Diffusion Coefficients in Hydrocarbon Systems

Methane in the Liquid Phase of the Methane-Cyclohexane System

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Molecular transport studies of the lighter paraffins in hydrocarbon mixtures were initiated by Pomeroy (*11*) and Lacey (*2,5,6,8*). These data have recently been supplemented by investigations of several binary paraffin hydrocarbon systems at elevated pressures (*12–16,18*). These studies indicate a rather systematic variation in the molecular transport characteristics of methane with an increase in molecular weight of the less volatile component. Furthermore, the Fick diffusion coefficient is markedly influenced by temperature and pressure, particularly near the critical state of the binary system in question.

It is beyond the scope of this article to consider the molecular transport investigations which have been made upon other substances. The studies of Tung and Drickamer (*25,26*) are offered as examples; Kirkwood (*7*) discussed some of the concepts associated with molecular transport, and Opfell (*10*) considered a number of relationships involved in the application of molecular diffusion coefficients to transport processes of industrial interest. Resistances at the interface (*24*) are probably not important for the pressure range of this investigation. Experimental studies at elevated pressures substantiate this conclusion (*23*). A short review of the background literature concerning this field (*14*), and an extensive bibliography (*4*) are available.

No data on the molecular transport of the paraffin hydrocarbons in the liquid phase of binary systems containing a cyclic compound were available, so methane in the liquid phase of the methane-cyclohexane system was investigated at pressures up to within 500 p.s.i. of the critical states of the system for the temperature interval between 100° and 280° F.

METHODS AND APPARATUS

A transient method involving the introduction of methane into an isochoric chamber containing a heterogeneous mixture of methane and cyclohexane was the basis for this study. The mixture of methane and cyclohexane was brought to physical equilibrium by mechanical agitation. The pressure was then raised a predetermined amount, and the quantity of methane required to maintain the system at this constant higher pressure was determined as a function of time.

A detailed description of the equipment is available (*14*). Some revisions were made, particularly in the control of pressure. The isochoric vessel contained many vertical tubes to decrease the influence of local accelerations upon the molecular transport phenomenon. This arrangement is shown schematically in Figure 1 as vessel *A*. The temperature of *A* was controlled by means of an agitated bath and was determined with a strain-free platinum resistance thermometer (*9*) which had been compared to a similar instrument calibrated by the National Bureau of Standards. The temperature of the isochoric vessel was known relative to the international platinum scale within 0.02° F. Variation in local temperature with time during the course of a single measurement was less than 0.005° F.

The 21 vertical tubes in the isochoric vessel were 0.374 inch in diameter and materially decreased the influence of local vibration and convection upon the molecular transport. The quantity of cyclohexane put in the apparatus was determined by weighing bomb techniques (*22*). This quantity was adjusted so that, as the volume in the liquid phase increased, the gas-liquid interface was always below the top of the vertical stainless steel tubes. The surface tension results in somewhat larger interfacial areas of contact between the gas and liquid than the net free area within and between the tubes. However, because the liquid phase near the surface rapidly comes to equilibrium with the gas phase, this increased interfacial area of contact exerts no influence upon the molecular transport process which controls the migration of methane into the liquid phase.

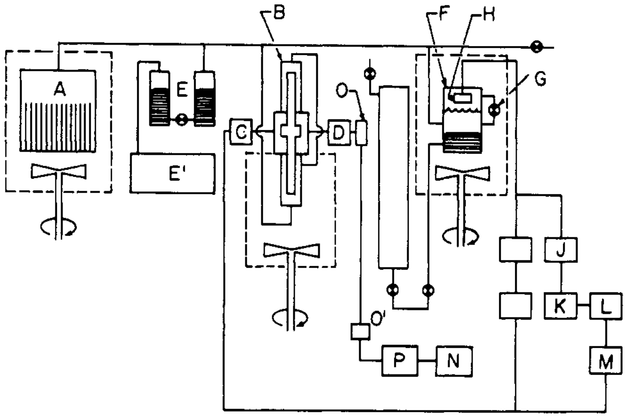

Figure 1. Schematic diagram of apparatus

The injector shown at *B* in Figure 1 is driven by a direct-current motor, *C*, through a worm-and-pinion combination (*14*). A counter, at *D*, permitted the position of the injector plunger to be determined with an uncertainty of approximately 10^{-4} inch. Discussion of the details of the injector, including pressure compensation for the packing and stress compensation for the instrument is available (*14*). The connection to the system which was used for pressure measurement was made through the mercury U-tube, *E*, in Figure 1. The left-hand limb of the U-tube connected to a pressure balance, *E'*, and was filled with oil. It is believed that the pressure relative to the vapor pressure of carbon dioxide at the ice point (*3*) was known within 0.1 p.s.i., or 0.05%, whichever was the larger measure of uncertainty.

The system must be maintained at very nearly isobaric conditions during the diffusion measurements. Otherwise, large uncertainties are introduced in the measurement of the diffusion rate. To improve the precision of such measurements, a manostat, at *F* in Figure 1, was used. The manostat consisted of a two-part vessel separated by a slack diaphragm; its position was determined within approximately 10^{-5} inch by a reluctance gage. The slack diaphragm was pressure-compensated so that only minor changes in the zero position were encountered upon change in pressure from atmospheric to 5000 p.s.i. The precision of this device was somewhat better than 10^{-3} p.s.i. The manostat was located in an agitated liquid bath in which the temperature variations with time were less than 0.002° F. After the pressure in the system was increased, and while some thermal effects were still recognizable within vessel *A*, valve *G* connecting the two parts of the manostat was closed. The output of the reluctance gage, *H*, passed through the amplifier, *J*, and the galvanometer, *K*, which was optically coupled through the photoelectric cell, *L*, to the modulating circuit, *M* (*19*). Response time of the various units in this feed-back circuit was such that variations in pressure during the course of a diffusion measurement were never more than 0.005 p.s.i. This represented perhaps one hundredth of the variation in pressure found with the manual control previously used (*14*). The position of the counter, *D*, was transmitted to a printer, *N*, through two self-synchronous repeaters, *O* and *O′* and a digitizer, *P*.

Methods of analysis similar to those of earlier studies (*12*–14) were used. The Fick diffusion coefficient was established from the experimental data by the following expression:

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

Asterisks in Equation 1 indicate average values of the quantity over the range of compositions encountered in the liquid phase during a particular measurement. Equation 1 takes into account the effect of hydrodynamic velocity (*14*) and the change in volume of the liquid phase, but does not include any effect of a resistance at the interface, which is not of sufficient magnitude to justify its consideration. Local equilibrium (*7*) was assumed—that is, the physical properties of the fluid at any point are those found at equilibrium. Recent data upon the volumetric behavior of the methane-cyclohexane system (*20*) and partial volumetric behavior of methane and cyclohexane in that system (*1*) were employed to determine the requisite partial volumetric and phase behavior.

The value of the first bracketed term of Equation 1, designated as the volumetric correction factor and concerned with the correction for the hydrodynamic velocity, is shown in Figure 2. Correspondingly, Figure 3 depicts the weight correction factor, which takes into account the difference between the weight of methane introduced into the isochoric chamber, *A*, of Figure 1 and that passing the interface of the heterogeneous system. The weight correction factor in this instance was small compared to that found for the methane-propane system (*18*) in which values as large as 3 were encountered and for which small uncertainties in this quantity were the primary source of error in the final values of the diffusion coefficient.

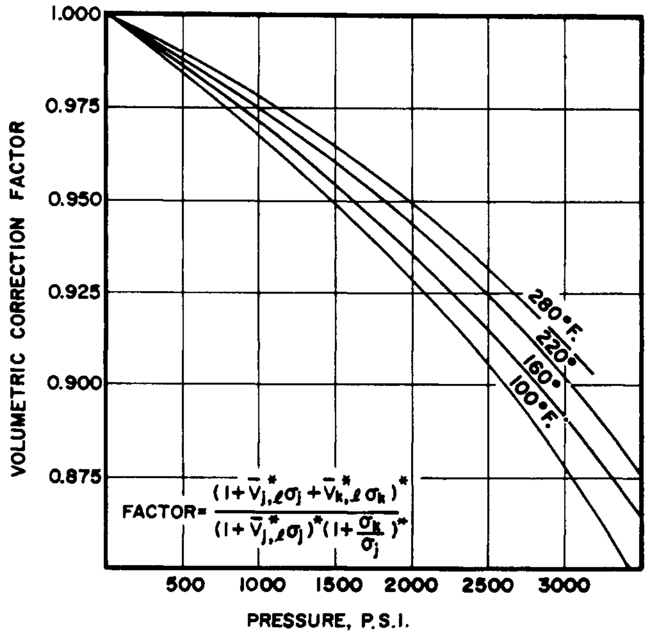

Figure 2. Volumetric correction factor for methane-cyclohexane system

MATERIALS

The cyclohexane was research grade from the Phillips Petroleum Co. and was reported to contain 0.0002 mole fraction of impurities. This material was dried and condensed under low pressure at the temperature of liquid nitrogen in order to remove noncondensable gases, and was then stored in a stainless steel container (*22*). Cyclohexane was introduced into the apparatus by distillation techniques.

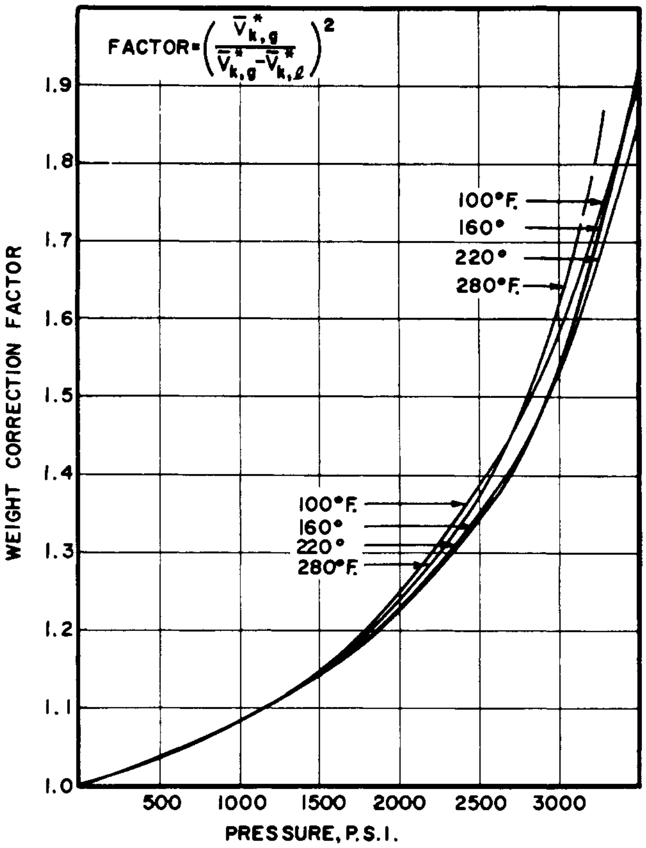

Figure 3. Weight correction factor for methane-cyclohexane system

A sample of the cyclohexane employed showed a value of 1.4238 for the index of refraction at 77° F. relative to the D-lines of sodium as compared to a value of 1.42354 reported by Rossini (*21*) for an air-saturated sample at the same temperature. The specific weight of the sample of deaerated cyclohexane at atmospheric pressure at 77° F. was 48.302 pounds per cubic foot compared to 48.311 pounds for air-saturated material at the same temperature reported by Rossini (*21*).

The freezing point of the cyclohexane in air at atmospheric pressure was 45.45° F. compared to a critically chosen value of 43.80° F. (*21*). The above information indicates that the sample of cyclohexane probably contained less than 0.003 mole fraction of material other than cyclohexane. The variation in freezing point indicates the presence of some impurities. As in a study of the volumetric behavior of cyclohexane (*17*), the purity of the sample as determined from mass spectrographic analysis was higher than would be expected considering the variation of freezing point from accepted values (*21*).

The methane was obtained from a producing well in the San Joaquin Valley of California and contained approximately 0.003 mole fraction carbon dioxide and traces of heavier hydrocarbons. It was in equilibrium with an aqueous phase at pressures of the order of 800 p.s.i. The gas was dried by passage over calcium chloride and anhydrous calcium sulfate; contact with activated charcoal and alumina removed the heavier hydrocarbons, and the carbon dioxide was absorbed by potassium hydroxide and Ascarite. These purification operations were carried out at pressures in excess of 500 p.s.i. The purified gas did not contain more than 0.001 mole fraction of material other than methane according to spectrographic analysis.

EXPERIMENTAL RESULTS

In Figure 4, the weight of methane added to the isochoric vessel is depicted as a function of time. Each point indicates a measurement of the position of the injector as a function of time. Only the change in the weight of methane per unit of square root time is important; therefore, the investigation at square root times less than 60 was omitted from the figure. The details of this typical series of experimental measurements are shown in Table I. The values in the second and fourth columns were obtained from digital recording equipment which permits values of the position of the counter, *D*, of Figure 1 to be recorded at stipulated time intervals. As expected, the quantity of methane was nearly a linear function of the square root of time over a substantial part of the total interval while diffusion was in progress. It is impossible to apply the simple methods of analysis of Equation 1 (*11,14*) when the quantity of diffusing component which has crossed the interface exceeds approximately half of that required for physical equilibrium.

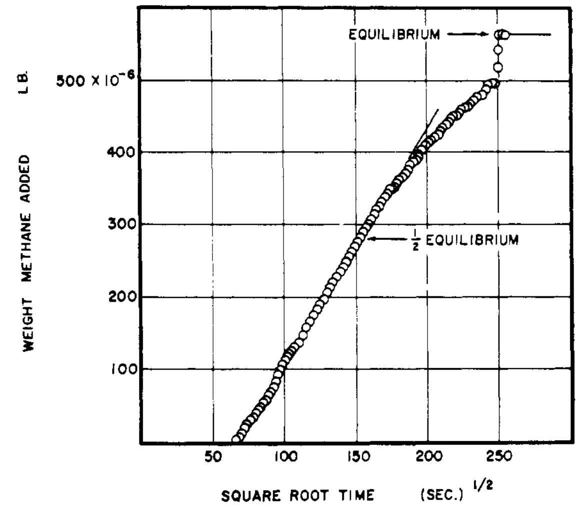

Figure 4. Typical experimental measurements at 220° F.

Table II summarizes the experimental results, including the initial and final pressures, equilibrium compositions and concentrations, and average values of the rate of change in the weight of methane squared with respect to time. The corresponding experimental standard error of estimate is included. This standard error is based upon the assumption that all of the uncertainty lies in the weight of methane involved and there are no errors in the associated variations in temperature and pressure. The corresponding volumetric correction factor has been included. The weight correction factor was used in evaluating the slope indicated in Table II. Values of the Fick diffusion coefficient uncorrected for the hydrodynamic velocity and those evaluated after correction for the hydrodynamic velocities are presented.

Utilizing this information, values of the Fick diffusion co-

Table I. Sample of Experimental Measurements

Pressure, P.S.I.A.	439.9[a]	740.5[b]
Weight Fraction Methane	0.015[a]	0.027[b]

Time, Sec.	Weight of Methane Added, Lb.[c]	Time, Sec.	Weight of Methane Added, Lb.[c]
0	. . .		
4,344	. . .	31,900	355.65 x 10^{-6}
4,420	1.735 x 10^{-6}	32,500	362.59
4,540	1.735	33,100	366.06
4,660	5.205	33,700	366.06
4,780	8.674	34,300	373.00
4,900	12.144	34,900	376.47
5,200	19.084	35,500	383.41
5,500	29.493	36,100	386.88
5,800	29.493	36,700	390.35
6,100	32.963	36,730	393.82
6,400	39.902	37,901	397.29
6,700	43.372	38,501	404.23
7,000	46.842	39,100	404.23
7,300	53.781	39,701	411.17
7,600	57.251	40,300	414.64
7,900	64.190	40,901	418.10
8,200	67.66	41,500	418.10
8,500	74.599	42,100	421.57
8,800	81.539	42,701	425.04
9,100	91.948	43,301	431.98
9,400	98.888	43,900	431.98
9,700	105.83	44,500	435.45
10,000	112.77	45,100	435.45
10,300	116.24	45,701	438.92
10,600	119.71	46,301	442.39
10,900	123.18	46,900	445.86
11,500	130.12	47,500	449.33
12,100	137.06	48,101	449.33
12,700	147.46	48,701	452.80
13,300	157.87	49,300	456.27
13,900	164.81	49,900	456.27
14,500	175.22	50,501	459.74
15,100	182.16	51,101	463.21
15,700	189.10	51,700	463.21
16,300	196.04	52,300	463.21
16,900	206.45	52,901	466.68
17,500	213.39	53,501	466.68
18,100	220.33	54,100	473.62
18,700	227.27	54,701	473.62
19,300	234.21	55,301	477.09
19,900	241.15	55,900	480.56
20,500	248.09	56,500	480.56
21,100	255.03	57,101	480.56
21,700	261.97	57,700	484.03
22,300	268.91	58,301	487.50
22,900	275.85	58,901	494.44
23,500	282.78	59,500	494.44
24,100	289.72	60,100	494.44
24,700	296.66	60,700	494.44
25,300	300.13	61,300	494.44
25,900	307.07	61,901	494.44
26,500	314.01	62,321	518.73
27,100	320.95	62,620	543.02
27,700	324.42	62,920	563.83
28,300	331.36	63,219	563.83
28,900	338.30	63,519	563.83
29,500	341.77	63,819	563.83
30,100	348.71	64,119	563.83
30,700	348.71	64,419	563.83
31,300	352.18	64,720	563.83

[a] Initial equilibrium pressure and composition.
[b] Constant operating pressure and associated composition at interface during diffusion.
[c] Weight added to heterogeneous, isochoric system.

Table II. Summary of Experimental Results

Pressure, P.S.I.A.		Methane in Liquid Phase: Comp. Wt. Fraction		Methane in Liquid Phase: Conc. Lb./Cu.Ft.		$\frac{(\Delta m_k)^{2}}{\theta}$[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
						100° F.				
80.5	391.7	0.004	0.017	0.144	0.758	9.408×10^{-12}	9.41×10^{-6}	0.9923	5.368×10^{-8}	5.327×10^{-8}
391.7	683.0	0.017	0.030	0.758	1.345	10.084	2.07	0.9829	6.437	6.327
682.3	983.7	0.030	0.044	1.345	1.969	10.884	1.75	0.9730	6.296	6.126
983.4	1285.0	0.044	0.060	1.969	2.595	9.240	1.93	0.9619	5.481	5.272
3092.4	3541.5	0.190	0.243	6.922	8.190	31.626	5.30	0.8590	7.363	6.325
						160° F.				
134.0	435.1	0.004	0.016	0.209	0.727	9.530×10^{-12}	1.11×10^{-6}	0.9918	7.670×10^{-8}	7.607×10^{-8}
1037.5	1338.7	0.042	0.057	1.800	2.365	12.123	1.58	0.9653	8.836	8.530
1339.1	1640.2	0.057	0.072	2.365	2.952	11.610	1.49	0.9554	8.117	7.755
1643.1	2144.9	0.073	0.102	2.957	3.970	31.851	3.42	0.9408	7.894	7.427
2144.8	2646.6	0.102	0.138	3.970	5.077	38.186	2.84	0.9204	8.661	7.972
2646.6	3148.8	0.138	0.183	5.077	6.322	40.111	3.90	0.8967	8.106	7.268
						220° F.				
141.0	441.2	0.004	0.015	0.168	0.641	11.172×10^{-12}	2.96×10^{-6}	0.9922	10.794×10^{-8}	10.710×10^{-8}
439.9	740.5	0.015	0.027	0.639	1.138	10.622	1.20	0.9838	9.537	9.383
2040.8	2532.1	0.091	0.123	3.376	4.337	33.459	15.74	0.9318	9.811	9.142
						280° F.				
147.4	450.0	0.003	0.014	0.116	0.560	15.384×10^{-12}	2.22×10^{-6}	0.9934	16.871×10^{-8}	16.760×10^{-8}
450.0	750.6	0.014	0.026	0.560	1.002	15.282	2.09	0.9876	17.286	17.071
751.4	1154.3	0.026	0.042	1.005	1.617	26.014	4.36	0.9782	15.851	15.505
2057.6	2554.4	0.089	0.123	3.098	3.978	36.309	31.41	0.9379	12.980	12.174
2552.1	3052.3	0.123	0.175	3.974	5.018	42.973	27.31	0.9194	12.560	11.548

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

efficient were smoothed with respect to pressure and temperature. Temperature and weight fraction methane in the liquid phase were chosen as parameters. The standard error of estimate arising from the smoothing operation with respect to both pressure and temperature was 0.4×10^{-8} square foot per second. This involves a relative uncertainty of approximately 5% based upon the median value of the coefficient. The influence of pressure and temperature upon this coefficient is shown in Figures 5 and 6, respectively. Limiting values estimated for the behavior at bubble point of cyclohexane and at the critical state of the system are included. The values near the critical state of the system are entirely estimates. Values of the Fick diffusion coefficient for methane in the methane-cyclohexane system are recorded in Table III.

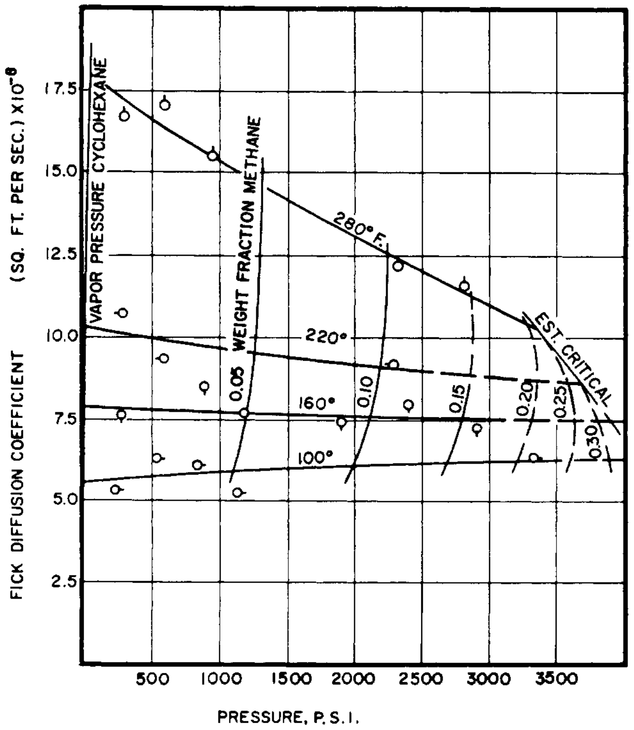

Figure 5. Effect of pressure upon Fick diffusion coefficient for methane

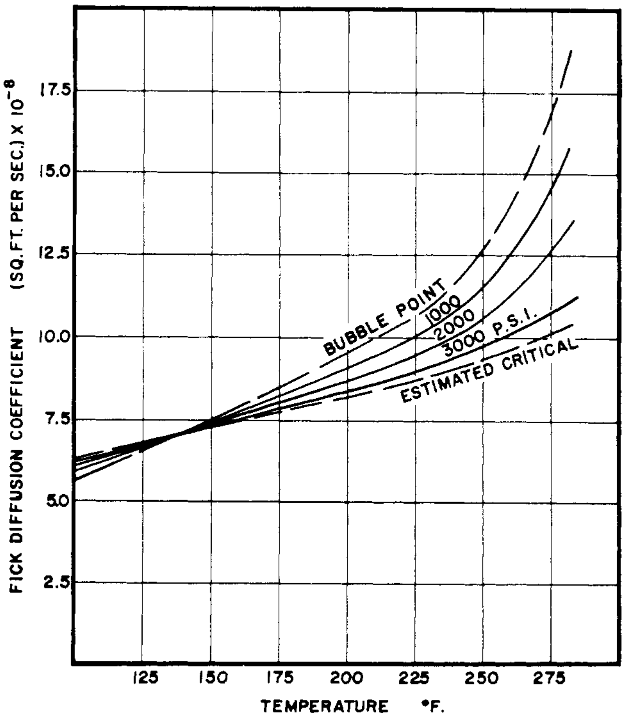

Figure 6. Influence of temperature upon Fick diffusion coefficient for methane

Table III. Fick Diffusion Coefficient for Methane

Pressure, P.S.I.A.	Methane in Liquid Phase: Comp., wt. fraction	Methane in Liquid Phase: Conc., lb./cu.ft.	Fick Diffusion Coefficient, sq.ft./sec.
	100° F.		
500	0.021	0.977	5.77×10^{-8}
1000	0.045	2.003	5.89
1500	0.071	3.067	5.98
2000	0.102	4.189	6.03
2500	0.137	5.371	6.11
3000	0.181	6.679	6.18
3500	0.237	8.060	6.22[a]
	160° F.		
500	0.019	0.846	7.19×10^{-8}
1000	0.040	1.732	7.74
1500	0.065	2.674	7.68
2000	0.093	3.679	7.63
2500	0.127	4.746	7.57
3000	0.168	5.944	7.51[a]
3500	0.228	7.264	7.45[a]
	220° F.		
500	0.018	0.734	9.97×10^{-8}
1000	0.038	1.538	9.68
1500	0.061	2.392	9.40
2000	0.088	3.307	9.18
2500	0.121	4.277	8.97[a]
3000	0.164	5.367	8.79[a]
3500	0.229	6.597	8.66[a]
	280° F.		
500	0.016	0.633	16.67×10^{-8}
1000	0.036	1.377	15.38
1500	0.059	2.169	14.20
2000	0.086	3.004	13.08
2500	0.118	3.877	11.99
3000	0.168	4.899	10.95[a]

[a] Extrapolated from data at lower pressures.

Figure 7 shows the comparative influence of temperature upon the Fick diffusion coefficient for methane in the liquid phase of the methane-cyclohexane system and that in the methane-*n*-heptane system. The information for the latter system was interpolated from results already available (*15*). In Figure 7, pressures of 500 and 1000 p.s.i. are the parameters.

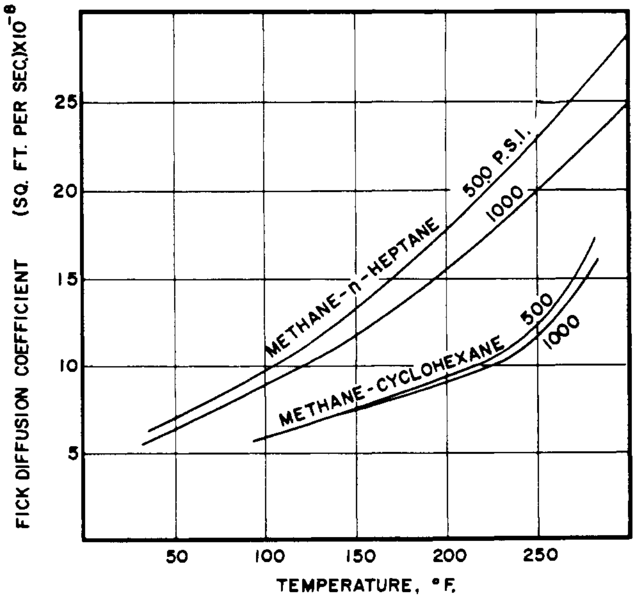

Figure 7. Comparison of Fick diffusion coefficients for methane

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.
$\underline{m}_k$ = total weight of component k crossing the interface, lb.
$\bar{V}_k$ = 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

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
o = initial conditions

ACKNOWLEDGMENT

This work constitutes a contribution from Project 37 of the American Petroleum Institute at the California Institute of Technology. The methane and its analysis were supplied through the courtesy of The Texas Co. Virginia Berry accomplished the calculations associated with the reduction of the experimental data, and B. Lawson Miller assisted in the preparation of the manuscript. W. N. Lacey contributed materially by his review of the manuscript and interest in the research program.

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Received for review February 12, 1959. Accepted February 27, 1959.