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Viscosity and Thermal Conductivity of Nitrogen—*n*-Heptane and Nitrogen—*n*-Octane Mixtures

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Measurements of the thermal conductivity and viscosity of *n*-heptane and *n*-octane in the gas phase were made at temperatures of 100° and 160°F. and at pressures below 1 atm. In addition, measurements of the viscosity and thermal conductivity of binary gas mixtures of nitrogen and *n*-heptane were made at 160°F. at pressures below 1 atm.

Only limited measurements of the viscosity and thermal conductivity of *n*-heptane and *n*-octane in the gas phase have been made. In the case of viscosity, these include the measurements of Lambert (*11*) and of Melaven (*13*). Moser (*14*) and Lambert (*11*) measured the thermal conductivity of these two aliphatic hydrocarbons in the gas phase. There appear to be no measurements of the viscosity or thermal conductivity of mixtures of these hydrocarbons with nitrogen or air.

The evaporation of *n*-heptane (*1, 2, 10*) and *n*-octane (*20*) into turbulent air streams has been studied in the course of experimental work on the material transport from spheres. In the analysis of the results, specific information concerning the viscosity and thermal conductivity of mixtures of these hydrocarbons with air was desirable. The available methods of predicting the viscosity and thermal conductivity of mixtures (*3, 12, 21*) are based primarily on the Chapman-Enskog theory (*9*) which is applicable to monatomic spherical species of molecular weights which do not differ markedly. Since the analysis of turbulent transport in air streams depends upon a knowledge of the transport properties of mixtures, limited measurements were made of the thermal conductivity and viscosity of binary gas mixtures of *n*-heptane with nitrogen at pressures between atmospheric and attenuation away from the dew point.

MIXTURE RULES

Chapman and Enskog (*9*) developed basic principles for behavior of mixtures of monatomic species involving spherical molecules in mixtures where the nature of the properties and molecular weights of each of the species do not differ greatly. Lindsay and Bromley (*12*) have suggested a mixture rule of the following form:

$$k_m = \frac{k_1}{1 + A_1(\eta_2/\eta_1)} + \frac{k_2}{1 + A_2(\eta_1/\eta_2)} \tag{1}$$

where

$$A_1 = \frac{1}{4}\left\{ 1 + \left[\frac{\eta_1}{\eta_2}\left(\frac{M_2}{M_1}\right)^{3/4} \frac{1+(S_1/T)}{1+(S_2/T)}\right]^{1/2}\right\}^2 \frac{1+(S_{12}/T)}{1+(S_1/T)} \tag{2}$$

A_2 corresponds to A_1 with the subscripts interchanged. Similar expressions may be used for viscosity (*21*). Under the circumstances where A_1 and A_2 are unity, Equation (1) corresponds to a linear variation in the thermal conductivity or viscosity with mole fraction of the component. In the case where $A_1 = M_2/M_1$ and $A_2 = M_1/M_2$, a linear variation with weight fraction results:

TABLE 1. PROPERTIES

	Purity,* mole fraction	Specific weight† Sample, lb./cu. ft.	Reference,‡ lb./cu. ft.	Index of refraction** Sample	Reference‡
Nitrogen—Prepurified					
Vendor: Matheson Co.	0.99996				
Chromatographic analysis	0.99969	0.07235¶	0.07242#		
n-Heptane—Research grade					
Vendor: Phillips Petroleum Co.	0.9989	42.426	42.419	1.3850	1.38511
n-Octane—Research grade					
Vendor: Phillips Petroleum Co.	0.9983	43.614	43.604	1.3948	1.39505

* Reported by vendor.
† Specific weight, air free, at 77°F.
‡ American Petroleum Institute Research Project 44, Chemical Thermodynamic Properties Center, Texas A & M University, "Selected Values of Properties of Hydrocarbons and Related Compounds."
** Index of refraction at 77°F. relative to D lines of sodium.
¶ Specific weight at 73°F. expressed in lb./cu. ft.
\# Hilsenrath (7).

$$k_m = n_1 k_1 + n_2 k_2 \tag{3}$$

It should be recognized that these simple mixture rules only apply to situations where the mixture is compatible with the assumptions to which the Chapman-Enskog analysis is applied. The Chapman-Cowling theory for nonuniform gas (5) affords, with the Lennard-Jones 6-12 potential (9), a more general approach to the effect of composition upon viscosity and thermal conductivity. One form of this theory may be expressed in terms of viscosity by

$$\frac{\beta_\eta}{\eta_m} = \frac{n_1^2}{\eta_1} + \frac{2\, n_1 n_2}{\eta_{12}} + \frac{n_2^2}{\eta_2} \tag{4}$$

It is beyond the scope of this discussion to consider the derivations or extensions of these mixture rules, since the emphasis is directed entirely to the experimental results obtained.

MATERIALS

The source and several properties of the materials are set forth in Table 1. Chromatographic analysis of these materials was employed to check the purity reported by the vendor. It appears that the hydrocarbons and nitrogen utilized were of sufficient purity as not to introduce a significant uncertainty in the reported values of the viscosity and thermal conductivity.

EXPERIMENTAL METHODS

The viscosity measurements were obtained with a rotating cylinder viscometer which has been described (*4*, *15*). The small variations in the calibration of the instrument with time were followed by the measurement of the viscosity of helium near atmospheric pressure. The critically chosen values for the viscosity of this gas reported by Hilsenrath and Touloukian (*8*) were used as a basis, and during the course of these measurements the variation in the behavior of the instrument was less than 0.1%. No difficulty was experienced in the operation of the equipment at pressures well below that of the atmosphere. The composition of the mixtures investigated was determined both by gravimetric methods employed in the introduction of the nitrogen and of the *n*-heptane and by the withdrawal of samples and determination of the composition by means of partial condensation (*16*) or chromatographic techniques (*6*). The reproducibility of the measurements was within 0.5%, and the accuracy is believed to be within 1% of the values reported.

The thermal conductivity measurements were made in a spherical cell which has been described in detail (*17* to *19*). The equipment was operated under steady state conditions, and no difficulties were experienced in carrying out measurements below atmospheric pressure. Again, the composition of the mixtures introduced was established by gravimetric techniques and checked by chromatographic measurements upon samples withdrawn from the equipment.

Particular care was exercised to insure that the samples of pure *n*-heptane and *n*-octane were not contaminated by residual traces of material in the apparatus or during the introduction process. It should be recognized that the quantities of these materials involved were much smaller during these measurements than was the case for measurements at higher pressures. In most cases the *n*-heptane and *n*-octane were introduced in sufficient quantity to yield a substantial amount of liquid within the equipment. Subsequently most of the material was removed by conventional vacuum techniques to obtain the desired amount of residual material. The composition of the pure components in both the thermal conductivity and viscosity equipment was within the limits of purity reported in Table 1.

RESULTS

By following the techniques which have been described (*4*, *15*, *17* to *19*), values of the viscosity and thermal conductivity for pure *n*-heptane and *n*-octane were obtained at 100° and 160°F. and at the pressures indicated in Table 2. The corresponding values of the viscosity and thermal conductivity for mixtures of nitrogen and *n*-heptane also are reported in this table. The range and detail of the data are insufficient to give meaningful values of the standard error of estimate from any type of analytical expression describing the effect of temperature upon the results. Experience with the equipment indicates that the values of viscosity and thermal conductivity reported in Table 2 did not involve uncertainties greater than 1%. The overall standard deviation of the viscosity measurements at each state was 0.20 micropoise. In the case of the data for thermal conductivity the overall standard deviation of the data at each state was 0.012×10^{-6} B.t.u./(sec.) (ft.) (°F.). There were an insufficient number of different states investigated to justify any statistical treatment of the smoothing with respect to temperature and composition.

Shown in Figure 1 are the variations of the thermal conductivity of the nitrogen–*n*-heptane system investigated at 160°F. The variations among the several combining rules are small, indicating that to a first-order approximation the use of the Lindsay-Bromley correlation (*12*) shown in Equation (1) is satisfactory when the coefficients A_1 and A_2 are established from Equation (2). The thermal conductivity of nitrogen shown in Figure 1 was taken from the data of Hilsenrath (*7*).

Similar information is shown in Figure 2 for the viscosity of the nitrogen–*n*-heptane system at 160°F. In this instance, the critically chosen value of viscosity of nitrogen from Hilsenrath (*7*) was employed.

The practical utilization of these data in experimental transport studies is often associated with the use of *n*-heptane–air mixtures and *n*-octane–air mixtures, rather

TABLE 2. EXPERIMENTAL RESULTS FOR NITROGEN-HYDROGEN MIXTURES

Temperature, °F.	Pressure, lb./sq. in. abs.	Mole fraction nitrogen	Independent variable	Number of measurements*	Standard deviation†
			n-Heptane Viscosity, micropoise		
100	0.398		62.4	5	0.21
160	0.398		69.4	3	0.14
			Thermal conductivity, B.t.u./(sec.)(ft.)(°F.)		
100	0.398		2.121×10^{-6}	6	0.008×10^{-6}
160	0.398		2.549	6	0.011
			n-Octane Viscosity, micropoise		
100	0.398		58.2	3	0.08
160	0.398		64.9	4	0.09
			Thermal conductivity, B.t.u./(sec.)(ft.)(°F.)		
100	0.398		1.983×10^{-6}	6	0.011×10^{-6}
160	0.398		2.389	6	0.014
			Nitrogen-*n*-Heptane system Viscosity, micropoise		
100	0.781	0.5152	104.0	4	0.16
160	2.574	0.8529	154.6	3	0.37
			Thermal conductivity, B.t.u./(sec.)(ft.)(°F.)		
100	0.796	0.4998	3.074×10^{-6}	6	0.012×10^{-6}
160	2.718	0.8536	3.899	6	0.014

* For each measurement of thermal conductivity, data were obtained at four different fluxes and extrapolated to zero flux. The individual measurements represent data obtained at different sectors of the spherical gap.

† Standard deviation is defined by

$$\sigma = \left[\frac{\sum_{1}^{N}(\eta_{av} - \eta)^2}{N}\right]^{1/2} \text{ or } \left[\frac{\sum_{1}^{N}(k_{av} - k)^2}{N}\right]^{1/2}$$

than the mixtures of the hydrocarbons with nitrogen. By assuming that the coefficient for the Chapman-Cowling analysis of the nitrogen–*n*-heptane system set forth in Equation (4) applies to the air–*n*-heptane and the air–*n*-octane systems, the viscosity and thermal conductivity of the latter mixtures were calculated. Values of the viscosity and thermal conductivity of *n*-heptane and *n*-octane and their mixtures with air are recorded in Tables 3 and 4, respectively, as a function of temperature and composition for attenuation. The small effect of pressure on the viscosity and thermal conductivity needed to evaluate the data for attenuation was established from experimental data for pure hydrocarbons. The viscosity and thermal conductivity of dry air were taken from the work of Hilsenrath (*7*).

The influence of temperature upon the viscosity of the hydrocarbon components of these systems was taken from a graphical evaluation of the effect of temperature upon the pure aliphatic hydrocarbons at attenuation by utilizing specifically the measurements of Lambert (*11*), Melaven (*13*), and Moser (*14*) for the viscosity and thermal conductivity of *n*-heptane and *n*-octane. It is beyond the scope of this discussion to present in detail the methods employed in evaluating the effect of temperature upon the viscosity and thermal conductivity of the components and the mixtures at attenuation. The values of viscosity reported in Table 3 and of thermal conduc-

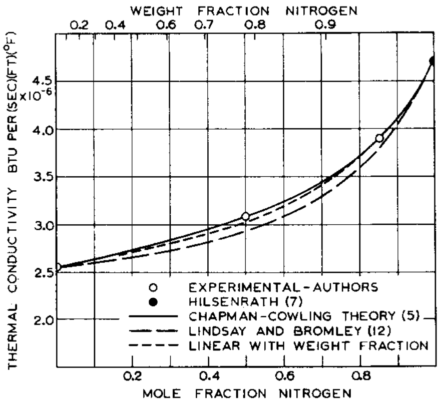

Fig. 1. Thermal conductivity of nitrogen–*n*-heptane system at 160°F.

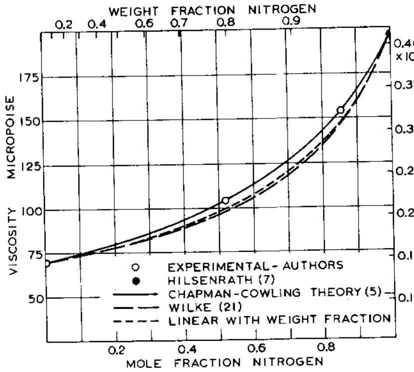

Fig. 2. Viscosity of nitrogen–*n*-heptane system at 160°F.

TABLE 3. VISCOSITY OF AIR-HYDROCARBON MIXTURES AT ATTENUATION

Mole fraction air	Temperature, °F.					
	70	100	130	160	190	220
	Viscosity, micropoise Air-*n*-Heptane					
0.0	58.77	62.40	65.80	69.41	72.76	76.43
0.1	63.08	66.93	70.55	74.37	77.93	81.80
0.2	68.01	72.11	75.97	80.02	83.81	87.99
0.3	73.74	78.12	82.25	86.57	90.61	94.99
0.4	80.49	85.19	89.63	94.24	98.58	103.24
0.5	88.60	93.66	98.44	103.40	108.07	113.06
0.6	98.54	104.01	109.22	114.55	119.61	124.98
0.7	111.08	117.02	122.71	128.49	134.00	139.78
0.8	127.42	133.91	140.18	146.45	152.49	158.75
0.9	149.69	156.80	163.76	170.58	177.23	183.96
1.0	181.94	189.70	197.45	204.80	212.15	219.40
	Air-*n*-Octane					
0.0	54.85	58.20	61.54	64.90	68.18	71.55
0.1	59.01	62.58	66.13	69.70	73.20	76.77
0.2	63.80	67.61	71.41	75.22	78.94	82.75
0.3	69.40	73.48	77.55	81.63	85.61	89.68
0.4	76.03	80.43	84.82	89.19	93.47	97.84
0.5	84.06	88.83	93.58	98.30	102.92	107.62
0.6	94.01	99.21	104.38	109.50	114.52	119.61
0.7	106.71	112.41	118.08	123.67	129.15	134.69
0.8	123.53	129.83	136.09	142.22	148.24	154.31
0.9	146.95	153.95	160.91	167.65	174.31	180.94
1.0	181.94	189.70	197.45	204.80	212.15	219.40

TABLE 4. THERMAL CONDUCTIVITY OF AIR-HYDROCARBON MIXTURES AT ATTENUATION

Mole fraction air	Temperature, °F. 70	100	130	160	190	220
	Thermal conductivity, B.t.u./(sec.)(ft.)(°F.)					
	Air-*n*-Heptane					
1.0	1.890×10^{-6}	2.121×10^{-6}	2.324×10^{-6}	2.549×10^{-6}	2.791×10^{-6}	2.994×10^{-6}
0.1	1.981	2.214	2.417	2.641	2.881	3.139
0.2	2.074	2.308	2.512	2.735	2.973	3.228
0.3	2.173	2.408	2.613	2.837	3.073	3.325
0.4	2.283	2.520	2.726	2.950	3.185	3.435
0.5	2.411	2.650	2.857	3.082	3.317	3.564
0.6	2.567	2.807	3.017	3.242	3.477	3.722
0.7	2.767	3.010	3.227	3.447	3.681	3.923
0.8	3.042	3.285	3.496	3.722	3.953	4.191
0.9	3.450	3.688	3.900	4.118	4.342	4.570
1.0	4.137	4.350	4.543	4.747	4.951	5.156
	Air-*n*-Octane					
0.0	1.804×10^{-6}	1.983×10^{-6}	2.179×10^{-6}	2.389×10^{-6}	2.591×10^{-6}	2.817×10^{-6}
0.1	1.897	2.079	2.277	2.488	2.690	2.915
0.2	1.991	2.177	2.377	2.588	2.791	3.015
0.3	2.092	2.281	2.482	2.695	2.900	3.123
0.4	2.204	2.397	2.600	2.814	3.020	3.244
0.5	2.334	2.531	2.737	2.953	3.161	3.387
0.6	2.493	2.695	2.904	3.122	3.332	3.558
0.7	2.699	2.906	3.117	3.338	3.550	3.775
0.8	2.982	3.196	3.408	3.630	3.844	4.069
0.9	3.408	3.636	3.836	4.056	4.270	4.489
1.0	4.137	4.350	4.543	4.747	4.951	5.156

tivity in Table 4 for the air–*n*-heptane and air–*n*-octane systems are recorded to at least one more significant figure than is justified by the accuracy of the experimental results.

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NOTATION

A_1, A_2 = interaction coefficients
k = thermal conductivity, B.t.u./(sec.)(ft.)(°F.)
M = molecular weight
N = number of experimental points
n = weight fraction
$\underset{\sim}{n}$ = mole fraction
S = Sutherland constant
T = absolute temperature, °R.

Greek Letters

β_η = molecular disparity function (9)
η = viscosity, micropoise
Σ = summation operator
σ = standard deviation defined in Table 2

Subscripts

1 = component 1
2 = component 2
av = average
m = mixture

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