Part I

PHASE EQUILIBRIA
MOLECULAR TRANSPORT
THERMODYNAMICS

Diffusion Coefficients in Hydrocarbon Systems

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

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EARLIER investigations of the molecular transport of the lighter paraffins in the liquid phase of hydrocarbon mixtures initiated by Lacey (2, 3, 4, 7) have been supplemented by more recent studies extending to higher pressures and temperatures. The experimental information available to date indicates a wide variation in the Fick diffusion coefficient with state. The possible resistance to diffusion at the gas-liquid interface (12) is not important at the pressures involved in this investigation. The present study is concerned with the molecular transport of ethane in the liquid phase of the ethane–n-pentane system at pressures up to 700 p.s.i.a. at temperatures between 40° and 280° F.

METHODS AND EQUIPMENT

In principle, the experimental methods involve the introduction of ethane at a known measured rate into a chamber of fixed volume containing a heterogeneous mixture of ethane and n-pentane, brought to physical equilibrium by mechanical agitation. Under quiescent conditions the pressure was raised a predetermined amount by the addition of ethane, and the quantity required to maintain an isobaric system at the elevated pressure was determined as a function of time.

The details of the equipment have been described (8, 9). Vertical tubes were provided to decrease the influence of local acceleration upon the molecular transport. The temperature measurement was established by a strain-free platinum resistance thermometer (6) recently compared with a similar calibrated instrument. The temperature was therefore known within 0.02° F.

The pressure within the isochoric vessel was measured by means of a balance involving a piston-sleeve combination and was known within 0.1 p.s.i.a. or 0.05%, whichever was a larger measure of uncertainty. A manostat (10) was employed to maintain isobaric conditions. The ethane was introduced by means of an injector (8). The indications of the position of the injector were recorded automatically in a digital fashion as a function of time (9). The speed of the injector was controlled from the indications of the manostat, and variations in pressure during a diffusion measurement were not more than 0.05 p.s.i.a.

Methods of analysis used in earlier studies (8) were followed. From the experimental data and a knowledge of the volumetric behavior of the system, including the assumption of steady local equilibrium (5) at the gas-liquid interface, the Fick diffusion coefficient was established by:

$$D_{f,k}^* = \left[\frac{(1 + V_{j,l\sigma_j}^* + V_{k,l\sigma_k}^*)^*}{(1 + V_{j,l\sigma_j}^*)^*[1 + (\sigma_k/\sigma_j)]^*} \right]^*$$

$$\left[\frac{\pi\, m_k^2}{4\theta(\sigma_{k,i,e} - \sigma_{k,o})^2} \right] \left[\frac{V_{k,s}^*}{V_{k,s}^* - V_{k,l}^*} \right]^2 \quad (1)$$

The asterisks in Equation 1 indicate average values of the quantity in question over the range of conditions existing within the liquid phase during a particular set of measurements. Equation 1 takes into account the effects of hydrodynamic velocity (8) and the change in volume of the liquid phase. This expression as written is limited to binary systems where the state of the liquid phase at the interface is established by the prevailing temperature and pressure.

Available experimental information (11) was the basis for establishing the partial volumetric behavior of ethane and of n-pentane in the liquid phase of the ethane–n-pentane system. The first bracketed term of Equation 1 (the volumetric correction factor) represents the correction for the hydrodynamic velocity and its value is presented in the

upper part of Figure 1. The last bracketed term accounts for the difference between the weight of ethane introduced into the isochoric diffusion vessel and that passing the interface of the heterogeneous system. The value of the weight correction factor is shown in Figure 1.

MATERIALS

The ethane was research grade from the Phillips Petroleum Co., containing less than 0.001 mole fraction of impurities, as confirmed by mass spectrographic techniques.

The n-pentane was Phillips Petroleum Co. pure grade, reported to contain less than 0.01 mole fraction of impurities. The refractive index at 77° F. was 1.3549 relative to
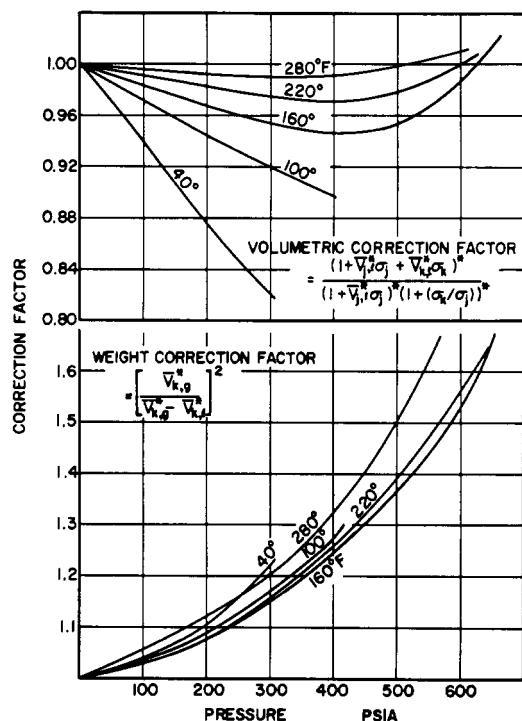

Figure 1. Volumetric and weight correction factors for ethane in the liquid phase of the ethane–n-pentane system

the D lines of sodium. This value compares favorably with 1.35472 reported by Rossini (1) for an air-saturated sample, which lends credence to the purity of the n-pentane employed. The samples of ethane and n-pentane were introduced into the diffusion cell and other parts of the apparatus by conventional high vacuum techniques.

EXPERIMENTAL RESULTS

Typical experimental results for a pressure of 199.8 p.s.i.a. and an initial weight fraction ethane of 0.09 at 160° F. are shown in Table I and Figure 2. The final equilibrium pressure was 216.6 p.s.i.a. and the final weight fraction ethane was 0.10. Each point represents an individual reading of the injector. It was not feasible to obtain satisfactory data at times less than 2000 seconds because of the significant energy dissipation and associated thermal gradients resulting from the abrupt increase in pressure from 199.8 to 216.6 p.s.i.a. The weight of ethane added was arbitrarily taken equal to zero at some appropriate time after the initial pressure transients had disappeared. In the derivation of Equation 1, constancy of the quotient of the square of the weight of ethane added with respect to time is to be expected only when less than one half the total quantity of ethane required to bring the system to final

Table I. Sample of Experimental Measurements at 160° F.

| | Pressure, p.s.i.a. | 199.8[a] | 216.6[b] |
| | Weight fraction ethane. | 0.089[a] | 0.098[b] |

Time, Sec.	Ethane Added,[c] Lb.	Time, Sec.	Ethane Added, Lb.
0	...	16,600	300.38 × 10⁻⁶
2,000	61.98 × 10⁻⁶	17,000	304.92
2,441	75.36	17,500	308.37
2,800	85.95	17,801	311.18
3,200	97.39	18,200	312.26
3,600	109.48	18,600	315.50
4,006	120.28	19,000	318.74
4,400	129.78	19,600	322.84
4,800	137.56	20,700	331.48
5,200	148.14	21,200	334.29
5,600	155.05	21,600	336.66
6,000	163.90	22,000	338.21
6,400	172.76	22,500	342.28
6,799	179.45	23,101	345.30
7,202	187.44	23,500	348.75
7,600	193.70	23,800	350.27
8,000	200.83	24,300	351.99
8,400	208.60	24,801	355.02
8,800	215.08	25,200	357.18
9,269	221.99	25,801	360.42
9,684	228.47	26,200	361.93
10,000	233.22	26,600	363.45
10,400	239.27	27,000	364.73
10,803	244.88	27,800	366.25
11,400	253.31	28,800	371.21
11,800	257.62	29,200	372.72
12,200	263.02	29,600	374.45
12,800	270.23	30,000	375.75
14,000	282.03	30,500	371.48
14,600	290.45	31,000	378.77
15,406	298.22	31,400	380.24
		31,800	382.01

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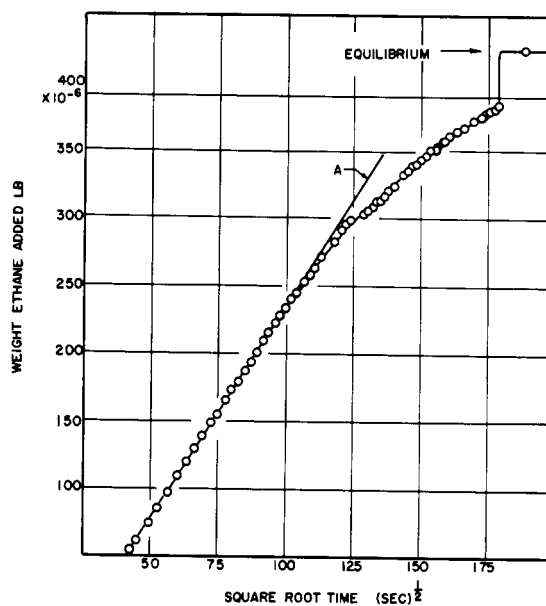

Figure 2. Typical experimental measurements at 160° F.

equilibrium has crossed the interface between the gas and liquid phase in the isochoric vessel.

The experimental results are summarized in Table II. A total of 26 independent measurements of the Fick diffusion coefficient were made. In Figure 2 the slope of the straight line, A, was established from data at weights of ethane added smaller than 215×10^{-6} pound, which corre-

sponds to approximately half the ethane required for equilibrium.

Figure 3 represents the influence of pressure on the Fick diffusion coefficient of ethane in the liquid phase of the ethane-n-pentane system. The standard error of estimate for the experimental points shown from the smooth curves was 5.1×10^{-8} sq. foot per second. The linear deviation with regard to sign of the points shown was 0.2×10^{-8} sq. foot per second. The relatively large standard error of estimate of the experimental data is in part associated with the unusually rapid change in the Fick diffusion coefficient with state. The cause of the minimum in the coefficient is not well understood.

Figure 4 depicts the effect of temperature upon the Fick diffusion coefficient of ethane in the liquid phase of the
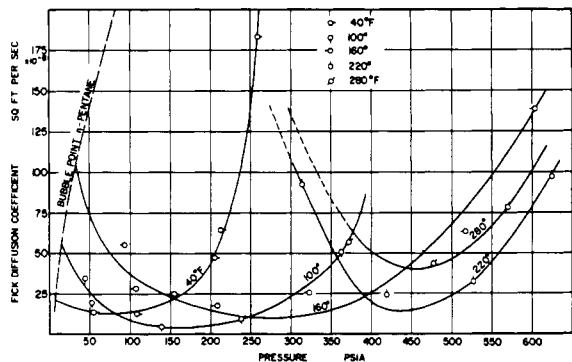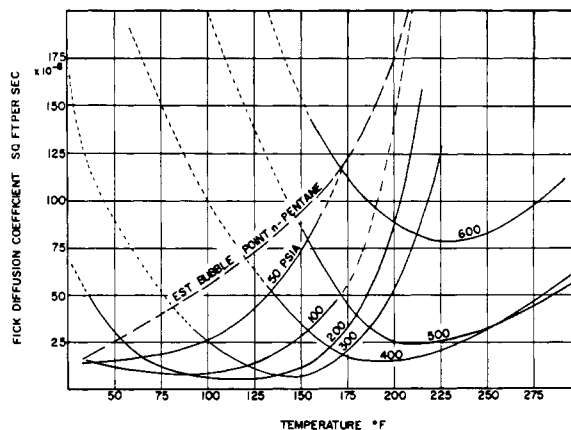

Figure 4. Effect of temperature upon Fick diffusion coefficient for ethane

ethane-n-pentane system and, as would be expected, there also exists a minimum in the coefficient with respect to change in temperature under isobaric conditions.

Table III sets forth smoothed values of the Fick diffusion coefficient for ethane in the liquid phase of the ethane-n-pentane system for a series of pressures and temperatures. The concentration of ethane in and the composition of the liquid phase have been included. These values correspond with the information presented in Figures 2 and 3. The rather complicated influence of enviroment upon the Fick diffusion coefficient of ethane indicates the limitation of

Figure 3. Influence of pressure upon Fick diffusion coefficient for ethane

Table II. Summary of Experimental Results

Pressure, P.S.I.A.		Ethane Compn., Weight Fraction		Ethane Concn., Lb./Cu. Ft.		$\dfrac{(\Delta \underline{m}_k)^2}{\theta}$, 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.										
51.8	56.6	0.067	0.076	2.56	2.86	5.946×10^{-12}	1.040×10^{-6}	0.971	14.265×10^{-8}	13.849×10^{-8}
104.0	112.9	0.152	0.168	5.64	6.20	19.592	2.764	0.938	13.821	12.959
150.3	160.4	0.248	0.264	8.62	9.29	54.982	1.377	0.906	27.770	25.159
198.2	211.0	0.350	0.382	12.07	13.01	202.495	3.289	0.874	53.899	47.081
209.5	214.8	0.377	0.390	12.89	13.30	52.904	4.941	0.862	74.486	64.214
257.0	261.9	0.508	0.522	16.07	16.48	148.173	10.648	0.842	217.76	183.25
291.3	295.0	0.616	0.630	18.48	18.74	301.359	11.797	0.826	1143.8	945.12
100° F.										
42.0	47.0	0.021	0.025	0.80	0.90	1.650	4.367	0.987	35.524	35.058
48.7	56.4	0.026	0.032	0.94	1.17	4.718	0.092	0.985	19.220	18.931
127.2	150.6	0.097	0.116	3.42	4.18	13.096	0.846	0.961	5.049	4.854
229.8	246.8	0.196	0.215	6.74	7.37	17.297	6.352	0.935	10.324	9.654
351.0	375.9	0.340	0.374	10.82	11.63	140.701	0.438	0.906	55.930	50.645
160° F.										
90.8	96.1	0.028	0.031	0.91	1.01	2.590	0.873	0.985	56.310	55.466
101.3	112.2	0.034	0.040	1.10	1.32	6.492	1.593	0.984	29.305	28.831
199.8	216.6	0.089	0.098	3.00	3.35	9.837	0.720	0.968	18.393	17.814
317.8	329.0	0.162	0.169	5.31	5.52	4.801	1.197	0.954	26.894	25.590
499.8	533.4	0.290	0.315	8.55	9.08	63.517	5.171	0.958	66.059	63.284
596.1	612.8	0.367	0.376	10.16	10.38	21.328	2.304	0.989	140.30	138.74
638.2	672.5	0.396	0.422	10.97	11.27	97.216	7.129	1.019	382.3	389.64
220° F.										
304.0	323.6	0.085	0.094	2.70	2.94	22.073	1.657	0.974	94.672	92.211
400.2	439.2	0.130	0.149	3.80	4.46	40.367	4.599	0.972	25.130	24.414
500.2	553.2	0.178	0.206	5.10	5.87	64.056	11.037	0.983	32.774	32.204
600.8	649.3	0.230	0.257	6.43	6.98	86.105	8.746	1.007	96.955	97.643
280° F.										
349.6	393.6	0.052	0.067	1.48	1.90	37.297	7.938	0.990	57.427	56.881
451.7	502.6	0.088	0.106	2.41	2.85	27.338	2.622	0.998	43.435	43.357
541.6	597.6	0.122	0.142	3.22	3.69	48.459	2.801	1.006	77.601	78.027

^{a} Effective cross-sectional area = 0.019187 sq. ft.

such a coefficient in adequately predicting the molecular transport of this hydrocarbon in a liquid phase.

As yet, sufficient experimental data are not accumulated to justify an attempt at relating the Fick diffusion coefficient of ethane to the properties of the less volatile component. However, the maximum values of the coefficient encountered in the work reported were at least five times those associated with the transport of ethane in a binary system involving a white oil having an average molecular weight of approximately 337.

ACKNOWLEDGMENT

Table III. Fick Diffusion Coefficient for Ethane

Pressure, P.S.I.A.	Ethane Compn., Weight Fraction	Ethane Concn., Lb./Cu. Ft.	Fick Diffusion Coefficient, Sq. Ft./Sec.
40° F.			
50	0.060	2.38	13.9×10^{-8}
100	0.145	5.32	13.8
150	0.242	8.57	20.6
200	0.352	12.2	44.2
250	0.479	15.5	141.1
100° F.			
50	0.026	0.98	25.7×10^{-8}
100	0.070	2.50	8.1
150	0.116	4.13	4.5
200	0.164	5.76	5.5
250	0.214	7.38	11.5
300	0.270	9.02	24.0
350	0.334	10.7	43.2
400	0.406	12.3	98.1
160° F.			
50	0.006	0.15	73.0×10^{-8}
100	0.033	1.07	36.7
150	0.060	2.00	22.6
200	0.088	2.99	14.7
250	0.119	4.00	10.5
300	0.151	4.99	10.7
350	0.182	5.94	15.2
400	0.216	6.83	25.6
450	0.250	7.71	43.8
500	0.287	8.56	67.3
550	0.325	9.40	98.5
600	0.365	10.2	136.0
220° F.			
300	0.083	2.69	106.7×10^{-8}
350	0.106	3.27	53.0
400	0.128	3.87	19.1
450	0.153	4.49	14.9
500	0.177	5.11	23.8
550	0.203	5.75	44.9
600	0.229	6.38	79.1
280° F.			
400	0.068	1.93	50.1×10^{-8}
450	0.086	2.38	40.6
500	0.104	2.82	46.5
550	0.123	3.27	67.6
600	0.143	3.71	101.2

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 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 liquid phase, lb./cu. ft.

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

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