Diffusion Coefficients in Hydrocarbon Systems

n-Heptane in the Gas Phase of the Ethane–*n*-Heptane and Propane–*n*-Heptane Systems

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Because little information is available concerning the behavior of hydrocarbons under conditions far from equilibrium, it appears desirable to obtain data for the diffusion coefficients of the lighter hydrocarbons in the gas phase.

The Maxwell diffusion coefficients of *n*-heptane in the gas phase of the ethane–*n*-heptane and propane–*n*-heptane systems were measured at temperatures from 100° to 220° F. and for pressures up to 60 lb./sq. in. The Fick diffusion coefficient was calculated as a function of state from these measurements.

The experimental results indicate that the interfacial resistance between the liquid and the gas phases into which the transport was taking place is small. It was found that pressure exerted a significant influence upon the Maxwell diffusion coefficient for both of the binary systems investigated. There is a marked decrease in the Maxwell diffusion coefficient with an increase in molecular weight of the stagnant component.

The evaluation of material transport in the gas phase as a result of a concentration gradient was placed on a surprisingly satisfactory basis by Maxwell (*12*) and Stefan (*18-21*). Chapman and Cowling (*7*) extended their treatment to include the effects of composition upon the diffusion characteristics of gaseous mixtures. Jost (*9*) reviewed the status of diffusion in gases, liquids, and solids. Kirkwood and Crawford (*10*) outlined the basic transport characteristics of homogeneous systems. A discussion of the application of diffusion coefficients was presented by Sherwood and Pigford (*17*). The relations of the several diffusion coefficients were recently reviewed (*13*) and it does not appear necessary to consider further the background of diffusion in gases beyond that associated with the paraffin hydrocarbons.

Wilke (*22*) reviewed the status of prediction of diffusion coefficients for the lighter gases and supplemented available correlations for gases at atmospheric pressure. Schlinger (*16*) established diffusion coefficients for *n*-heptane and *n*-hexane in air and reviewed the literature concerning the experimental determination of Maxwell diffusion coefficients. The coefficients for *n*-heptane in the gas phase of the methane–*n*-heptane system at pressures up to 60 lb./sq. in. are available (*5*) and measurements of the diffusion of *n*-hexane in the gas phase of the methane–*n*-hexane, ethane–*n*-hexane, and propane–*n*-hexane systems were reported (*6*). In each of these cases it was found that the Maxwell hypothesis, with either partial pressure or fugacity as the potential, did not fully describe the transport process even at pressures below 60 lb./sq. in. The present work is concerned with the measurement of the Maxwell diffusion coefficient for *n*-heptane in the gas phase of the ethane–*n*-heptane and the propane–*n*-heptane systems for temperatures from 100° to 220°F. and at pressures from 14 to 60 lb./sq. in. abs. Throughout this discussion and in the associated figures the pressures are reported in pounds per square inch absolute or pounds per square foot absolute.

METHODS AND APPARATUS

The experimental approach to this investigation involved an adaptation of the classical diffusion cell of Stefan (*18*). The gas phase filled the diffusion path and the *n*-heptane was introduced as a liquid into the lower part of the chamber through a fritted-glass disk. Steady state conditions were indicated by the constancy of the capillary depression within the fritted disk. The concentration of the *n*-heptane in the gas phase at the top of the diffusion cell was maintained at a steady value by circulation across the top of the cell of a gas phase which was at equilibrium with *n*-heptane liquid at 32° F.

The apparatus, which is rather complicated, has been described in detail (*4*, *5*). Appropriate corrections were made for the end effects associated with the introduction of *n*-heptane through the fritted-glass disk and its withdrawal by gas circulation at the top of the cell. The methods for evaluation of these corrections have been described (*4*). The pressures were measured within 0.01 lb./sq. in. and the temperatures with an uncertainty of 0.01° F. relative to the international platinum scale. The estimated uncertainty in each of the variables pertinent to these measurements is available (*5*).

It has been shown (*16*) that for measurements of this kind the Maxwell diffusion coefficient may be evaluated from the following expression in which *T* refers to the temperature of the transport path:

$$D_{M,k} = \frac{\overset{\circ}{m}_k b_k T(l_G - l_c)}{Z\left(\frac{f_k^0}{P}\right) \ln\left(\frac{f_k^0 - f_{k,t}}{f_k^0 - f_{k,i} + b_k T r_{i,k} \overset{\circ}{m}_k}\right)} \qquad (1)$$

Equation (1) is based upon an assumption that the gas phase is an ideal solution, and fugacity is chosen as the potential. It takes into account end corrections to the length of the diffusion path which amounted to less than 1.5% of the average transfer distance. The resistance in the interface shown in Equation (1) was found to be negligibly small and has not been presented in this discussion because with the accuracy of evaluation of this effect attainable its existence was uncertain. In any event the total influence of the resistance in the interface was in no case more than 1% of the total resistance to transport, and a first order correction was made for its influence as indicated in Equation (1).

If the gas phase is treated as a perfect gas, Equation (1) assumes the form

$$D_{M,k} = \frac{\overset{\circ}{m}_k b_k T(l_G - l_c)}{\ln\left(\frac{p_{i,t}}{p_{i,i} + b_k T r_{i,k} \overset{\circ}{m}_k}\right)} \qquad (2)$$

If length corrections and interfacial resistance are neglected, Equation (2) assumes the conventional form

$$D_{M,k} = \frac{\overset{\circ}{m}_k b_k T l}{\ln\left(\frac{p_{i,t}}{p_{i,i}}\right)} \qquad (3)$$

The values of the length correction were determined from experimental data already available (*4*). It was assumed that this correction was solely a function of the Reynolds number of the flow at the exit to the transport path. The diameter of the exit tubes was used as a characteristic length. In the present instance the effective transport length was described by (*5*).

$$l = l_G - 4.90 \times 10^{-4} \frac{\eta_r}{\eta} \underline{\overset{\circ}{m}}_t \qquad (4)$$

In Equation (4) the reference viscosity corresponds to that of pure methane at 100°F. and atmospheric pressure.* The viscosity at the state in question was determined from available information concerning the influence of pressure and temperature upon the behavior of methane (*15*). In estimating the viscosity of the gas phase no regard was taken of the effect of small quantities of *n*-heptane present in the recirculating gas.

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*The dimensional constant 4.90×10^{-4} is expressed in (ft.)(sec.)/lb.

MATERIALS

The *n*-heptane employed for this study was obtained as research grade from the Phillips Petroleum Company. The air-free sample had a specific weight of 42.4229 at 77° F., which compares satisfactorily with a value of 42.417 reported by Rossini (*14*) for an air-saturated sample at the same temperature. The index of refraction for the *D* lines of sodium was found to be 1.3852, in comparison with a value of 1.38517 reported by Rossini for 77° F. It appears that the sample of *n*-heptane used in this investigation was relatively free of impurities and probably contained more than 0.998 mole fraction *n*-heptane.

TABLE 1. EXPERIMENTAL MAXWELL DIFFUSION COEFFICIENTS FOR *n*-HEPTANE

Pressure, lb./sq. ft.	Temperature transport path, °F.	Diffusion coefficient Perfect gas, lb./sec.	Diffusion coefficient Ideal solution, lb./sec.
	Ethane–*n*-Heptane		
2,393	100.56	0.0929	0.0951
3,620	100.56	0.0986	0.1002
2,429	99.96	0.1154	0.1173
2,226	160.60	0.1353	0.1397
2,287	160.50	0.1447	0.1496
3,019	160.61	0.1377	0.1422
7,223	160.02	0.1230	0.1289
4,402	160.01	0.1228	0.1271
7,353	160.02	0.1096	0.1143
5,113	190.00	0.1537	0.1617
7,791	190.05	0.1445	0.1533
4,422	189.99	0.1451	0.1556
5,992	219.98	0.1701	0.1834
8,482	220.05	0.1681	0.1806
5,071	220.03	0.1738	0.1779
	Propane–*n*-Heptane		
2,122	100.70	0.0623	0.0636
2,158	130.57	0.0829	0.0851
2,314	130.64	0.0881	0.0913
4,382	130.59	0.0655	0.0684
4,375	160.59	0.0831	0.0849
3,058	160.58	0.0945	0.0982
4,469	160.66	0.0778	0.0817
6,627	160.60	0.0660	0.0702
6,696	190.63	0.0838	0.0899
4,392	190.62	0.1038	0.1100
3,561	190.65	0.1117	0.1176
6,644	220.55	0.1256	0.1362
8,370	220.58	0.0945	0.1032
4,952	220.66	0.1137	0.1223
7,137	220.63	0.1130	0.1224

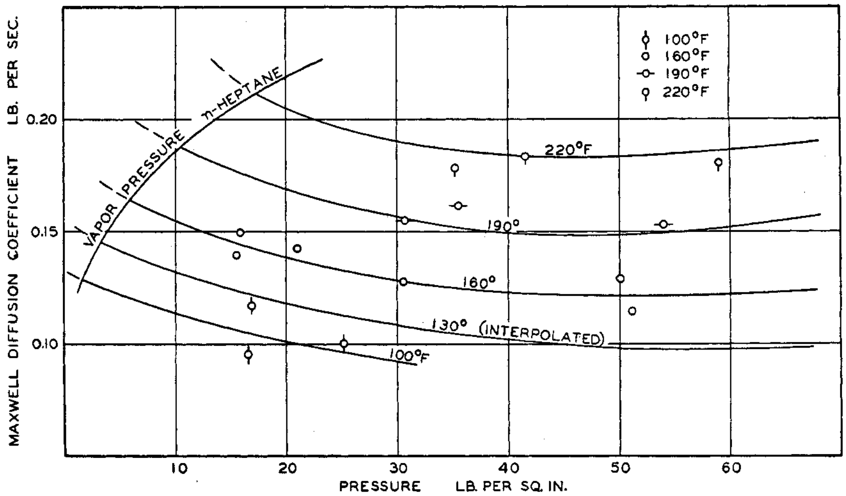

Fig. 1. Effect of pressure upon the Maxwell diffusion coefficient for *n*-heptane in the gas phase of the ethane–*n*-heptane system.

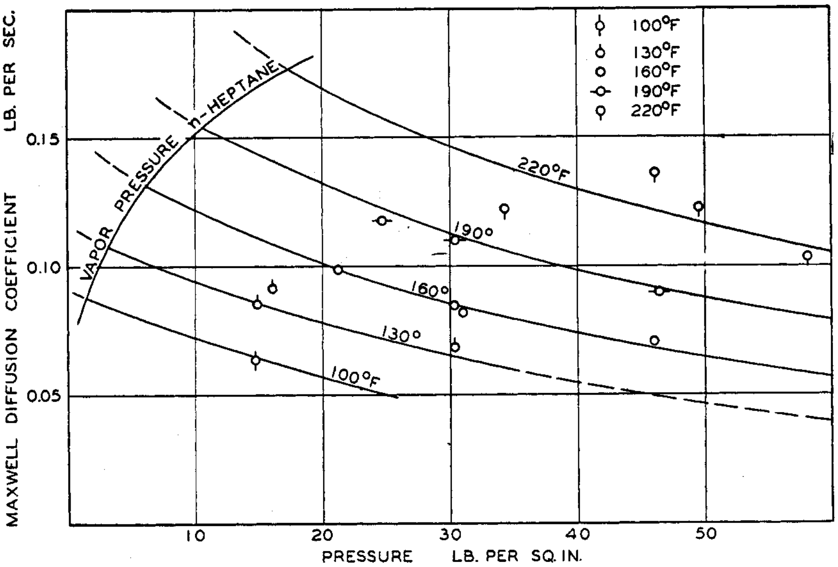

Fig. 2. Effect of pressure upon the Maxwell diffusion coefficient for *n*-heptane in the gas phase of the propane–*n*-heptane system.

The sample of ethane utilized in the study of the ethane–*n*-heptane system was obtained from Phillips Petroleum Company as research grade and was reported to contain not more than 0.0006 mole fraction impurities. A mass spectrometric analysis of this sample of ethane indicated that the dried material contained less than 0.00028 mole fraction of material other than compounds containing two carbon atoms. Care was exercised to avoid contamination of the sample during introduction to the apparatus, but no purification of the ethane was made other than to dry it over anhydrous calcium sulfate.

The propane was also obtained from Phillips Petroleum Company as pure grade. This material was subjected to mass spectrometric analysis, and the dried sample was found to contain less than 0.0002 mole fraction of impurities. The impurities present were compounds containing four carbon atoms. Before introduction into the diffusion apparatus, this material was carefully dried by passage over anhydrous calcium sulfate at pressures in excess of 100 lb./sq. in.

EXPERIMENTAL RESULTS

In the investigation of the Maxwell diffusion coefficient for *n*-heptane in the ethane–*n*-heptane and in the propane–*n*-heptane systems, the minimum pressure studied was fixed by approach to the vapor pressure of *n*-heptane where uncertainties as to the behavior at the interface became important. As a result of the relatively high rate of diffusion of ethane and propane into the *n*-heptane liquid some difficulties were experienced from the transport of ethane and propane through the fritted-glass disk at the higher pressures. For example, it was necessary to limit the measurements at 100° F. to pressures below 25 lb./sq. in. Throughout the temperature interval investigated it was not possible to make measurements at pressures much below twice the vapor pressure of *n*-heptane at the temperature in question.

The results of the experimental measurements with the ethane–*n*-heptane and the propane–*n*-heptane systems are available (*3*). Each measurement of diffusion coefficients required approximately 14 hr. for its completion. The information available (*3*) is sufficient to establish the Maxwell diffusion coefficients of *n*-heptane in these systems when taken with the collateral thermodynamic properties of the gas phase, the vapor pressure, and fugacity of *n*-heptane. The Maxwell diffusion coefficients were calculated from the available data (*3*) on the basis of Equations (1) and (2) and are recorded in Table 1. The difference in the Maxwell diffusion coefficients computed on the basis of ideal solutions and of perfect gases is not significant at the lowest temperature but becomes of significant interest at the higher temperatures.

The fugacity and compressibility factor of *n*-heptane and the compressibility factors of ethane and propane were obtained by application of the Benedict equation of state (*1*, *2*, *8*). The vapor pressure of *n*-heptane

Table 2. Maxwell Diffusion Coefficients for n-Heptane in the Ethane–n-Heptane System

Temperature, °F.	Pressure, lb./sq. in. 14.696	20	30	40	50	60
100	0.1070*	0.1010	0.0920			
130	0.1250	0.1179	0.1081	0.1019	0.0980	0.0979
160	0.1468	0.1385	0.1280	0.1235	0.1220	0.1220
190	0.1789	0.1690	0.1565	0.1500	0.1484	0.1520
220	—	0.2050	0.1901	0.1840	0.1840	0.1869

*Maxwell diffusion coefficients expressed in lb./sec.

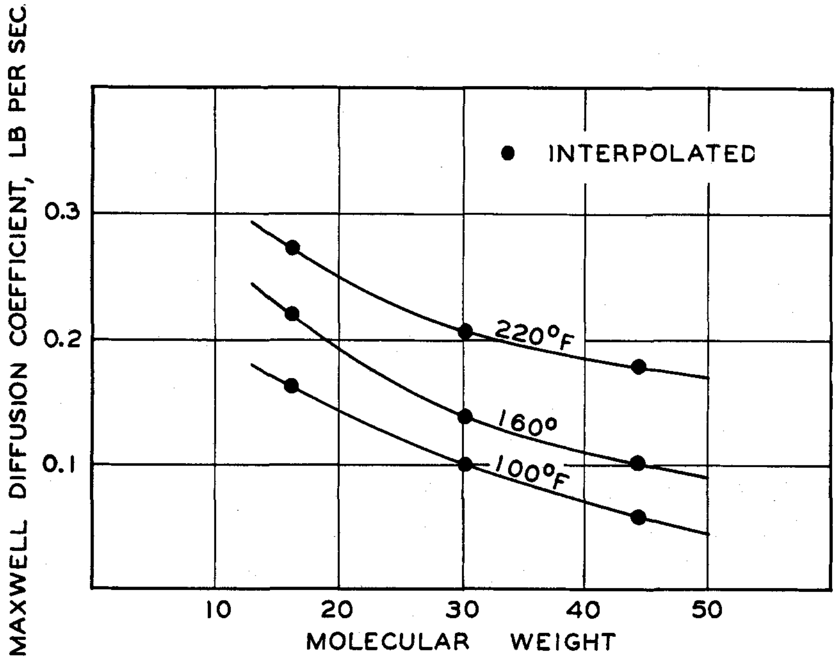

Fig. 3. Effect of molecular weight of stagnant component on diffusion coefficients for n-heptane.

was taken from a critical review of Rossini (*14*), supplemented by the experimental measurements of Young (*23*). The values of vapor pressure employed were associated with the temperature of the interface. This interfacial temperature differs slightly from that of the transport path. The composition of the gas phase at the interface and in the condenser was estimated from ideal solutions (*11*) and fugacity data calculated from the Benedict equation of state (*2*). It was predicated upon the existence of local equilibrium (*10*).

The experimental results for the Maxwell diffusion coefficients for n-heptane in the ethane–n-heptane system are shown in Figure 1. The behavior at 130° F. was interpolated from measurements at the other temperatures. The standard deviation of the experimental data shown from the smoothed curves of Figure 1 was 0.00686 lb./sec. and the corresponding average deviation without regard to sign was 0.00565 lb./sec. Smoothed values of the Maxwell diffusion coefficients for n-heptane in the gas phase of the ethane–n-heptane system are given in Table 2. These data were interpolated from the experimental results shown in Figure 1. The minima shown in the curves of Figure 1 resulted from fitting a three-coefficient curve to the data by least squares methods. The existence of this minimum may be open to some question, but this representation yields a much smaller standard deviation than does a linear presentation.

The experimental measurements upon the transport of n-heptane in the gas phase of the propane–n-heptane system are shown in Figure 2. In this case measurements were obtained at five temperatures evenly spaced between 100° and 220° F. The experimental data indicate a progressive decrease in the Maxwell diffusion coefficients with an increase in pressure for this system. The standard deviation of the measurements shown in Figure 2 and recorded in a part of Table 1 from the smoothed curve was 0.00692 lb./sec. The corresponding average deviation without regard to sign was 0.00447 lb./sec. The data for 130° F. were extended in Figure 2 to pressures somewhat above the range of the experimental measurements. The added uncertainty in this region has been indicated by a dashed curve. Likewise, the curves have been extended to pressures below the vapor pressure of n-heptane to indicate that the boundary of the heterogeneous region is not a limitation of the region of pressure and temperature in which the Maxwell diffusion coefficients may be employed. Smoothed values of the Maxwell diffusion coefficients for n-heptane in the gas phase of the propane–n-heptane system are shown in Table 3.

It should be emphasized that throughout the analysis of the experimental data it was assumed that the Maxwell hypothesis is descriptive of the transport of n-heptane at a specified pressure and temperature throughout the composition interval encountered in the apparatus. It is probable that some improvement in the description of the experimental results could have been obtained by use of the methods suggested by Chapman and Cowling (*7*), but such refinements were not justified in the present instance because of the uncertainties in the primary measurements. As more is learned concerning the transport characteristics of the hydrocarbons of intermediate molecular weight, corrections for the effect of composition upon the Maxwell diffusion coefficients can be made. The experimental data available (*3*) permit the reader to make such calculations if they should be of interest. Likewise a comparison with the predicted effect of pressure (*7*) upon the Maxwell diffusion coefficient can well await the accumulation of additional experimental facts over a wider range of pressure than was studied in the present instance.

Available information concerning the diffusion of n-heptane in the gas phase of the methane–n-heptane system (*5*) together with the information presented here permits the effect of the nature of the stagnant component on the transport characteristics of this paraffin hydrocarbon to be estimated. Figure 3 presents interpolated values of the Maxwell diffusion coefficients at 20 lb./sq. in. for n-heptane in the gas phase of the methane–n-heptane, ethane–n-heptane, and the propane–n-heptane systems. The points shown are the experimental data for each of the several binary systems interpolated to a pressure of 20 lb./sq. in. The data indicate a rather marked decrease in the Maxwell diffusion coefficient with an increase in the molecular weight of the stagnant component. This effect is more pronounced at the lower temperatures. The behavior depicted in Figure 3 for n-heptane is similar to that found for n-hexane in the corresponding binary systems (*6*).

TRANSPORT CHARACTERISTICS

For perfect gases the Fick diffusion coefficient is related to the Maxwell diffusion coefficient in the following way (*5, 13*):

$$D_{F,k} = \left(\frac{n_i}{n_j}\right)\frac{D_{M,k}}{P} \tag{5}$$

Equation (5) was utilized to compute values of the Fick diffusion coefficient for n-heptane. These are available (*3*) for the ethane–n-heptane and the propane–n-heptane systems, respectively. The variation in composition with position in a transport path may be determined from Equation (2). The values of the Fick diffusion coefficient were calculated from the foregoing expression as a function of composition and pressure on the assumption that the Maxwell diffusion coefficient was independent of composition. The Fick diffusion coefficients are a marked function of composition, pressure, and temperature of the phase at the point at which the transport takes place. The effect of temperature on the product of pressure and the Fick diffusion coefficient for n-heptane is shown in Figure 4. The behavior of n-heptane in the methane–n-heptane system (*5*) was included for comparison. There is a progressive decrease in the Fick diffusion coefficient

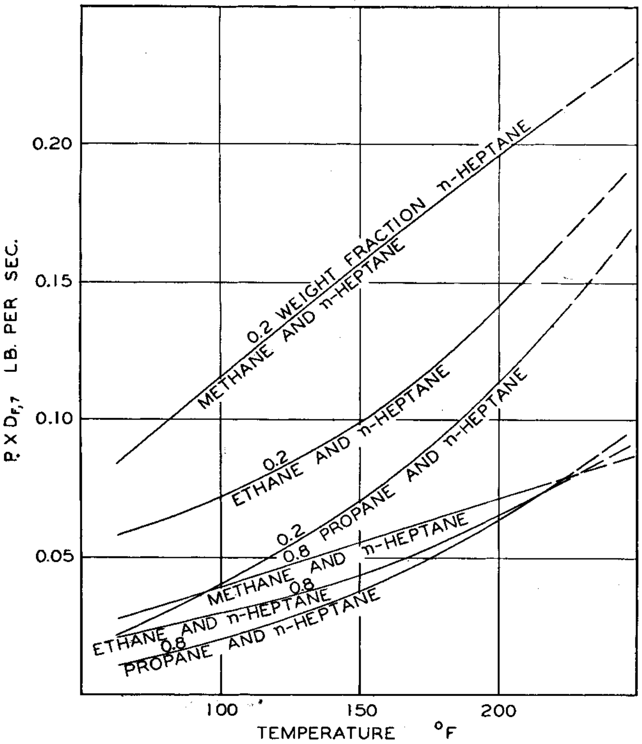

Fig. 4. Fick diffusion coefficients for *n*-heptane in the gas phase at 20 lb./sq. in.

with an increase in molecular weight of the stagnant component.

The coefficients for the components of an ideal solution are related by the following expression:

$$D_{F,i} = \frac{\sigma_k^0}{\sigma_i^0} D_{F,k} \qquad (6)$$

By use of Equation (6) the values for the Fick diffusion coefficients of ethane and propane in the systems studied were computed and are available (*3*).

ACKNOWLEDGMENT

This work is a contribution from Project 37 of the American Petroleum Institute at the California Institute of Technology. Jacques Bodes assisted with the experimental work, Betty Kendall carried out the calculations, and Elizabeth McLaughlin contributed to the preparation of the manuscript, which was reviewed by W. N. Lacey.

NOTATION

b_k = specific gas constant of component *k*, ft./°R.
$D_{F,k}$ = Fick diffusion coefficient of component *k*, sq. ft./sec.
$D_{M,k}$ = Maxwell diffusion coefficient of component *k*, lb./sec.
f_k = fugacity of component *k*, lb./sq. ft.
f_k^0 = fugacity of component *k* in pure state, lb./sq. ft.
l = effective transport length, ft.
l_c = effective correction to gross transport length, ft.
l_G = gross transport length, ft.
ln = natural logarithm
$\overset{\circ}{m}_k$ = weight rate of transport of component *k*, lb./(sq. ft.)(sec.)
$\underline{\overset{\circ}{m}}$ = total weight rate of transport, lb./sec.
n_k = weight fraction of component *k*
η_k = mole fraction of component *k*
p_k = partial pressure of component *k*, $(P\eta_k)$, lb./sq. ft.
P = pressure, lb./sq. ft. abs.
r_i = interfacial resistance, sec./ft.
T = thermodynamic temperature, °R.
Z = compressibility factor of gas phase
η = absolute viscosity of gas phase, (lb.)(sec.)/sq. ft.
σ_k = specific weight of component *k*, lb./cu. ft.

Superscript

0 = pure substance

Subscripts

i = conditions at interface
j = stagnant component
k = diffusing component
r = reference state
t = conditions at exit of transfer section

Table 3. Maxwell Diffusion Coefficients for *n*-Heptane in the Propane–*n*-Heptane System

Temperature, °F.	Pressure, lb./sq. in. 14.696	20	30	40	50	60
100	0.0645*	0.0569				
130	0.0860	0.0780	0.0650	0.0549		
160	0.1119	0.1010	0.0854	0.0740	0.0648	0.0569
190	0.1459	0.1329	0.1130	0.0982	0.0880	0.0789
220	—	0.1696	0.1471	0.1302	0.1161	0.1055

*Maxwell diffusion coefficients expressed in lb./sec.

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