient for methane at a pressure of 500 pounds per square inch is shown in Figure 5 as a function of the molecular weight of the less volatile component. Measurements of the Fick diffusion coefficient in the methane-*n*-butane (*16*), methane-*n*-pentane (*13*), methane-*n*-heptane (*17*), methane-*n*-decane (*15*), and methane-white oil (*14*) systems were included in this comparison.

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NOMENCLATURE

$D_{F,k}$ = Fick diffusion coefficient of component k, square feet per second
m_k = weight of component k added per unit area of interface, pounds per square foot
$\underline{m}_k$ = weight of component k added to interface, pounds
$\overline{V}_k$ = partial specific volume of component k, cubic feet per pound
Δ = difference in
θ = time, seconds
σ_k = concentration of component k, pounds per cubic foot

Superscript

$*$ = average condition

Subscripts

e = conditions at equilibrium
g = gas phase
i = conditions at interface
j = component j, stagnant component
k = component k, diffusing component
l = liquid phase
o = initial conditions

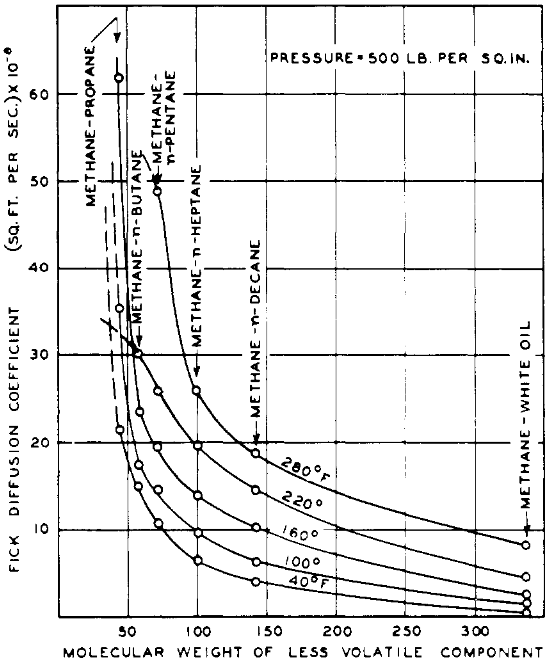

Figure 5. Effect of molecular weight of less volatile component upon Fick diffusion coefficient for methane in the liquid phase

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