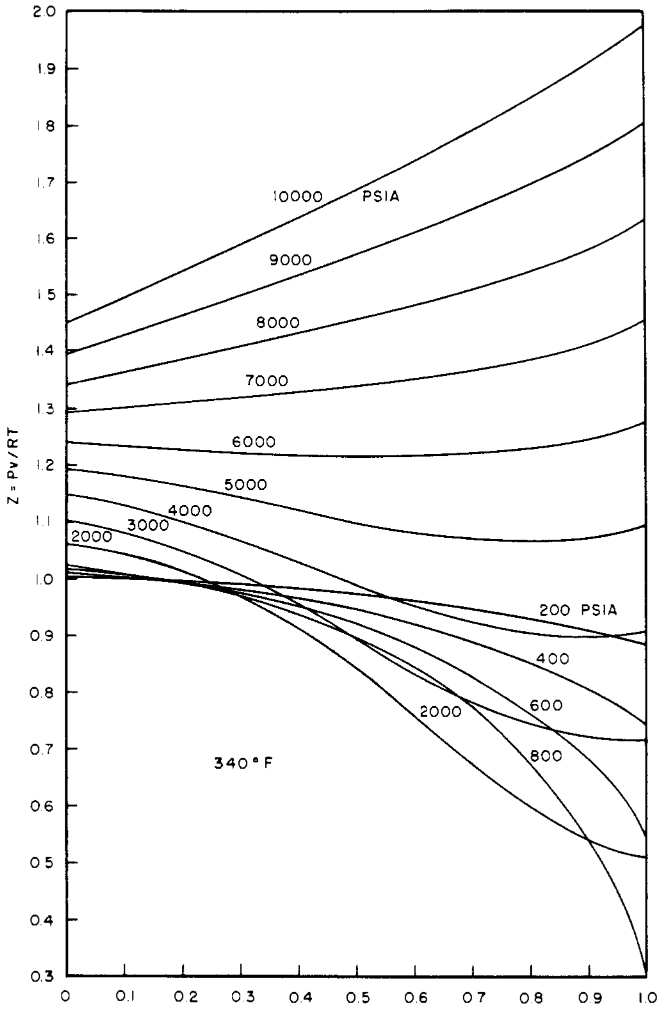

Figure 2. Compressibility factors vs. mole fraction of n-butane at constant pressures

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Diffusion Coefficients in Hydrocarbon Systems

Methane–n-Butane–Methane in Liquid Phase

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There is insufficient information about the diffusion coefficients of the lighter hydrocarbons in the liquid phase for predicting the nonequilibrium behavior of petroleum during production and refining operations.

By following methods established earlier, the Fick diffusion coefficient of methane in the liquid phase of the methane-n-butane system was determined at pressures up to nearly 2000 pounds/square inch in the temperature interval between 10° and 220° F. The results are presented as a function of the state of the phase.

These measurements indicate that the composition and temperature of the liquid phase have a significant influence on the Fick diffusion coefficient. The magnitude of variations in the coefficient within the range of temperatures and compositions investigated makes it necessary to take both of these factors into account in treating many physical situations of industrial interest.

INTRODUCTION

A knowledge of the molecular transport characteristics of the lighter hydrocarbons is of value in many operations associated with the production and refining of petroleum. Little experimental work is available in this field except the early measurements of Pomeroy (9) and of Lacey and coworkers (1,4,5,7). Kirkwood (6) has assembled the basic relations of transport and these have been applied to a number of situations of engineering interest (8). Drickamer made a number of investigations of transport in liquid and gas phases at elevated pressures, of which his studies of diffusion through an interface (18, 19) are given as examples. There has been increasing interest in resistances at interfaces (2) but, in the case of hydrocarbon systems involving transfer from a liquid to a gas phase (16), it appears that this resistance is not large. Such behavior is

TABLE I. DIFFUSION OF METHANE INTO THE LIQUID PHASE OF THE METHANE-BUTANE SYSTEM (EXPERIMENTAL MEASUREMENTS)

Pressure, Lb./Sq. Inch Absolute	Time, Sec.	Wt. Methane Added^{a}, Lb.
10° F.		
83.8^{b}	0	-
284.5^{c}	280	0
	720	84.84×10^{-6}
	1200	148.02
	1690	199.59
	2222	249.88
	3070	311.25
	3920	370.43
	4870	425.49
	5730	470.10
	6760	523.74
	7760	564.99
	8880	608.83
	9970	651.12
	10960	688.64
	12600	735.19
	14730	808.30
	15710	829.31
	17070	867.09
	18530	898.55
	19900	932.33
	21120	957.09
	23170	993.83
	24340	1012.66
	25510	1028.90
	26200	1040.25
	27960	1063.72
	28870	1308.95
	29760	1313.72
	32050	1313.72
298.7^{b}	0	-
499.4^{c}	290	0
	520	71.93×10^{-6}
	780	120.03
	1160	175.77
	1630	220.17
	2140	271.05
	2870	327.95
	3600	374.67
	4540	448.67
	5640	507.19
	6680	562.92
	7720	613.34
	8770	662.14
	10000	713.25
	11510	768.76
	12590	806.92
	13670	843.46
	14640	876.30
	15610	905.21
	16490	929.03
	17250	949.62
	18230	976.21
	20910	1042.13
	22120	1068.03
	23310	1093.93
	24130	1109.20
	25430	1531.04
	28090	1531.04
449.4^{b}	0	-
700.1^{c}	530	0
	890	105.45×10^{-6}
	1330	168.59
	2340	269.74
	2800	315.69
	3230	351.39
	3980	408.58
	4550	443.62
	5110	482.96
	6910	582.79
	7910	636.67
	8760	674.03
	9670	714.69
	10600	756.01
	11460	787.41
	12380	825.10
	13840	880.30
	14750	910.38
	16350	962.28
	17290	992.04
	19660	1061.12
	21910	1119.64
	22790	1140.46
	23510	1761.60
	23830	1771.18
	26160	1771.18
40° F.		
100.6^{b}	0	-
301.4^{c}	580	0
	1220	82.08×10^{-6}
	2030	163.07
	2840	223.54
	4100	302.89
	6459	421.50
	8458	503.58
	9704	548.32
	10465	575.54
	11830	616.45
	13394	660.91
	15280	707.01
	17020	745.05
	19000	778.43
	20290	1051.22
	22008	1053.82
	24717	1053.82
302.0^{b}	0	-
603.0^{c}	690	0
	970	90.56×10^{-6}
	1575	206.80
	2590	346.16
	3590	453.09
	4590	545.34
	5670	632.24
	6660	704.18
	8330	811.95
	10150	916.05
	12180	1017.33
	14630	1124.82
	16920	1212.84
	20050	1314.97
	22480	1382.96
	24120	1424.15
	26170	1848.74
	28760	1851.28
	32170	1851.28
602.3^{b}	0	-
903.4^{c}	510	0
	782	164.71×10^{-6}
	1640	365.06
	2235	460.66
	3210	575.83
	3841	641.45
	5470	784.43
	6625	874.83
	8368	992.60
	9720	1075.17
	11537	1183.38
	13390	1268.56
	15260	1357.66
	17400	1442.40
	20280	1554.52
	22880	1640.57
	25050	2365.47
	27410	2367.64
	30880	2367.64
1019.9^{b}	0	-
1220.6^{c}	540	0
	960	169.46×10^{-6} -
	1550	271.37
	2840	408.27
	3810	484.85
	4930	559.63
	6570	651.30
	7940	720.65
	9340	778.54
	10780	838.85
	12320	895.53
	13740	943.78
	16440	1032.43
	17730	1066.80
	18960	1103.59
	20700	1150.02
	22150	1185.60
	23940	1234.95
	25950	1279.68
	27980	1316.46
	30070	1358.68
	33150	1418.38
	36510	1473.86
	40410	1537.78
	43780	1577.59
	46540	1618.59
	50240	1663.82
	50420	1902.03
	50580	2012.99
	50690	2027.46
	52580	2027.46
1219.4^{b}	0	-
1420.1^{c}	550	0
	1090	120.27×10^{-6}
	2770	371.88
	5160	532.31
	6840	622.69
	8810	705.24
	10690	790.64
	12520	862.52
	13950	922.29
	15130	960.72
	16370	999.15
	17720	1043.99
	19190	1090.24
	20806	1134.36
	22320	1169.23
	24020	1211.93
	25420	1253.92
	27230	1301.60
	29760	1367.78
	31770	1414.04
	33840	1459.59
	35870	1505.13
	44130	1659.14
	44490	2304.31
	44660	2350.57
	45010	2357.68
	48690	2357.68
100° F.		
297.4^{b}	0	-
598.5^{c}	850	0
	1410	91.23×10^{-6}
	2290	208.20
	3840	368.27
	5360	482.45
	7960	641.96
	10100	755.01
	11750	837.00
	14560	950.34

TABLE I. DIFFUSION OF METHANE INTO THE LIQUID PHASE OF THE METHANE-BUTANE SYSTEM (EXPERIMENTAL MEASUREMENTS) (Contd.)

Pressure, Lb./Sq. Inch Absolute	Time, Sec.	Wt. Methane Added^{a}, Lb.
	16270	1018.06
	19250	1119.92
	20910	1173.09
	22980	1229.06
	25310	1286.15
	26070	1734.74
	28080	1751.53
	28910	1751.53
592.9^{b}	0	-
894.0^{c}	610	0
	770	65.33×10^{-6}
	1420	183.08
	2180	285.37
	3330	403.13
	3990	462.44
	4950	533.35
	5930	604.26
	7170	677.32
	8420	751.67
	9310	795.94
	11050	883.61
	12790	969.57
	15320	1080.45
	17750	1171.56
	21110	1290.61
	22720	1334.88
	23870	2172.08
	24710	2173.37
	54610	2173.37
598.6^{b}	0	-
899.7^{c}	790	0
	1060	78.74×10^{-6}
	1470	153.15
	1890	215.02
	2750	316.26
	3960	431.34
	5170	531.71
	6570	619.96
	8960	773.98
	11860	921.94
	14030	1014.53
	16910	1136.96
	19420	1225.65
	21210	1283.63
	23830	2045.93
	25060	2045.93
	26990	2045.93
894.3^{b}	0	-
1195.4^{c}	430	0
	650	25.91×10^{-6}
	980	104.24
	1480	197.89
	2080	272.69
	4310	482.36
	5260	548.91
	6330	619.58
	6860	655.51
	8350	743.85
	9170	792.15
	9860	825.13
	10870	873.42
	11710	922.30
	12990	978.26
	14260	1031.26
	15530	1085.45
	17170	1151.41
	18780	1207.94
	20050	1257.42
	23540	1372.27
	24500	2469.49
	26690	2500.71
	27450	2500.71
	29080	2500.71
894.6^{b}	0	-
1193.7^{c}	950	0
	1390	107.12×10^{-6}
	2130	214.82
	2770	290.74
	4660	465.54
	6520	603.26
	8440	719.21
	11240	858.69
	12910	933.44
	15880	1056.44
	19680	1190.63
	22740	2280.62
	25580	2280.62
	27400	2280.62
160° F.		
245.4^{b}	0	-
446.1^{c}	520	0
	820	26.30×10^{-6}
	1760	68.63
	3255	166.23
	4655	238.36
	5900	291.78
	7855	365.14
	9060	404.18
	11230	462.13
	11950	480.83
	14390	532.40
	15050	751.86
	15230	764.19
	17510	764.19
847.6^{b}	0	-
1048.3^{c}	610	0
	1380	118.46×10^{-6}
	2220	181.78
	2860	223.65
	3260	246.12
	4260	296.16
	5250	340.07
	7260	420.75
	9030	480.49
	11070	544.32
	14260	630.10
	17370	705.16
	20540	764.91
	21760	1065.66
	24120	1080.47
	25810	1080.47
	28780	1080.47
1048.8^{b}	0	-
1249.5^{c}	500	0
	1080	44.25×10^{-6}
	1670	165.12
	2700	240.56
	3350	278.28
	4520	333.32
	6270	403.82
	8910	491.02
	10850	546.68
	12760	601.10
	15300	656.13
	17700	706.22
	19850	745.80
	22280	783.53
	23060	1155.19
	25790	1163.23
	27560	1174.98
	32880	1174.98
1249.4^{b}	0	-
1450.2^{c}	490	0
	770	60.44×10^{-6}
	1570	145.64
	2290	203.16
	3350	269.43
	4020	308.02
	4940	349.53
	6520	419.43
	7300	443.46
	8130	470.40
	9590	522.10
	11520	565.07
	13460	611.67
	14750	639.34
	16000	662.64
	16620	679.39
	17240	1224.07
	17730	1294.70
	21850	1294.70
220° F.		
414.9^{b}	0	-
615.6^{c}	460	0
	2080	19.03×10^{-6}
	2320	42.68
	2850	78.44
	3650	117.37
	4270	149.09
	5020	183.69
	5730	210.22
	6980	257.23
	7550	275.69
	8290	298.75
	8830	314.32
	9930	346.62
	12650	406.60
	13400	418.14
	14360	433.42
	17220	471.78
	19320	496.00
	21810	526.85
	25360	543.58
	27870	605.00
	31690	605.00
	33930	605.00
1018.0^{b}	0	-
1218.8^{c}	380	0
	530	37.33×10^{-6}
	1040	69.85
	1810	115.01
	3330	189.67
	4460	236.03
	5670	279.99
	7410	337.19
	8200	360.67
	9730	405.23
	12110	458.22
	13220	482.30
	14970	513.61
	15910	531.08
	18010	568.41
	19130	584.06
	20920	609.96
	23480	639.46
	25560	660.53
	27130	895.36
	31090	895.36

[a] Weight added to heterogeneous isochoric system.
[b] Initial equilibrium pressure.
[c] Constant operating pressure during diffusion.

in accordance with the predictions of Schrage (17), who indicated that interfacial resistance would be important only when the mean-free path of the molecules approached the dimensions of the interface. A more extended review of the literature applying to material transport is available (11).

A review of the available information indicated the need for data concerning the diffusion of methane in the quiescent liquid phase of the methane-n-butane system. This report describes experimental measurements of the Fick diffusion coefficient by transient methods for pressures within 500 pounds/square inch of the critical pressures of the methane-n-butane system at temperatures between 10° and 220° F.

METHODS AND APPARATUS

The method employed involves the introduction of methane into an isochoric vessel which is partially filled with a heterogeneous mixture of methane and n-butane. The pressure was suddenly raised from the equilibrium value to some predetermined higher level. It was maintained at this level, and the quantity of methane introduced was determined as a function of time. The details of the equipment have already been described (11). The standard error of estimate for the weight of methane added was approximately 0.3 x 10^{-6} pounds. Time was measured with a maximum uncertainty of two seconds in a period of about eight hours. The pressure was maintained at a constant value within 0.1 pound/square inch and was known within 0.05%. Temperatures were determined with strain-free platinum resistance thermometers which were compared to a similar set of instruments calibrated by the National Bureau of Standards. The temperatures of the bath surrounding the isochoric vessel were related to the international platinum scale within 0.02° F. Small vertical tubes were placed in the isochoric vessel to decrease the influence of local vibration and convection in the liquid phase. The quantity of n-butane introduced was determined by weighing bomb techniques (15) and no measurements were made when the change in volume of the liquid phase from the solution of methane raised the interface above the upper end of the vertical tubes.

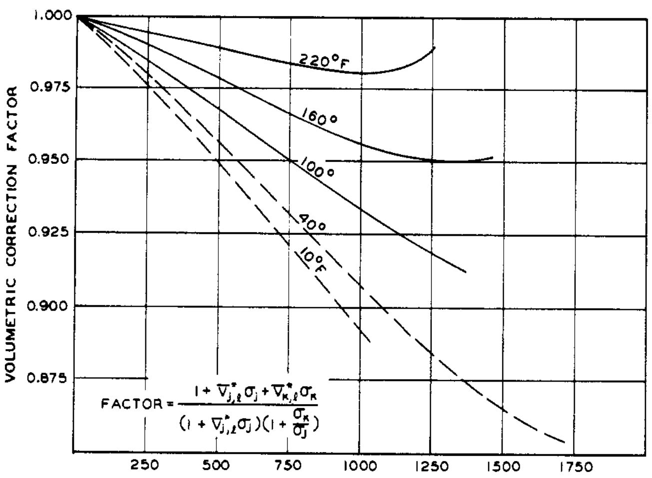

Figure 1. Effect of hydrodynamic velocity on experimental Fick diffusion coefficient

Following methods of analysis which have already been described (11), the Fick diffusion coefficient was calculated from the experimental measurements by means of the following expression:

$$D_{F,k} = \left[\frac{(1+\bar{V}^*_{j,l}\sigma_j+\bar{V}^*_{k,l}\sigma_k)}{(1+\bar{V}^*_{j,l}\sigma_j)\left(1+\frac{\sigma_k}{\sigma_j}\right)}\right]^* \left[\frac{\pi m^2_{k,c}}{4\theta(\sigma_{k,i,e}-\sigma_{k,0})}\right]\left[\frac{\bar{V}^*_{k,g}}{\bar{V}^*_{k,g}-\bar{V}^*_{k,l}}\right]^2 \qquad (1)$$

Equation 1 takes into account the change in volume of the liquid phase and the hydrodynamic velocity (8) but neglects the resistance at the interface. The asterisk on the bracketed first term and in the last term indicates an average over the range of conditions encountered in a particular measurement. Expressions taking the resistance into account can be derived, but in the present instance the resistance does not appear great enough to permit its accurate evaluation.

In order to evaluate the terms in Equation 1, earlier measurements upon the volumetric and phase behavior of the methane-n-butane system at equilibrium were employed (10, 12, 13). The magnitude of the first bracketed term in Equation 1 which takes into account the hydrodynamic velocity is shown in Figure 1 where it is designated as the volumetric correction factor. The magnitude of this correction is significant, particularly at the lower temperatures. The correction for the change in volume of the liquid phase as it is employed in the last bracket of the equation is shown in Figure 2 where it is designated as the weight correction factor since it takes into account the difference in weight of methane introduced and that passing the interface. In this instance the correction is of similar magnitude but is greater than unity. Thus, it is seen that the two corrections tend to compensate one another. It should be emphasized that Equation 1 and the application of the corrections from Figures 1 and 2 are based entirely upon the assumption of local equilibrium (3, 6) throughout the phase.

MATERIALS

The methane employed in this investigation was obtained from a well in the San Joaquin Valley of California and contained approximately 0.003 mole fraction of carbon dioxide, traces of heavier hydrocarbons, and was saturated with water. The gas was dried by passage over anhydrous calcium sulfate and the carbon dioxide and heavier hydrocarbons were removed by contact with potassium hydroxide, activated charcoal, Ascarite, and alumina. The gas employed did not contain more than 0.001 mole fraction of material other than methane. The n-butane was purchased as pure grade from the Phillips Petroleum Co. and was reported to contain less than 0.01 mole fraction of material other than n-butane. The n-butane was fractionated once

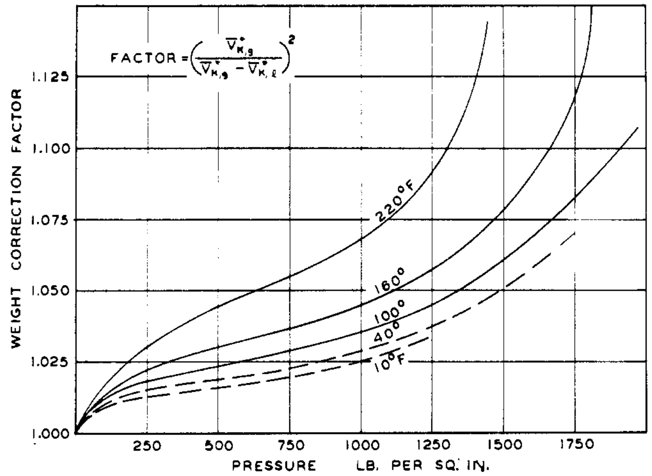

Figure 2. Influence of change in volume of the liquid phase on the weight of methane crossing interface

TABLE II. SUMMARY OF EXPERIMENTAL RESULTS

Pressure, Lb./Sq. Inch Absolute		Composition Methane, Weight Fraction		Concentration Methane, Lb./Cu. Ft.		$\frac{\Delta m^2}{\theta}$[a]	Standard Error of Estimate, Lb.	Volumetric Correction Factor	Fick Diffusion Coefficient, Sq. Ft./Sec.	
Initial	Final	Initial	Final	Initial	Final	Lb.^{2}/Sec.			Uncorrected	Corrected
10° F.[b]										
83.8	284.5	0.011	0.038	0.361	1.311	59.753 x 10^{-12}	2.5 x 10^{-6}	0.9724	14.161 x 10^{-8}	13.770 x 10^{-8}
298.7	499.4	0.040	0.069	1.380	2.360	68.393	3.1	0.9498	15.320	14.551
499.4	700.1	0.069	0.098	2.360	3.363	73.102	5.7	0.9269	15.644	14.500
40° F.[b]										
100.6	301.4	0.009	0.035	0.360	1.221	52.998 x 10^{-12}	1.1 x 10^{-6}	0.9753	15.316 x 10^{-8}	14.938 x 10^{-8}
302.0	603.0	0.035	0.074	1.226	2.580	130.188	3.2	0.9468	15.232	14.422
602.3	903.4	0.074	0.117	2.578	3.912	144.000	6.6	0.9178	17.568	16.124
1019.9	1220.6	0.135	0.169	4.506	5.441	66.260	4.5	0.8873	16.631	14.757
1219.4	1420.1	0.168	0.214	5.436	6.382	68.724	5.0	0.8713	16.906	14.730
100° F.										
297.4	598.5	0.025	0.060	0.870	1.970	100.000	9.5 x 10^{-6}	0.9613	17.900 x 10^{-8}	17.207 x 10^{-8}
592.9	894.0	0.059	0.098	1.947	3.070	105.678	3.1	0.9411	18.282	17.205
598.6	899.7	0.060	0.099	1.970	3.090	108.994	5.7	0.9407	18.965	17.840
894.3	1195.4	0.098	0.144	3.070	4.208	105.473	3.2	0.9220	17.930	16.531
894.6	1193.7	0.098	0.144	3.090	4.206	104.653	8.0	0.9220	18.419	16.982
160° F.										
245.4	446.1	0.012	0.031	0.361	0.949	39.188 x 10^{-12}	0.8 x 10^{-6}	0.9816	24.610 x 10^{-8}	24.157 x 10^{-8}
847.6	1048.3	0.075	0.100	2.150	2.756	37.454	1.2	0.9548	22.510	21.493
1048.8	1249.5	0.100	0.129	2.759	3.367	35.284	2.5	0.9511	21.241	20.202
1249.4	1450.2	0.129	0.164	3.367	3.975	34.222	7.5	0.9514	20.841	19.828
220° F.										
414.9	615.6	0.016	0.035	0.429	0.929	35.402 x 10^{-12}	4.2 x 10^{-6}	0.9870	31.366 x 10^{-8}	30.958 x 10^{-8}
1018.0	1218.8	0.080	0.109	1.949	2.460	27.353	2.5	0.9869	23.879	23.566

[a] Effective cross-sectional area = 0.019262 sq. ft.

[b] Values of phase composition, concentration, and volumetric correction factor are extrapolated from data at higher temperatures.

and collected under vacuum at liquid nitrogen temperature. Its vapor pressure at 160° F. was within 0.1 pound/square inch of a critically chosen value (14).

EXPERIMENTAL MEASUREMENTS

A series of measurements of the quantity of methane introduced as a function of time were made for several different compositions of the liquid phase at each of five temperatures between 10° and 220° F. inclusive. In this investigation nonequilibrium pressure differentials from 100 to 200 pounds/square inch were employed. As would be expected, for each measurement which covered only a small range in composition, the weight of methane added was nearly a linear function of the square root of time. The measurements were usually carried to such a point that approximately 50% of the methane required to bring the system to equilibrium, was added. As pointed out by Pomeroy (9), beyond this point it is impossible to treat the liquid phase as an infinite body, and simple relationships between quantity of methane added and time no longer exist. The results of experimental measurements are given in Table I.

Table II summarizes the experimental results obtained in this investigation. The deviation of the experimental points from a line of constant value of $\Delta m_k/\theta^{1/2}$ has been included for each set of measurements. In this instance it was assumed that all of the error was associated with the weight of methane added and none with the time. The average standard error of estimate for all the experimental data was 4.2 x 10^{-6} pounds. The Fick diffusion coefficient was evaluated through Equation 1, utilizing the equilibrium data in Figures 1 and 2.

From the values of the Fick diffusion coefficient recorded in Table II the influence of state on this coefficient can be seen. The experimental results are shown in Figure 3 as a function of the mean of the initial and final pressure associated with each measurement. The measured Fick diffusion coefficients were assumed to apply at this mean pressure. The smooth curves drawn through the experimental points have been located so as to yield the minimum standard error of estimate. The small number of experimental points obtained at 220° F. resulted in greater uncertainty than that for the lower temperatures. Lines of

TABLE III. DEVIATIONS OF EXPERIMENTAL MEASUREMENTS FROM SMOOTHED DATA

Temp., ° F.	Average Difference		Standard Deviation, Sq. Ft./Sec.	Relative Deviation, %
	With sign	Without sign		
10	0.01 x 10^{-8}	0.29 x 10^{-8}	0.38 x 10^{-8}	2.66
40	-0.05	0.52	0.69	4.63
100	-0.07	0.30	0.42	2.44
160	0.06	0.28	0.44	2.04
220	-0.36	1.24	1.02	3.76
Av.	-0.08	0.53	0.59	3.11

constant composition have been included in Figure 3, together with an estimate of the location of the critical state. A summary of deviations in the individual measurements of the Fick diffusion coefficient from the smoothed data is presented in Table III. It appears that the relative standard deviation is about 3.1%, which is somewhat smaller than would be expected considering the uncertainties in the individual measurements. The effect of temperature upon the Fick diffusion coefficient is shown in Figure 4. At the lower temperatures an increase in pressure results in an increase in the diffusion coefficient. However, for temperatures above approximately 80° F. an increase in pressure results in a significant decrease in the Fick diffusion coefficient. The approximate position of the limiting curve associated with the critical state has been included. Table IV presents smoothed values of the Fick diffusion coefficient as a function of state. For the convenience of the reader, the composition, pressure, and temperature of the phase have been indicated. The relation of these variables was taken from earlier studies of the equilibrium behavior of the methane-n-butane system (10, 12, 13). The results obtained in this investigation are in accord with other studies of the transport characteristics of methane in the liquid phase of other binary hydrocarbon systems.

TABLE IV. FICK DIFFUSION COEFFICIENT FOR METHANE

Pressure, Lb./Sq. Inch Absolute	Concn., Lb./Cu. Ft.	Compn., Weight Fraction	Fick Diffusion Coefficient, Sq. Ft./Sec.
		10° F.[a]	
19[b]	0	0	14.1×10^{-8}
250	1.146	0.034	14.2
500	2.359	0.069	14.3
750	3.619	0.105	14.4
1000	4.871	0.145	14.5[c]
1250	6.146	0.190	14.6[c]
1500	7.399	0.258	14.8[c]
		40° F.[a]	
26[b]	0	0	14.9×10^{-8}
250	1.001	0.028	14.9
500	2.112	0.061	15.0
750	3.258	0.094	15.0
1000	4.410	0.131	15.1
1250	5.578	0.174	15.2
1500	6.759	0.234	15.4[c]
		100° F.	
51.5[b]	0	0	17.6×10^{-8}
250	0.699	0.020	17.5
500	1.601	0.048	17.4
750	2.529	0.079	17.2
1000	3.468	0.114	17.1
1250	4.418	0.154	17.0[c]
1500	5.346	0.203	16.9[c]
		160° F.	
120.6[b]	0	0	25.3×10^{-8}
250	0.376	0.012	24.7
500	1.112	0.036	23.5
750	1.860	0.064	22.4
1000	2.609	0.094	21.2
1250	3.366	0.128	20.1
1500	4.124	0.174	19.0[c]
		220° F.	
241.2[b]	0	0	32.6×10^{-8}
250	0.019	0.001	32.5
500	0.640	0.023	30.2
750	1.267	0.049	28.0
1000	1.904	0.078	26.1
1250	2.541	0.114	24.1[c]
1500	3.178	0.177	22.3[c]

[a] Composition and concentration values were extrapolated from data at higher temperatures.
[b] Vapor pressure of n-butane expressed in lb./sq. inch.
[c] Values were obtained from extrapolation of experimental data at lower pressures.

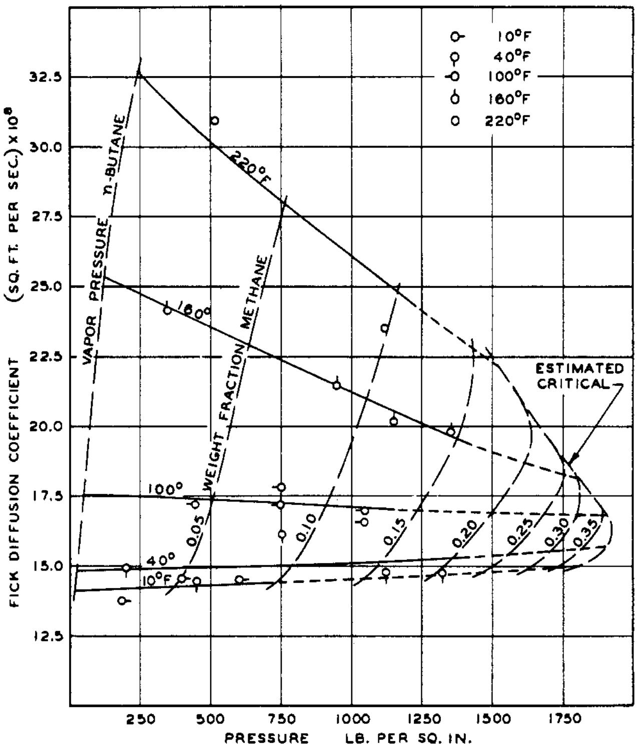

Figure 3. Influence of pressure on Fick diffusion coefficient

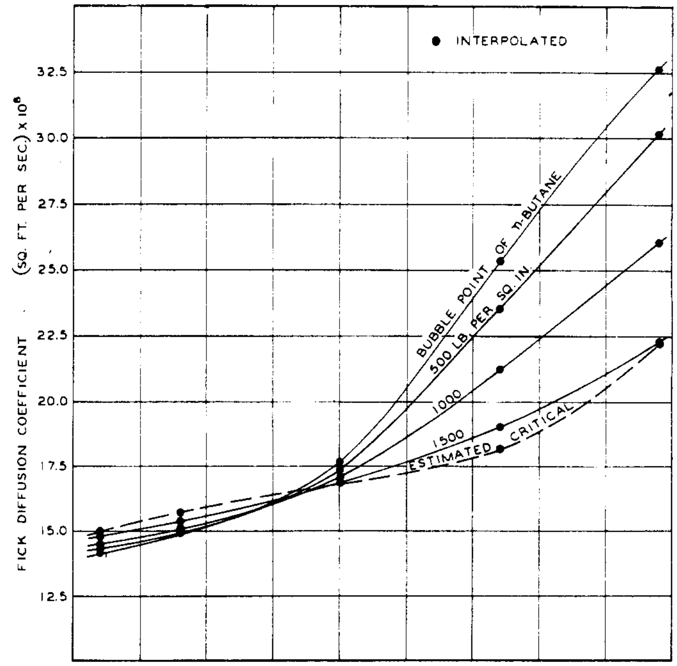

Figure 4. Effect of temperature on Fick diffusion coefficient

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NOMENCLATURE

$D_{F,k}$ = Fick diffusion coefficient of component k, sq. ft./sec.
m_k = weight of component k added per unit area of interface, lb./sq. ft.
V_k = partial specific volume of component k, cu. ft./lb.
Δ = difference in
θ = time, sec.
σ_k = concentration of component k, lb./cu. ft.

Superscript
$*$ = average condition

Subscripts
c = diffusion cell
e = conditions at equilibrium
g = gas phase
i = conditions at interface
j = component j, the stagnant component
k = component k, the diffusing component
l = liquid phase
0 = initial conditions

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Generalized Charts of Detonation Parameters for Gaseous Mixtures

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Where detonative combustion is involved, it is frequently desirable to visualize the relationships among various detonation parameters. To fulfill this need, generalized charts of detonation parameters for all gaseous mixtures, involving only nondimensional quantities, are given. The chief usefulness of these plots of generalized equations, derived directly from the classical equations of detonation, is to provide a means for visualizing relationships among the detonation parameters for all gaseous mixtures on a small number of Mollier-type diagrams. Application of these generalized charts is illustrated by means of several examples.

There is need of simplified methods for determining and visualizing values of detonation parameters for all gaseous mixtures. Considerably more information on detonation parameters is required before the advantageous application of supersonic burning in propulsive devices can be realized. Such information may also have direct application in understanding instability phenomena (such as screech) in ramjet, turbojet, afterburner, and rocket engines. These instability phenomena and their possible association with detonative combustion have been discussed in the literature (6, 8).

To provide simplified means for analytically determining values of detonation parameters, the classical equations of detonation were previously rearranged (2), and also a calculation procedure based on the resulting generalized equations, involving only nondimensional quantities, was devised. During the process of generalizing the detonation equations it became apparent that it would be extremely useful if the detonation parameters for all gaseous mixtures could be presented in nondimensional form on a Mollier-type diagram. This would aid considerably in visualization of relationships among the various detonation parameters. It was found that the generalized detonation equations could be utilized for the graphical presentation of the detonation parameters on a small number of Mollier-type diagrams.

In this article, derivation of the generalized detonation equations is summarized, and the method of constructing the generalized charts based on these equations is described. Application of the generalized detonation charts is illustrated by means of several examples.

DERIVATION OF EQUATIONS FOR THE GENERALIZED CHARTS

The assumptions utilized in the derivation following are generally introduced where required. It is assumed