Diffusion Coefficients in Hydrocarbon Systems: Methane in the Liquid Phase of the Methane–*n*-Heptane System

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The production and refining of petroleum involve many processes in which conditions deviate markedly from equilibrium. For prediction of the behavior of such nonequilibrium systems, information concerning the molecular-transport characteristics of the paraffin hydrocarbons is of practical interest.

Fick diffusion coefficients for methane were measured in the liquid phase of the methane–*n*-heptane system at temperatures between 40° and 340°F. at pressures up to 3,500 lb./sq. in., but the pressure range was limited at the higher temperatures by approach to the critical state of this binary system.

The measurements obtained confirmed the fact that the Fick diffusion coefficients for methane decrease with an increase in the concentration of this component and increase rapidly with an increase in temperature for a constant composition. These data together with similar information for other binary paraffin hydrocarbon systems indicate that the Fick diffusion coefficients for methane decrease with an increase in the molecular weight of the less volatile component.

A knowledge of the molecular transport in hydrocarbon liquids is useful in predicting behavior under nonequilibrium conditions, but the experimental background regarding diffusion in hydrocarbon liquids is limited. Pomeroy (*10*), Hill (*5*, *6*) and Bertram (*2*) investigated the diffusion of methane and propane into a number of hydrocarbon liquids at pressures below 500 lb./sq. in., Kirkwood (*7*) reviewed the relationship of molecular transport, and Drickamer (*21*, *22*) reported numerous investigations of molecular transport in and between liquid and gas phases and found a resistance to material transport at the interface.

Measurements were made of the Fick diffusion coefficients for methane in the liquid phase of the methane–*n*-decane (*13*) and the methane–*n*-pentane systems (*11*) for pressures up to within 500 lb./sq. in. of the critical pressures at temperatures from 40° to 280°F. Similar measurements were reported for methane in the liquid phase of the methane–*n*-butane system (*14*) at pressures up to nearly 2,000 lb./sq. in. in the temperature interval between 10° and 220°F. The current study presents measurements of the Fick diffusion coefficient for methane in the liquid phase of the methane–*n*-heptane system. In this instance data were obtained at temperatures from 40° to 340°F. and at pressures up to 3,500 lb./sq. in. At the higher temperatures it was not possible to reach this pressure because of approach to the critical pressure (*16*) of the system.

METHODS AND APPARATUS

The method employed was similar to that used by Pomeroy (*10*) and involved the measurement of the rate of introduction of methane into a quiescent, heterogeneous, isochoric mixture of methane and *n*-heptane. The heterogeneous system was brought to equilibrium at a chosen state and the pressure of the quiescent system was then increased rapidly to a predetermined level. The quantity of methane required to maintain the variable-weight system under isobaric-isothermal conditions was determined as a function of time. A description of the equipment and the method of interpretation of the results is available in reference *13*.

The quantity of methane introduced was determined by means of a volumetric injector (*13*) operated at a known rate by a motor, the speed of which was controlled by a quartz oscillator (*15*). Experience indicated that uncertainty in the introduction of methane was less than 0.1% of the total quantity added during the period of measurement. The quantity of *n*-heptane employed was determined gravimetrically by weighing-bomb techniques (*19*). The uncertainty in the quantity of *n*-heptane introduced was less than 0.05%.

Pressure in the isochoric diffusion vessel was determined by means of a balance (*19*) with a probable error of 0.1 lb./sq. in. or 0.05%, whichever was the larger measure of uncertainty. Variations in pressure during the diffusion process were less than 0.2 lb./sq. in. Temperatures were measured with platinum resistance thermometers of the strain-free type (*8*), which were compared with reference resistance thermometers calibrated by the National Bureau of Standards. The temperature of the bath within which the diffusion vessel was located was controlled with a variation of less than 0.005°F. The calibration of the resistance thermometers was made with sufficient care and frequency so that the temperature of the system was related to the international platinum scale within 0.02°F. Somewhat larger uncertainties in temperature may have existed during the short period required to raise the pressure from the initial to the final value. Time intervals during the sequence of measurements were established with an uncertainty of 3 sec.

Experimental measurements yielded values of the weight of methane introduced into the isochoric vessel as a function of time. The Fick diffusion coefficient was related to the average conditions obtaining during such measurements in the following way (*13*):

$$D^*_{F,k} = \left[\frac{(1+\bar{V}^*_{j,l}c_{j,l}+\bar{V}^*_{k,l}c_{k,l})}{(1+\bar{V}^*_{j,l}c_{j,l})^*\left(1+\frac{c_k}{c_j}\right)^*}\right] \cdot \left[\frac{\pi m_k^{\,2}}{4\theta(c_{k,i,e}-c_{k,0})^2}\right] \cdot \left[\frac{\bar{V}^*_{k,g}}{\bar{V}^*_{k,g}-\bar{V}^*_{k,l}}\right]^2 \qquad (1)$$

Local equilibrium was assumed (*7*) and the first and third brackets of Equation (1) could be evaluated from available equilibrium data (*9*, *16*). The first bracket is a correction for the hydrodynamic velocity (*13*) in the liquid phase. This velocity cor-

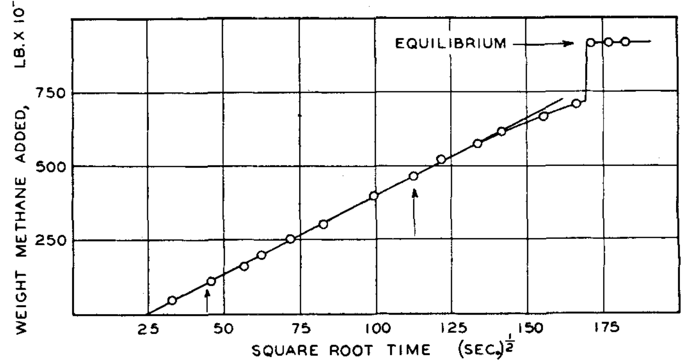

Fig. 1. Typical experimental measurements at 160°F.

TABLE 1. SAMPLE OF DETAILED EXPERIMENTAL MEASUREMENTS

Pressure, lb./sq. in. abs.	Weight fraction methane	Time, sec.	Weight of methane added, lb.
		160°F.	
*411.0**	0.020	0	
766.2†	0.039	510	—
		1050	49.871×10^{-6}
		2070	110.662
		3190	160.532
		3880	201.303
		5100	251.902
		6860	307.232
		9880	400.421
		12690	466.309
		14860	521.276
		17940	575.879
		20410	614.464
		24090	668.339
		27600	708.018
		29480	911.868
		31420	911.868
		33380	911.868

*Initial equilibrium pressure.

†Pressure remained constant throughout the measurements.

responds to the momentum of the fluid during diffusion. The second bracket involves the measurements of the weight of methane as a function of time and is obtained from the diffusion data. The third bracket represents a correction to the weight of material introduced into the isochoric vessel to establish that crossing the liquid-gas interface. Detailed discussion of the derivation of Equation (1) is available (*13*).

More complicated expressions taking the resistance at the interface into account are also available (*13*). Experience with measurements of this type indicates that the resistance at the interface for similar systems (*20*) is so small that it can safely be neglected in these studies. The deviation from the linear relationship between the weight of methane transported across the interface and the square root of time was sufficiently small to confirm this point of view. The resistance of the gas phase may be disregarded, since, if local equilibrium (*7*) exists, the composition on the liquid-phase side of the interface is solely a function of the prevailing temperature and pressure.

A typical record of the experimental data obtained in a particular situation is depicted in Figure 1 for a temperature of 160°F. The standard deviation of the experimental points from a straight line was 5.2×10^{-6} lb. for the time period indicated between the two vertical arrows. This measure of deviation assumed that there was no uncertainty in the measurement of time. The quantity of methane entering the liquid phase to obtain equilibrium is indicated by the location of the horizontal arrow.

MATERIALS

The sample of *n*-heptane employed in this investigation was purchased as pure grade from the Phillips Petroleum Company and was reported to contain less than 0.01 mole fraction of material other than *n*-heptane. The *n*-heptane was dried with sodium and subjected to two fractionations at a reflux ratio of 20 in a column containing sixteen glass plates, the central 80% portion of the overhead being retained from each fractionation. The product from the second fractionation was passed as a liquid over activated alumina and deaerated by refluxing at reduced pressure. The sample had a specific weight of 42.429 lb./cu. ft. as compared with a value of 42.419 lb./cu. ft. reported by Rossini (*18*) for an air-saturated sample at 77°F. The index of refraction relative to the *D* lines of sodium at this same temperature was 1.3852. This value is in close agreement with a value for air-saturated *n*-heptane at 77°F. of 1.38511, selected by Rossini (*18*). The close agreement of the measured specific weight and index of refraction for this sample with critically chosen values for the pure hydrocarbon and the statements of the supplier leads the authors to believe that the sample of *n*-heptane contained less than 0.001 mole fraction of impurities.

Methane was obtained from a well in the San Joaquin Valley of California. The sample received at the laboratory contained approximately 0.001 mole fraction of carbon dioxide with traces of heavier paraffin hydrocarbons and was in equilibrium in an aqueous phase at a pressure of approximately 1,400 lb./sq. in. The nearly pure methane was passed over calcium chloride, activated charcoal, potassium hydroxide, Ascarite, and anhydrous calcium sulfate. Spectroscopic analysis indicates that methane obtained from this well after being subjected to the treatment

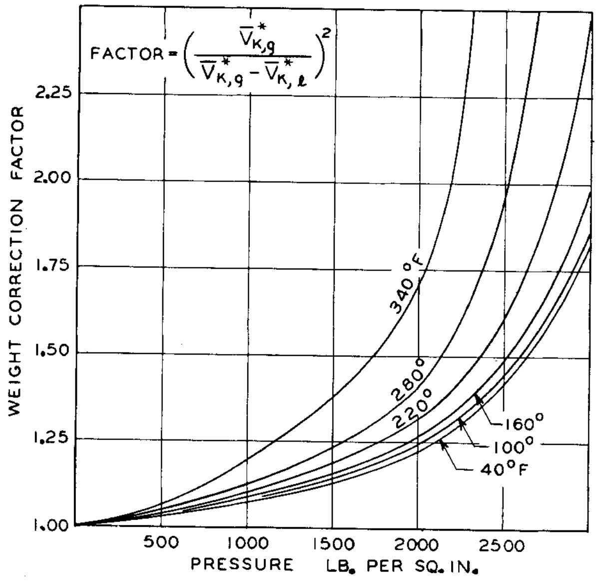

Fig. 2. Weight-correction factor for methane–*n*-heptane system.

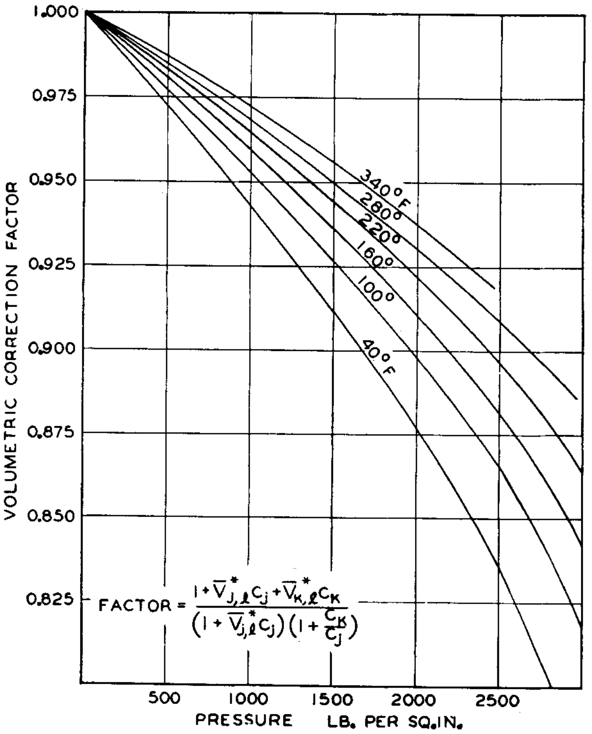

Fig. 3. Volumetric correction factor for methane–*n*-heptane system.

Table 2. Summary of Experimental Results

Pressure, lb./sq. in. abs.		Composition methane weight fraction		Concentration methane lb./cu. ft.		$\frac{(\Delta m_k)^2}{\theta}$* lb.²/sec.	Standard error of estimate, lb.	Volumetric correction factor	Fick diffusion coefficient, sq. ft./sec.	
Initial	Final	Initial	Final	Initial	Final				Uncorrected	Corrected
						40° F.				
59.4	410.6	0.004	0.027	0.167	1.139	29.160×10^{-12}	2.6×10^{-6}	0.9785	6.651×10^{-8}	6.508×10^{-8}
410.6	761.8	0.027	0.052	1.139	2.147	28.409	9.3	0.9578	6.210	5.948
762.8	1114.0	0.052	0.079	2.148	3.180	27.668	3.7	0.9362	5.993	5.611
1114.1	1465.3	0.079	0.109	3.180	4.219	27.773	13.2	0.9138	6.188	5.654
1465.3	1816.6	0.109	0.140	4.219	5.240	25.705	5.1	0.8903	6.203	5.522
1818.9	2170.1	0.140	0.178	5.250	6.325	18.404	12.2	0.8645	4.299	3.717
2849.2	3049.9	0.278	0.326	8.768	9.695	12.250	6.6	0.7669	5.670	4.349
						100°F.				
34.6	335.7	0.003	0.014	0.076	0.751	22.090×10^{-12}	3.4×10^{-6}	0.9863	10.468×10^{-8}	10.325×10^{-8}
724.8	1062.4	0.042	0.064	1.654	2.459	24.502	3.4	0.9503	8.732	8.298
1075.0	1426.3	0.065	0.089	2.489	3.347	25.705	3.1	0.9310	8.426	7.845
1426.3	1777.6	0.089	0.117	3.347	4.222	23.912	8.3	0.9110	7.915	7.210
1791.0	2142.2	0.118	0.149	4.259	5.179	28.090	23.2	0.8886	9.051	8.042
2152.4	2503.6	0.150	0.188	5.208	6.225	25.100	17.0	0.8622	7.397	6.378
						160°F.				
59.8	411.0	0.003	0.020	0.110	0.786	27.668×10^{-12}	9.0×10^{-6}	0.9848	13.330×10^{-8}	13.128×10^{-8}
411.0	766.2	0.020	0.039	0.786	1.489	27.458	5.2	0.9696	12.537	12.156
766.2	1117.5	0.039	0.059	1.489	2.163	28.196	5.3	0.9585	14.479	13.878
1470.8	1822.1	0.081	0.106	2.971	3.682	18.062	11.1	0.9203	9.242	8.506
1823.6	2184.2	0.107	0.136	3.686	4.518	26.522	8.9	0.9010	10.802	9.733
2184.1	2535.3	0.136	0.172	4.518	5.381	25.908	39.7	0.8791	11.120	9.775
2535.9	2877.1	0.172	0.217	5.382	6.311	16.728	26.2	0.8530	7.459	6.362
						220°F.				
753.7	1104.9	0.035	0.054	1.259	1.890	26.214×10^{-12}	5.9×10^{-6}	0.9604	15.582×10^{-8}	14.965×10^{-8}
1119.4	1470.6	0.055	0.076	1.918	2.581	30.581	10.5	0.9463	17.422	16.486
1454.0	1805.2	0.075	0.099	2.554	3.249	26.522	7.1	0.9314	14.717	13.708
1806.0	2157.3	0.099	0.127	3.250	3.996	27.878	13.9	0.9147	14.633	13.385
2164.2	2515.4	0.128	0.163	4.010	4.803	23.620	9.5	0.8960	12.833	11.498
2310.7	2511.4	0.141	0.162	4.323	4.797	7.453	12.4	0.8963	11.329	10.154
						280°F.				
418.7	759.9	0.027	0.033	0.582	1.120	30.140×10^{-12}	2.7×10^{-6}	0.9775	23.919×10^{-8}	23.381×10^{-8}
758.7	1109.9	0.033	0.050	1.118	1.677	31.136	1.7	0.9691	24.258	23.508
1110.5	1461.8	0.050	0.071	1.677	2.250	28.516	7.7	0.9527	22.505	21.440
1461.7	1812.9	0.071	0.094	2.250	2.867	29.052	6.5	0.9385	21.374	20.059
1814.0	2165.3	0.094	0.124	2.869	3.549	25.604	6.6	0.9245	17.877	16.527
2198.4	2399.1	0.127	0.148	3.622	4.039	6.502	5.1	0.9144	14.161	12.949
2598.2	2799.0	0.175	0.216	4.500	5.046	4.928	2.9	0.8948	12.242	10.953
						340°F.				
717.0	1018.1	0.029	0.045	0.925	1.377	21.068×10^{-12}	6.9×10^{-6}	0.9715	26.219×10^{-8}	25.472×10^{-8}
1323.4	1624.4	0.063	0.082	1.840	2.308	15.524	3.5	0.9510	21.577	20.520
1624.2	1925.2	0.082	0.105	2.308	2.809	19.272	7.4	0.9403	26.493	24.912

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*Effective cross-sectional area = 0.019262 sq. ft.

described above contains less than 0.002 mole fraction of material other than methane.

EQUILIBRIUM DATA

As indicated in Equation (1), a rather detailed knowledge of the equilibrium volumetric and phase behavior of this system is required in order to interpret the diffusion measurements. Initially an effort was made to employ the measurements of Boomer and coworkers (*3*) upon the methane-nitrogen-heptane system to evaluate these quantities. However it was found that the data of Boomer, because of limited composition and temperature range, did not permit the evaluation of the partial volumes of the components in the liquid and gas phases with an accuracy comparable to the rate measurement obtained. For this reason the volumetric and phase behavior of the methane–*n*-heptane system was investigated (*9*, *16*). These data are in good agreement with the measurement of Beattie (*1*) upon pure *n*-heptane and in fair agreement with the earlier measurements of Boomer. The recent data (*16*) were employed to evaluate the partial volumes required to obtain the Fick diffusion coefficients from Equation (1). In this instance the graphical method of Roozeboom (*17*) was employed to determine the partial volume in the liquid phase as a function of pressure, temperature, and composition. Figure 2 depicts the weight-correction factor which is made necessary by the increase in volume in the liquid phase and the consequent decrease in the volume of the gas phase. It is apparent that at the higher pressures this correction becomes of importance and its accurate evaluation is a necessary part of the determination of the Fick diffusion coefficient from the experimental measurements. Figure 3 shows the volumetric correction factor which accounts for the hydrodynamic velocity (*13*). This effect is much smaller than the weight-correction factor shown in Figure 2 but is of sufficient magnitude to justify its inclusion in the evaluation of the Fick diffusion coefficient. The data of Figures 2 and 3 were employed in connection with the present experimental measurements to determine the Fick diffusion coefficient.

EXPERIMENTAL RESULTS

Measurements of the rate of solution of methane in the liquid phase of the

TABLE 3. FICK DIFFUSION COEFFICIENT FOR METHANE

Pressure, lb./sq.in. abs.	Composition methane weight fraction	Concentration methane, lb./cu. ft.	Fick diffusion coefficient, sq. ft./sec.
	40°F.		
500	0.036	1.373	6.4
1,000	0.070	2.835	5.8
1,500	0.112	4.312	5.2
2,000	0.160	5.799	4.5
2,500	0.220	7.437	3.9
3,000	0.313	9.465	3.2*
	100°F.		
500	0.028	1.110	9.7
1,000	0.060	2.313	8.8
1,500	0.095	3.527	7.8
2,000	0.136	4.788	6.8
2,500	0.188	6.212	5.9*
3,000	0.264	7.916	4.8*
3,500	0.395	9.818	3.9*
	160°F.		
500	0.025	0.950	13.9
1,000	0.052	1.945	12.3
1,500	0.083	2.974	10.7
2,000	0.121	4.098	9.2
2,500	0.168	5.301	7.8
3,000	0.238	6.686	6.4*
3,500	0.372	8.411	5.1*
	220°F.		
500	0.022	0.811	19.6
1,000	0.048	1.706	17.2
1,500	0.078	2.636	14.7
2,000	0.114	3.661	12.3
2,500	0.161	4.767	10.0*
3,000	0.238	6.078	8.0*
	280°F.		
500	0.020	0.696	26.2
1,000	0.045	1.503	22.7
1,500	0.073	2.320	19.3
2,000	0.109	3.224	16.0
2,500	0.161	4.266	12.8
	340°F.		
500	0.019	0.610	33.0
1,000	0.044	1.346	28.4
1,500	0.074	2.104	23.9
2,000	0.113	2.962	19.6*

*Values were obtained by extrapolation of experimental data at lower pressures.

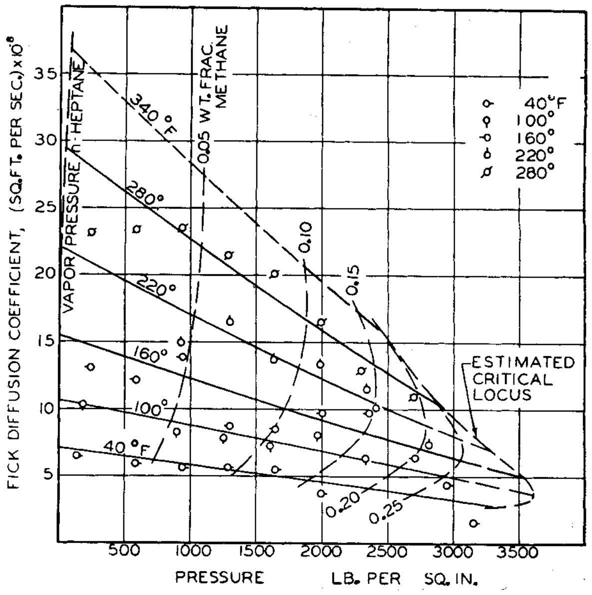

Fig. 4. Fick diffusion coefficients for methane.

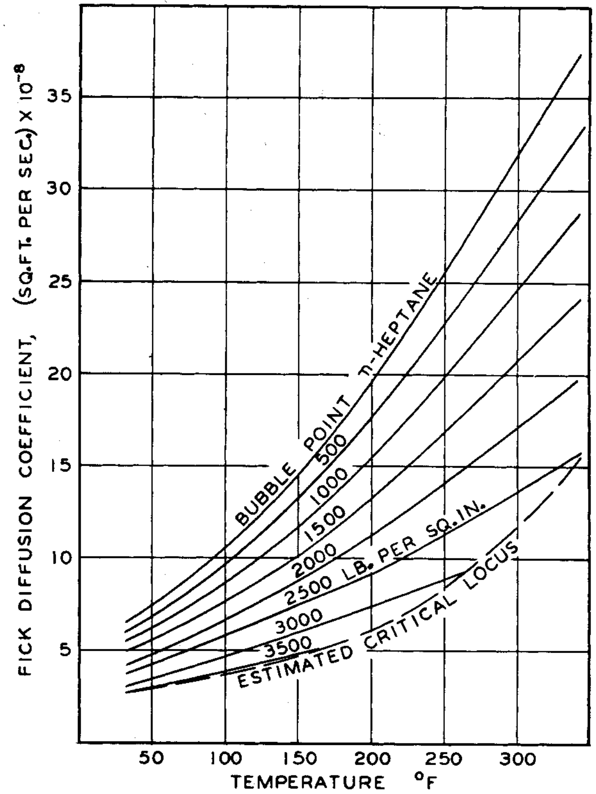

Fig. 5. Influence of temperature upon Fick diffusion coefficient for methane.

methane–*n*-heptane system were carried out at six temperatures between 40° and 340°F. in accordance with procedures already described (*13*). A sample of these experimental data constitutes Table 1 and the entire set of experimental measurements is available (*4*). The experimental results are recorded in terms of the weight of methane added per unit area of gas-liquid interface as a function of time. Table 2 records for each set of measurements the information necessary for the solution of Equation (1). In this table values of the Fick diffusion coefficient determined with and without the correction for the hydrodynamic velocity were included. Values of the standard error of estimate, also included in Table 2, were determined from the deviations of the experimentally measured weight of methane added from the straight line drawn through the data, as is shown in the example of Figure 1. The standard error of estimate was evaluated upon the assumption that all the uncertainty was associated with the weight of methane added and none with the time. The average relative percentage of deviation was 1.3.

The experimental results for the Fick diffusion coefficient with the hydrodynamic velocity taken into account are shown in Figure 4. Lines of constant composition have been included on this diagram along with the estimated locus of critical states. The latter data were obtained from available equilibrium measurements (*16*). In Figure 4 the experimental points were located at the linear average of the initial and final pressures used in each measurement. The deviation of the experimental points from the simple curves is due in a large measure to the severe requirements for accuracy

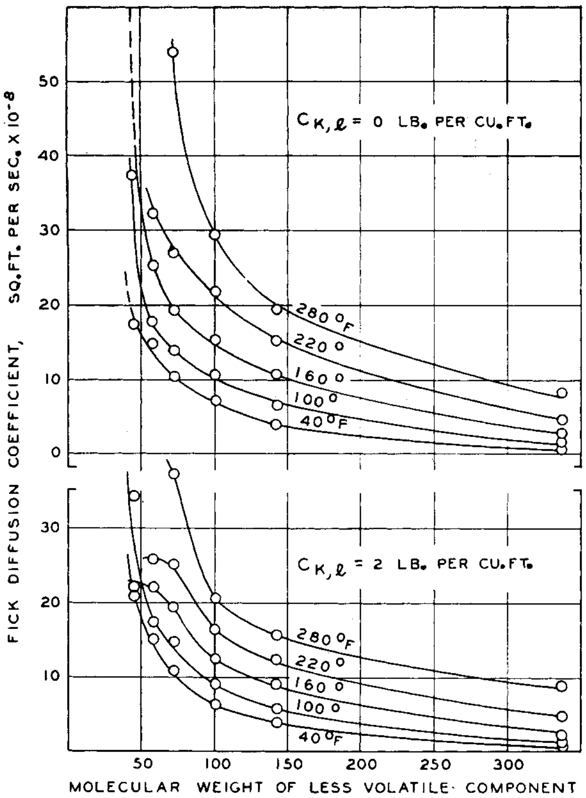

Fig. 6. Effect of molecular weight of less volatile component upon Fick diffusion coefficient for methane.

that are placed on the equilibrium data (*16*). The uncertainties in evaluating the concentrations and the partial volumes required in the solution of Equation (1) contribute a large part of the variation shown in Figure 4. The effect of temperature upon the Fick diffusion coefficient is presented in Figure 5. At the low temperatures there is only a small decrease in the coefficient with an increase in pressure. At the higher temperatures the coefficient decreases rapidly with an increase in pressure.

Smoothed values of the Fick diffusion coefficient for methane in the liquid phase of the methane–*n*-heptane system are recorded in Table 3. The concentration of methane and its weight fraction as determined for equilibrium conditions (*16*) at the indicated pressure and temperature have been included. Standard deviation of the experimental measurements shown in Figure 4 from smoothed data of Table 3 was 0.97 × 10^{-8} sq. ft./sec. This evaluation was made on the assumption that all the uncertainty existed in the Fick diffusion coefficient and none in the determination of the temperature, pressure, or concentration.

The experimental data presented in this discussion followed the same trend as was found for the Fick diffusion coefficients for methane in the liquid phase of the methane–*n*-decane (*13*) and the methane–*n*-pentane (*11*) systems. The behavior in the vicinity of the critical state is only an estimate, as it was not possible to determine experimentally the transport characteristics near this state by the methods exmployed here.

The effect of the molecular weight of the less volatile component upon the Fick diffusion coefficient of methane at a pressure of 2,000 lb./sq. in. is shown in Figure 6. The data include information for the methane–*n*-pentane (*11*), methane–*n*-decane (*13*), and methane–white-oil (*12*) systems. It is seen that there is a marked change in the Fick diffusion coefficient with the molecular weight of the less volatile component.

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NOTATION

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

Superscript

$*$ = average condition

Subscripts

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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