Diffusion Coefficients of Ethane in the Liquid Phase of The Ethane–White Oil System

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INVESTIGATION of the molecular transport of the lighter paraffins in the liquid phase of hydrocarbon mixtures was initiated by Lacey in collaboration with Pomeroy, Scudder, Stapp, Hill, and Bertram (*1, 3, 4, 7*), with primary emphasis upon the transport of methane. These early studies have been supplemented by further investigations over a wider range of pressures and temperatures. The data indicate a systematic but large variation in the Fick diffusion coefficient of methane with variations in the concentration and molecular weight of the less volatile component.

The extensive background of molecular transport investigations of substances other than hydrocarbons has not been reviewed. The resistance to diffusion at the interface (*15*) between gas and liquid phases is not important for the range of pressures involved in this investigation.

As a result of the marked variation in the Fick diffusion coefficient for methane with the nature of less volatile component in binary systems, the molecular transport of ethane in the liquid phase of the ethane–white oil system was studied at pressures up to 1000 p.s.i. in the temperature interval between 40° and 400° F.

METHODS AND EQUIPMENT

The experimental approach involved the introduction of ethane into an isochoric chamber which contained a heterogeneous mixture of ethane and white oil. Initially, the mixture was brought to physical equilibrium by mechanical agitation. The pressure was then raised a predetermined amount by addition of ethane, and the quantity of ethane required to maintain the system at a higher pressure under isobaric conditions was determined as a function of time.

Some revisions of the original equipment (*8*) were made, including introduction of a number of vertical tubes within the isochoric vessel (*11*), to decrease the influence of local accelerations upon the molecular transport.

The temperature was determined by a strain-free, platinum resistance thermometer (*6*), recently compared to the indications of 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. Change in local temperature with time during a single measurement was less than 0.003° F.

The quantity of white oil introduced into the apparatus was determined gravimetrically. The volume of the liquid phase was adjusted so that the gas-liquid interface was always below the top of the vertical stainless steel tubes. The surface tension resulted in somewhat larger interfacial areas of contact between the gas and liquid phases than the net free cross-sectional area between and within the tubes. The composition of the fluid adjacent to the meniscus near the tube walls was nearly constant. As a result, increase in interfacial area had no influence on the molecular transport process associated with the migration of ethane into the liquid phase.

The quantity of ethane introduced was determined by an automatically controlled injector (*8*) driven by a direct current motor at such a rate as to maintain isobaric conditions within the isochoric vessel, and was known within 0.2%. The indications of the injector were recorded automatically in a digital fashion as a function of time (*11*).

The pressure within the isochoric vessel was measured by

Earlier publications from these laboratories on liquid diffusion are "Relations in Material Transport," Opfell and Sage, *Ind. Eng. Chem.* **47**, 918 (1955) and a series of articles, "Diffusion Coefficients in Hydrocarbon Systems," Reamer, Sage, and coworkers, *Ind. Eng. Chem.* **48**, 275, 282, 285 (1956); *A.I.Ch.E. Journal* **3**, 449 (1957); *Ind. Eng. Chem., Chem. Eng. Data Ser.* **1**, 71 (1956); **3**, 54 (1958); *J. Chem. Eng. Data* **4**, 15, 296 (1959).

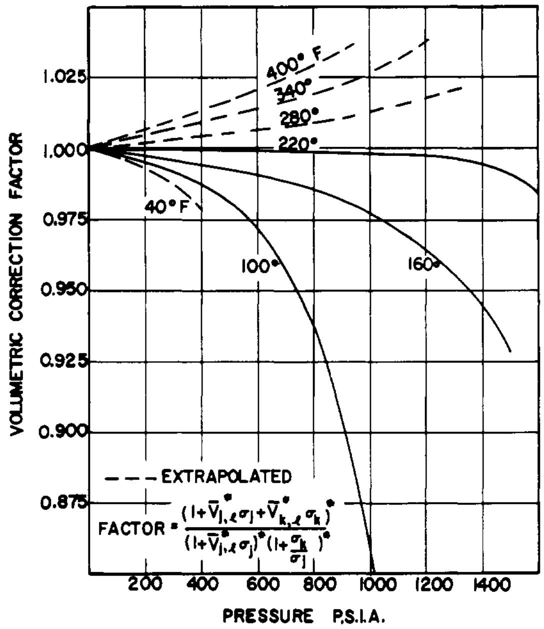

Figure 1. Volumetric correction factor in ethane–white oil system

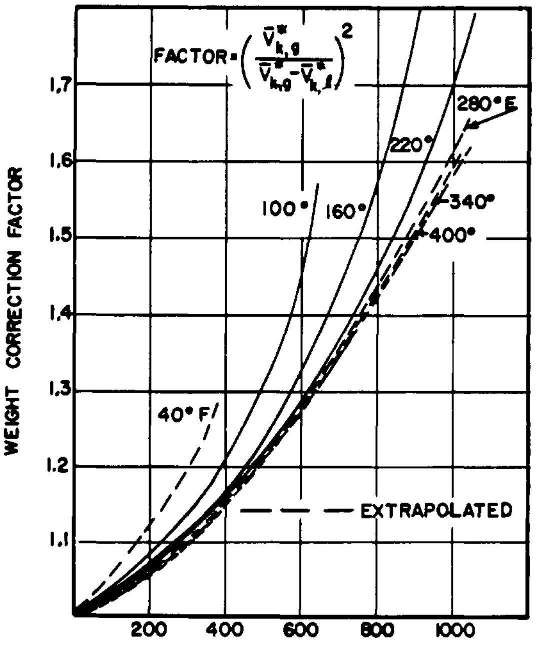

Figure 2. Weight correction factor in ethane–white oil system

a pressure balance calibrated against the vapor pressure of carbon dioxide at the ice point (*2*), and was known within 0.1 p.s.i. or 0.05%, whichever was the larger measure of uncertainty.

To improve the precision with which isobaric conditions were maintained during the diffusion process, a manostat (*12*) was employed. The slack diaphragm in the manostat was balanced against helium maintained in an isochoric, isothermal chamber. The precision of the manostat was somewhat better than 10^{-3} p.s.i. After the pressure in the diffusion vessel had been raised by the introduction of ethane, and while some thermal gradients were still recognizable within the diffusion vessel, the manostat was attached to the system, and the output of the reluctance transducer used in connection with the slack diaphragm was employed to control the direct current motor driving the injector. This procedure permitted automatic maintenance of isobaric conditions with precision throughout the diffusion process. It is estimated that the variations in pressure during a diffusion measurement were not more than 0.005 p.s.i. The use of this manostat reduced the variations in pressure encountered in earlier diffusion operations (*8*) by a factor of at least 100.

Methods of anlysis used in earlier studies (*8*) were followed. The Fick diffusion coefficient was established from the experimental data by application of the following expression:

$$D^{*}_{F,k} = \left[\frac{(1 + \overline{V}^{*}_{j,l}\sigma_j + \overline{V}^{*}_{k,l}\sigma_k)^{*}}{(1 + \overline{V}^{*}_{j,l}\sigma_j)^{*}(1 + \sigma_k/\sigma_j)^{*}}\right] \left[\frac{\pi m_k^2}{4\theta(\sigma_{k,i,e} - \sigma_{k,0})^2}\right]\left[\frac{\overline{V}^{*}_{k,g}}{\overline{V}^{*}_{k,g} - \overline{V}^{*}_{k,l}}\right]^2 \tag{1}$$

where the asterisks indicate average values of the quantity in question over the range of compositions encountered in the liquid phase during a particular set of measurements. The foregoing relationship takes into account the effect of hydrodynamic velocity (*8*) and the change in volume of the liquid phase, but not resistance at the interface. It was assumed that local equilibrium (*5*) existed.

Experimental information (*13, 14*) was used to predict values of the partial volume of ethane and of white oil in the liquid phase of the ethane–white oil system. The value of the first bracketed term of Equation 1, which is concerned with the correction for the hydrodynamic velocity, is shown in Figure 1. This term has been called the "volumetric correction factor." The data were extrapolated to some of the states because of the small magnitude of the correction. Figure 2 depicts the weight correction factor, which takes into account the difference between the weight of ethane introduced into the isochoric vessel and that passing the interface of the heterogeneous system. The change in volume of the liquid phase is of primary concern in this connection.

MATERIALS

The physical properties of the white oil, which has been used in other investigations (*13, 14*), are reported in Table I. It was de-aerated and used without further purification. The naphthenic-base hydrocarbon is essentially nonvolatile and nearly colorless, and has been employed as an approximate representative of the heavier hydrocarbons encountered in practice.

The ethane was of research grade from the Phillips Petroleum Co. and was reported to contain less than 0.0006 mole fraction of impurities; this was confirmed by mass spectrographic analysis. The sample was introduced into the injector and other parts of the apparatus by conventional high vacuum techniques.

EXPERIMENTAL RESULTS

A typical set of experimental results for one set of conditions is shown in Figure 3. The initial pressure was 348.6 p.s.i. and the final pressure was 453.4 p.s.i. The isochoric vessel was maintained at 220° F. Each experimental point indicates the reading of the counter on the injector as a function of time. This sample of experimental results, recorded in Table II, indicates the extent of experimental measurements obtained for each experimental point. The relatively even values of time result from the automatic digital recording equipment, which permits reading of the counter at any predetermined time interval. Data obtained at values of the square root of time less than 44 have been omitted, because the thermal gradients existing in the liquid phase as a result of the rapid rise in pressure make the data of little consequence. It is clear from Figure 3 that the quantity of ethane added was nearly a linear function of the square root of time over a substantial part of the total interval. Because of the assumptions made in the derivation of Equation 1, a systematic deviation from linearity is to be

Table I. Some Properties of White Oil

Sample Oil Before Aniline Extn. (1671) Extract	Aniline, Vol. %	Temp. of Extn., ° F.	Recovery, Vol. %	Gravity, °API at 60° F.	Refractive Index[a]	Viscosity, Saybolt Universal Sec. at 210° F.	Viscosity Gravity Constant, VGC
...	...	...	...	31.1	1.4743	37.35	0.825
1	120	115	3.35	26.7	1.4847	38.5	0.853
2	100	115	2.69	27.2	1.4823	38.2	0.850
3	100	116	2.79	27.1	1.4825	38.4	0.852
4	100	116	2.38	27.2	1.4821	38.4	0.850
5	100	146	4.92	28.1	1.4801	38.2	0.844
6	100	145	4.58	28.4	1.4800	38.2	0.843
7	100	147	4.87	28.6	1.4788	38.2	0.841
8	75	170	5.60	29.3	1.4775	38.4	0.834
9	75	171	5.75	29.6	1.4769	38.3	0.832
10	75	170	6.55	29.9	1.4763	38.1	0.831
11	75	199	13.16	31.1	1.4742	38.0	0.824
12	75	200	13.08	31.3	1.4735	38.0	0.822
13	75	200	12.68	31.8	1.4721	37.9	0.818
14	75	200	10.81	32.9	1.4704	38.4	0.810
		(by difference)	6.79				
Raffinate	...	(recovered)	5.09	34.0	1.4677	38.9	0.800

[a] Relative to *D* lines of sodium at 68° F.

Table II. Sample of Experimental Measurements

Pressure, p.s.i.a.	348.6[a]	453.4[b]
Weight fraction ethane	0.034[a]	0.046[b]
Temp. 220° F.		

Time, Sec., θ	Ethane Added[c], Lb.	Time, Sec., θ	Ethane Added[c], Lb.
0	...		
2,000	48.766×10^{-6}	25,400	337.384×10^{-6}
2,400	59.714	26,000	343.853
2,800	71.159	27,800	344.848
3,200	76.633	28,400	349.327
3,800	90.068	29,000	349.824
4,400	100.518	31,400	366.246
5,000	113.456	33,200	375.700
5,600	121.418	33,800	379.682
6,200	136.347	34,400	386.150
6,800	145.304	35,000	389.634
7,400	155.256	35,600	394.112
8,000	165.208	36,200	395.108
8,600	170.185	36,800	401.079
9,400	178.644	37,400	403.567
9,800	186.606	38,000	409.041
10,400	194.070	38,600	411.031
11,000	197.056	39,200	416.505
11,600	202.530	39,800	418.993
12,200	212.482	40,400	422.974
12,800	214.970	41,000	426.955
13,400	219.449	41,600	431.891
14,000	230.396	42,200	433.383
14,600	235.870	42,800	437.862
15,200	241.344	43,400	440.349
16,400	251.794	44,000	443.832
17,000	259.258	44,600	443.832
17,600	269.210	45,200	447.315
18,200	278.168	45,800	820.990
18,800	289.613	46,400	841.391
20,600	293.594	47,000	842.883
22,400	311.508	47,600	845.371
23,600	320.963	48,200	845.371
24,200	329.422	48,800	845.371
24,800	332.906	49,400	845.371

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

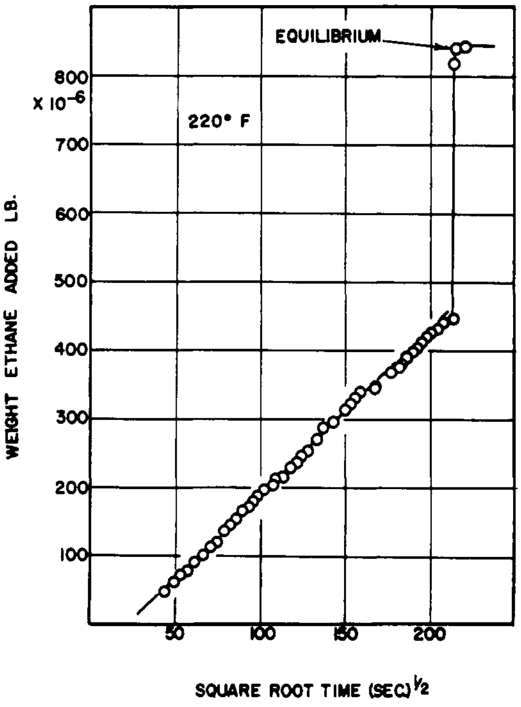

Figure 3. Typical experimental results used in evaluating Fick diffusion coefficient

expected when the quantity of ethane which has crossed the interface is in excess of 50% of the equilibrium value. Only the data in the linear part of the curve were used in evaluating the diffusion coefficient. Typical information is shown in Table II and Figure 3.

Experimental measurements are summarized in Table III. The reported standard error of estimate for the weight

Table III. Summary of Experimental Results

Pressure, P.S.I.A.		Ethane Compn., Weight Fraction		Ethane Concn., Lb./Cu. Ft.		$\frac{(\Delta \underline{m}_k)^2}{\theta}$, Lb.²/Sec.[a]	Standard Error of Estimate, Lb.	Volumetric Correction Factor	Fick Diffusion Coefficient, Sq. Ft./Sec.	
Initial	Final	Initial	Final	Initial	Final				Uncorrected	Corrected
						40° F.				
66.3	80.4	0.016	0.022	1.04	1.27	0.283×10^{-12}	12.27×10^{-6}	0.998	1.164×10^{-8}	1.162×10^{-8}
94.6	112.3	0.028	0.034	1.54	1.90	0.544	7.47	0.997	0.947	0.944
147.3	172.2	0.053	0.068	2.60	3.22	2.007	5.22	0.995	1.215	1.209
201.0	234.9	0.086	0.112	4.03	5.13	9.728	3.18	0.992	1.943	1.928
254.0	279.7	0.130	0.158	5.87	6.83	13.026	3.03	0.989	3.519	3.480
						100° F.				
99.5	122.8	0.014	0.019	0.96	1.20	0.624×10^{-12}	2.83×10^{-6}	0.997	2.407×10^{-8}	2.399×10^{-8}
194.6	218.4	0.038	0.044	2.02	2.34	1.007	6.03	0.995	2.274	2.263
307.0	330.0	0.072	0.079	3.61	3.98	1.449	5.63	0.991	2.597	2.574
418.5	451.2	0.109	0.121	5.40	5.94	3.827	10.53	0.985	5.696	5.610
562.2	596.5	0.167	0.182	7.90	8.53	9.501	73.95	0.973	7.243	7.047
						220° F.				
101.2	142.6	0.008	0.012	0.48	0.70	0.468×10^{-12}	2.04×10^{-6}	1.000	2.137×10^{-8}	2.137×10^{-8}
348.0	453.4	0.034	0.046	1.73	2.25	5.665	5.17	1.000	5.166	5.166
701.4	802.4	0.074	0.086	3.53	4.07	10.74[b]	23.52	0.999	11.074	11.063
1016.0	1113.4	0.113	0.126	5.29	5.85	9.6[b]	14.30	0.998	11.822	11.799
						280° F.				
228.6	288.7	0.018	0.022	0.92	1.15	1.436×10^{-12}	2.42×10^{-6}	1.003	6.263×10^{-8}	6.282×10^{-8}
						340° F.				
208.8	264.0	0.014	0.017	0.71	0.88	0.755×10^{-12}	1.046×10^{-6}	1.006	5.945×10^{-8}	5.981×10^{-8}
493.5	600.0	0.032	0.039	1.60	1.95	6.570	4.292	1.013	14.188	14.372
						400° F.				
249.8	319.0	0.014	0.018	0.72	0.94	1.446×10^{-12}	1.144×10^{-6}	1.010	6.940×10^{-8}	7.010×10^{-8}

[a] Effective cross sectional area = 0.019187 sq. ft.

[b] These values are subject to much more uncertainty than the remainder of the data reported. The possibility of two liquid phases exists.

of ethane added was computed upon the assumption that all uncertainty lies in the weight of ethane and that there were no errors in the associated variations in temperature and pressure. The weight correction factor shown in Figure 2 was employed in evaluating the weight of ethane crossing the interface, and thus is implicity included in the evaluation of the slope indicated in a portion of Table III. From the data recorded values of the Fick diffusion coefficient were smoothed with respect to pressure and temperature. The linear average of the initial equilibrium pressure and the pressure existing in the isochoric vessel during diffusion was used to characterize the pressure of measurement.

Fick diffusion coefficients are presented in Figure 4 as a function of pressure. The curves present smoothed values and the points shown are those determined experimentally and recorded in Table III. Dotted curves of constant weight fraction ethane have been included in Figure 4. Weight fractions of ethane indicated correspond to a linear average of the weight fraction ethane in the liquid phase under the initial equilibrium conditions and that existing at the interface during the transient diffusion process. Standard error of estimate for the 18 experimental points shown from the smooth curves was 0.8×10^{-8} square foot per second. In evaluating this quantity, it was assumed that all the error was in the Fick diffusion coefficient and none in the prevailing pressure and temperature. It was not possible to

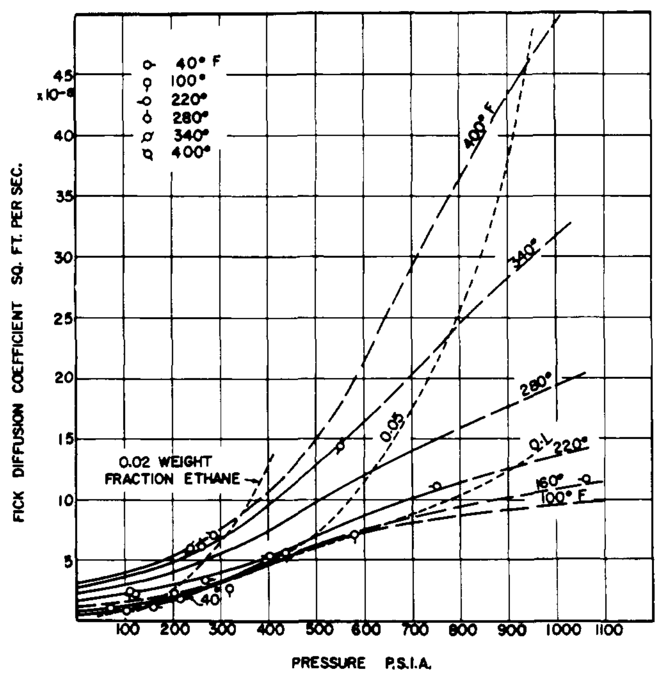

Figure 4. Effect of pressure upon Fick diffusion coefficient

Table IV. Fick Diffusion Coefficients for Ethane

Pressure, P.S.I.A.	Ethane Compn., Weight Fraction	Ethane Concn., Lb./Cu. Ft.	Fick Diffusion Coefficient, Sq. Ft./Sec.
		40° F.[a]	
100	0.030	1.64	0.9×10^{-8}
200	0.085	4.02	1.8
300	0.185	7.55	3.2
400			
500			
600			
700			
800			
900			
1000			
		100° F.	
100	0.014	0.96	1.2×10^{-8}
200	0.040	2.08	2.1
300	0.068	3.52	3.2
400	0.102	5.11	4.7
500	0.140	6.80	6.2
600	0.184	8.60	7.3[b]
700	0.232	10.79	8.0[b]
800	0.285	12.12	8.6[b]
900	0.345	13.81	9.1[b]
1000	0.407	15.57	9.5[b]
		160° F.[c]	
100	0.011	0.64	1.5×10^{-8}
200	0.024	1.30	2.3
300	0.040	2.07	3.4
400	0.058	2.92	4.8
500	0.076	3.76	6.3
600	0.095	4.64	7.6
700	0.116	5.51	8.5
800	0.136	6.41	9.3
900	0.158	7.28	10.1
1000	0.180	8.19	10.8
		220° F.	
100	0.008	0.49	2.2×10^{-8}
200	0.018	0.98	3.0
300	0.029	1.48	4.1
400	0.040	1.98	5.3
500	0.051	2.50	7.0
		220° F. Continued	
600	0.062	3.00	8.7
700	0.073	3.51	10.1
800	0.085	4.06	11.4
900	0.098	4.62	12.8
1000	0.111	5.20	14.2
		280° F.[a]	
100	0.007	0.41	2.9×10^{-8}
200	0.015	0.80	4.1
300	0.023	1.19	5.6
400	0.032	1.56	7.5[b]
500	0.040	1.94	9.9
600	0.047	2.32	12.1
700	0.056	2.71	14.1
800	0.064	3.11	16.0
900	0.072	3.51	17.7
1000	0.080	3.92	19.3
		340° F.[a]	
100	0.006	0.34	3.5×10^{-8}
200	0.013	0.67	4.9
300	0.019	0.99	6.9
400	0.026	1.31	9.6
500	0.032	1.62	13.0
600	0.039	1.93	16.5
700	0.045	2.24	20.4[b]
800	0.051	2.56	24.6
900	0.058	2.90	28.2
1000	0.064	3.24	31.6
		400° F.[a]	
100	0.005	0.29	3.9×10^{-8}
200	0.012	0.58	5.4
300	0.017	0.87	7.7
400	0.022	1.15	10.8
500	0.027	1.43	14.9[b]
600	0.032	1.70	21.4
700	0.037	1.95	29.3
800	0.042	2.22	36.6
900	0.048	2.49	43.4
1000	0.053	2.78	49.2

[a] Values of composition and concentration extrapolated from data at higher or lower temperatures.

[b] Values of Fick diffusion coefficient at these and higher pressures extrapolated from data at lower pressures.

[c] Values of Fick diffusion coefficient interpolated.

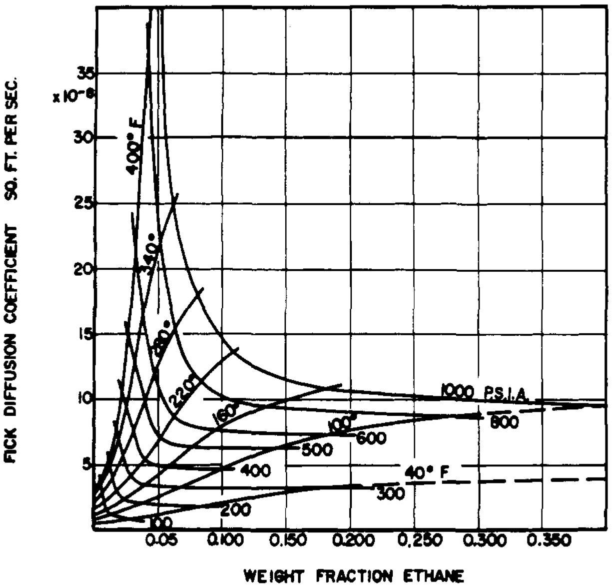

Figure 5. Effect of weight Fraction ethane upon Fick diffusion coefficient

obtain the same precision of measurement in the study with ethane as in corresponding studies with methane (*8–11*). Large changes in the Fick diffusion constant with state contributed materially to the difficulty.

The influence of the weight fraction ethane upon the Fick diffusion coefficient is shown on Figure 5. Marked increase in this coefficient at the higher pressures and temperatures is evident. Table IV records smoothed values of the Fick diffusion coefficient as a function of pressure and temperature in the ethane–white oil system.

Experimental data concerning the Fick diffusion coefficient of ethane in binary hydrocarbon systems are insufficient at this time to justify any attempt to relate the diffusion coefficient to the characteristics of the less volatile component. However, additional information upon the molecular transport characteristics of ethane should make this possible, as has been done for methane (*10*).

ACKNOWLEDGMENT

The assistance of John Lower in connection with the experimental work is acknowledged. Virginia Berry carried out the calculations associated with resolution of the data, and B. Lawson Miller contributed to the preparation of the manuscript.

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.
$\overline{V}_k$ = partial specific volume of component k, cu. ft./lb.
Δ = difference in
θ = time, sec.
σ_k = concentration of component k in the liquid phase, 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
0 = initial conditions

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Partial Volumetric Behavior in Hydrocarbon Systems

Ethane and *n*-Pentane in the Liquid Phase of the Ethane–*n*-Pentane System

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RECENTLY, the volumetric and phase behavior of the ethane–*n*-pentane system was investigated (*3*). In addition, the phase behavior of the methane-ethane–*n*-pentane system has been studied over a limited range of temperatures (*1*). On the basis of the foregoing data, with primary reference to the recent study of the volumetric behavior of the the ethane–*n*-pentane system (*3*), the values of the partial volumes of ethane and *n*-pentane were evaluated.

The partial molal volume (hereafter referred to as the partial volume) is defined by the equation,

$$\overline{V} = \left(\frac{\partial V}{\partial m_k}\right)_{T,P,m_j} \quad (1)$$

Articles from these laboratories on partial volume have been published in *Drilling and Production Practice* pp. 402–20 (1939), and pp. 641–652 (1940); *California Oil World* **34**, 31 (1941); and in the *Journal of Chemical and Engineering Data* **4**, 98, 204 (1959).