The Thermal Conductivity of Hydrocarbon Gases at Normal Pressures

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Dimensional analysis has been applied for the correlation of the thermal conductivity of a gas to its temperature, molecular weight, heat capacity, and critical constants. This approach indicates that the group $k^*\lambda/C_p$ should be a function of z_c and T_R, where $\lambda = M^{1/2}T_c^{1/6}/P_c^{2/3}$. Experimental thermal conductivities of hydrocarbons at normal pressures (approximately 0.2 to 5 atm.) have been used to develop two relationships. The first is applicable to all types of hydrocarbons for $0.6 < T_R < 3.0$ with the exception of methane and the cyclic hydrocarbons below $T_R = 1.0$, for which the other relationship is applicable. These two relationships have been used to calculate thermal conductivities for twenty-eight gaseous hydrocarbons for which experimental data are available. Calculated values for normal paraffins, isoparaffins, olefins, diolefins, acetylenes, naphthenes, and aromatics produce an average deviation of 2.4% from experimental values for 154 points considered.

The principles of kinetic theory lead to the following expression for the thermal conductivity of a gas having rigid spherical molecules:

$$k^* = 19.891 \times 10^{-5} \frac{\sqrt{T/M}}{\sigma^2} \qquad (1)$$

In order to account for the nonrigid nature of real molecules Hirschfelder, Bird, and Spotz (*8, 9*) introduced the correction factor $\Omega^{(2,2)*}[T_N]$ for σ^2. This factor is known as the *collision integral* and is a function of temperature. Thus the first approximation of thermal conductivity for monatomic real gases is given by Hirschfelder, Curtiss, and Bird (*10*) as

$$[k]_1 = 19.891 \times 10^{-5} \frac{\sqrt{T/M}}{\sigma^2 \Omega^{(2,2)*}[T_N]} \qquad (2)$$

Collision integrals for the Lennard-Jones potential have been developed and are presented elsewhere (*10*).

To account for the internal degrees of freedom of polyatomic gases Eucken (*3, 4*) proposed the factor $\left[\frac{4}{15}\frac{C_v}{R} + \frac{3}{5}\right]$ in order to obtain the thermal conductivity of polyatomic gases from values determined from the rigid spherical molecule model. The application of the Eucken factor to Equation (*2*) produces thermal conductivities that are reliable only for the simple gases. For triatomic and polyatomic gases the Eucken factor fails to produce thermal conductivities that are in agreement with experimental data, particularly at elevated temperatures (*21*).

To overcome some of the simplifications assumed by Eucken (*3, 4*) Hirschfelder (*7*) developed a correction factor similar to that of Eucken. The Hirschfelder correction factor $\left[0.354\frac{C_p}{R} + 0.115\right]$ includes as a variable the heat capacity.

Bromley (*2*) modifies Eucken's relation by introducing separately the different energy terms in order to predict thermal conductivities for complex molecules from the Maxwell relationship $k/C_v\mu$.

It is apparent from the background already presented that the thermal conductivity of a polyatomic gas is directly related to its heat capacity. This interdependence is not unexpected, since the factors influencing heat capacity are the same as those which influence thermal conductivity. Thus the rotational and vibrational energies at elevated temperatures become more important at these levels and influence this transport property. Consequently the use of heat capacity becomes useful to account for variation in the thermal conductivity of gases at atmospheric pressure.

DIMENSIONAL ANALYSIS

Thermal conductivity at normal pressures (approximately 0.2 to 5.0 atm.) has been assumed to depend on the following variables:

$$k^* = \alpha M^a T^b_c T^c P^d_c v^e_c C^f_p R^g \qquad (3)$$

where α and the exponents are constants to be established. In Equation (3) the heat capacity of the substance has been included as a variable as a result of the previous discussion. When one uses the fundamental dimensions of mass, length, time, and temperature and applies a dimensional analysis approach, these exponents defined in terms of c, f, and g become

$$a = -\frac{1}{2} \qquad d = \frac{3}{2} - f - g$$

$$b = -1 - c + f + g \quad e = \frac{5}{6} - f - g$$

These values when substituted into Equation (3) produce the following relationship:

$$k^* \frac{M^{1/2}T_c^{1/6}}{P_c^{2/3}} = \beta T^c_R C^f_p z_c^{5/6-f-g} \qquad (4)$$

where $z_c = P_c v_c / RT_c$. The group $M^{1/2}T_c^{1/6}/P_c^{2/3}$ is constant for a substance and will be designated as λ. Thus the product $k^*\lambda$ is directly related to the heat capacity, reduced temperature, and critical compressibility factor. In order to determine α and the exponents c, f, and g it becomes necessary to utilize available heat capacities and experimental thermal conductivities.

TREATMENT OF EXPERIMENTAL THERMAL CONDUCTIVITIES

A comprehensive literature search of thermal conductivities has been carried out for the collection of available information on hydrocarbons. As a result of the search values were obtained for twenty-eight hydrocarbons of different types including normal paraffins, isoparaffins, olefins, diolefins, acetylenes, naphthenes, and aromatics. The references for the values for each hydrocarbon are presented in Table 1.

The thermal conductivity values for each hydrocarbon were plotted against reduced temperature. This information was most plentiful for methane and ranged from $T_R = 0.50$ to $T_R = 3.0$. Thermal conductivities for the other hydrocarbons fell within this temperature interval. For several, only a single value was available.

With the exception of methane the thermal conductivity of hydrocarbons produce linear relationships when plotted against temperature on log-log coordinates. This linear relationship is exhibited by ethane for temperatures up to $T_R = 1.7$ and suggests the possibility of short-range extrapolations for substances having a limited amount of experimental data. Since thermal

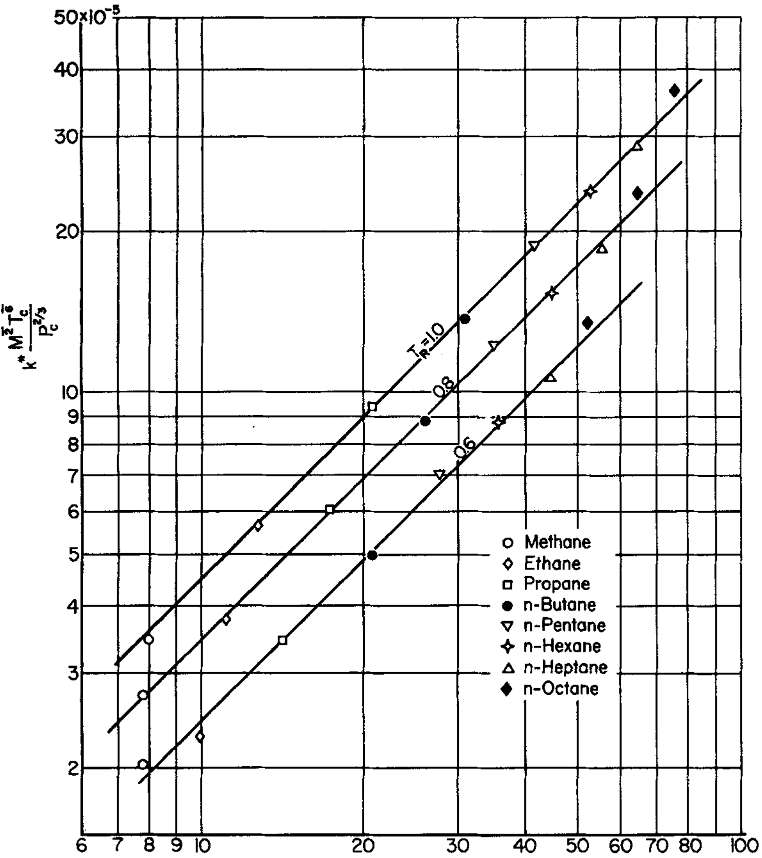

Fig. 1. Relationships of $k^* \lambda$ vs. C_p for the normal paraffins at different reduced temperatures.

conductivities are available mostly for the normal paraffins, this class of compounds was arbitrarily selected as representative of all hydrocarbons at the temperature levels of $T_R = 0.6$, 0.8 and 1.0.

The critical constants required to produce the quantity λ were obtained for the most part from the compilation of Kobe and Lynn (*14*). If constants were unavailable, critical values were calculated according to the methods of Lydersen (*22*) and Forman and Thodos (*5*). The λ values resulting from these critical constants are presented in Table 1 for all the hydrocarbons considered in this study.

The heat capacities of hydrocarbons presented by Souders, Matthews, and Hurd (*28*) were used exclusively in this study. The product $k^*\lambda$ when related to the heat capacity at the three temperature levels, $T_R = 0.6$, 0.8, and 1.0, produced on log-log coordinates the relationships of Figure 1. These relationships can be represented by straight lines having a slope of 1 and thus establish the exponent f of Equation (4) to be 1. This exponent has been used to calculate the quantity $k^*\lambda/C_p$ for all the hydrocarbons included in this study. This quantity $k^*\lambda/C_p$ was found to be essentially independent of z_c, the critical compressibility factor at fixed reduced temperatures. To illustrate this behavior values of $k^*\lambda/C_p$ are presented for the normal paraffins from methane through n-octane at $T_R = 0.6$, 0.8 and 1.0. These values are as follows:

	z_c	$(k^*\lambda/C_p) \times 10^5$		
		$T_R = 0.6$	$T_R = 0.8$	$T_R = 1.0$
Methane	0.289	0.259	0.350	0.434
Ethane	0.285	0.231	0.342	0.441
Propane	0.277	0.244	0.349	0.451
Butane	0.274	0.241	0.339	0.441
Pentane	0.269	0.253	0.350	0.453
Hexane	0.264	0.248	0.344	0.453
Heptane	0.260	0.239	0.335	0.447
Octane	0.258	0.259	0.364	0.483

Since the quantity $k^*\lambda/C_p$ is essentially constant for each reduced temperature, it can be concluded that the exponent of the critical compressibility factor in Equation (4) is zero. Thus it follows that

$$\frac{k^*\lambda}{C_p} = \beta T^c_R \qquad (5)$$

Values of $k^*\lambda/C_p$, calculated from experimental thermal conductivities were related to reduced temperature for all the hydrocarbons of this study. The normal paraffins, with the exception of methane, the isoparaffins, olefins, diolefins, and acetylenes exhibit an identical behavior. On the other hand naphthenes, aromatics, and methane follow a behavior that is unique to these substances. The compilation for the several types of hydrocarbons is presented in Figure 2. It is suggested that the different behavior of methane, naphthenes, and aromatics results from their configurational structure. These substances are relatively compact and possess small energies of internal rotation and vibration. The relationship below $T_R = 1.0$ for this class of hydrocarbons is

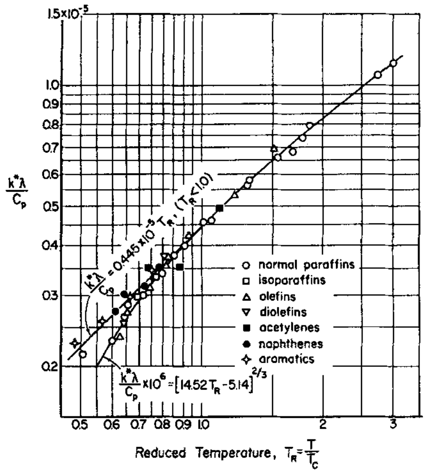

Fig. 2. Relationships of $k^* \lambda/C_p$ vs. T_R for all types of hydrocarbons.

$$\frac{k^*\lambda}{C_p} = 0.445 \times 10^{-5}\, T_R \qquad (6)$$

The relationship applicable to aliphatic hydrocarbons from $T_R = 0.5$ to $T_R = 3.0$ can be conveniently expressed in equation form as

$$\frac{k^*\lambda}{C_p} \times 10^6 = [14.52\, T_R - 5.14]^{2/3} \qquad (7)$$

Equation (7) suggests that exponent c in Equation (4) is not a constant but depends on the reduced temperature. Equation (7), above $T_R = 1.5$, has been based on the high-temperature data of methane, since thermal conductivities at these temperatures are not available for other hydrocarbons. The thermal-conductivity data of the hydrocarbons at higher temperatures

Table 1. Values of Parameter λ and Temperature Range of Thermal Conductivities

	λ	T_R	References
Normal paraffins			
Methane	0.694	0.51-3.0	*4, 6, 11, 12, 13, 16, 19, 20, 23, 29, 32*
Ethane	1.072	0.89-1.71	*12, 16, 18, 20, 23, 26, 27, 31*
Propane	1.469	0.75-1.14	*16, 18, 23, 27, 31*
n-Butane	1.800	0.65-0.81	*16, 23, 26, 27*
n-Pentane	2.279	0.58-0.72	*16, 24*
n-Hexane	2.717	0.54-0.81	*16, 17, 24, 31*
n-Heptane	3.165	0.63	*16*
n-Octane	3.634	0.60	*16*
Isoparaffins			
Methylpropane	1.896	0.67	*25*
2-Methylbutane	2.302	0.59-0.99	*16, 24*
2, 2-Dimethylpropane	2.337	0.77	*16*
2, 2-Dimethylbutane	2.658	0.93	*16*
2, 4-Dimethylpentane	3.115	0.65	*16*
2, 2, 4-Trimethylpentane	3.518	0.62	*16*
Olefins			
Ethylene	0.989	0.97-1.51	*4, 6, 12, 15, 16, 19, 26, 27, 29, 32*
Propylene	1.355	0.75-0.94	*16, 25, 26, 27*
1-Butene	1.762	0.65-0.82	*25, 27*
2-Butene (cis)	1.718	0.63-0.78	*16, 25*
2-Butene (trans)	1.769	0.64-0.79	*16, 25*
2-Methylpropene	1.762	0.65	*25*
Hexene	2.592	0.54-0.74	*24*
Diolefins			
1, 3-Butadiene	1.653	0.64-0.81	*16, 25, 27*
Acetylenes			
Ethyne	0.853	0.88-1.11	*4, 27*
Vinyl Acetylene	1.487	0.74	*27*
Naphthenes			
Cyclopentane	1.880	0.64	*16*
Cyclohexane	2.240	0.61-0.79	*16, 17, 24, 31*
Aromatics			
Benzene	0.901	0.49-0.86	*1, 17, 24, 31*
Xylene	2.758	0.764	*1*

follow the same pattern as exhibited by methane; therefore it can be assumed that this behavior is common and that Equation (7) applies to all types of hydrocarbons above $T_R = 1.0$, while it applies only to aliphatic hydrocarbons below $T_R = 1.0$.

COMPARISON OF RESULTS

The validity of Equations (6) and (7) has been tested by calculating thermal conductivities and comparing them with the corresponding experimental values. Equation (6) produced for thirty values of methane, cyclopentane, cyclohexane, benzene, and xylene an average deviation of 1.8%. For the remaining twenty-three aliphatic hydrocarbons, including methane, 116 experimental values were considered. Equation (7) reproduces these values with an average deviation of 2.6%. These comparisons indicate that a reasonable order of accuracy can be anticipated from Equations (6) and (7), in spite of inherent uncertainties in critical constants for the establishment of λ, in heat capacity values, and experimental errors associated with the original measurements of thermal conductivities. These equations are convenient for the rapid estimation of thermal conductivities at normal pressures (0.2 to 5.0 atm.) once heat capacity values are available.

NOTATION

$a,b,c,d,e,f,$ = exponents, [Equation (3)]
C_p = heat capacity at constant pressure, cal./g.-mole °K.
C_v = heat capacity at constant volume, cal./g.-mole °K.
k = thermal conductivity, cal./sec. cm. °K.
$[k]_1$ = first approximation of thermal conductivity, cal./sec. cm. °K.
k^* = thermal conductivity at normal pressures, cal./sec. cm. °K.
M = molecular weight
P_c = critical pressure, atm.
R = gas constant, 1.987 cal./g.-mole °K.
T = absolute temperature, °K.
T_c = critical temperature, °K.
T_N = normalized temperature, $T/\frac{\epsilon}{\kappa}$
T_R = reduced temperature, T/T_c
v_c = critical volume, cc./g.-mole
z_c = critical compressibility factor, $P_c v_c/RT_c$

Greek Letters

α = constant, [Equation (3)]
ϵ = maximum energy of attraction for Lennard-Jones potential, erg.
κ = Boltzmann constant, 1.3805×10^{-16} erg./°K.
λ = characteristic constant, $T_c^{1/6}/M^{1/2}P_c^{2/3}$
μ = viscosity, g./sec. cm.
σ = collision diameter for Lennard-Jones potential, Å.
$\Omega^{(2,2)*}[T_N]$ = collision integral function

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Volumetric Properties of Gas Mixtures at Low Temperatures and High Pressures by the Burnett Method: the Hydrogen-Methane System

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A Burnett type of apparatus for the study of the volumetric behavior of gases at low temperatures and high pressures was constructed. The apparatus was used to study the volumetric behavior of methane and four mixtures of hydrogen and methane from +50° to —200°F. and pressures as high as 7,000 lb./sq. in.

The experimental data were used to obtain the second virial coefficients for pure methane and for the mixtures. The results of approximately 600 experimental points were used to obtain a table of compressibility factors for methane and the mixtures at even increments of pressure and temperature.

HISTORICAL BACKGROUND

In 1936 E. S. Burnett introduced a method for determining compressibility factors without directly measuring either volume or mass (*3*). The apparatus as described was to be applied to a homogeneous gaseous phase only. Following the introduction of this apparatus by Burnett many investigators have applied the apparatus to study the compressibility of gases. The wide range of conditions over which the Burnett apparatus has been applied to obtain compressibility factors attests to the versatility of the method (*2, 12, 5, 8, 14, 15, 18, 4, 16, 17*).

ADVANTAGES AND DISADVANTAGES OF THE BURNETT METHOD

In the most commonly used experimental techniques for Z value measurement it is necessary to determine temperature and pressure for a fixed amount of gas in a measured volume. Accurate volume measurements may be made with high accuracy and precision at low pressures, but high-pressure measurements become much less certain. It is also necessary in these techniques to know the mass of the sample under observation; this is determined either directly by differential weighings of a sample bomb before and after material has been removed, or by measuring the gas volume at a low pressure where the compressibility of the material studied is accurately

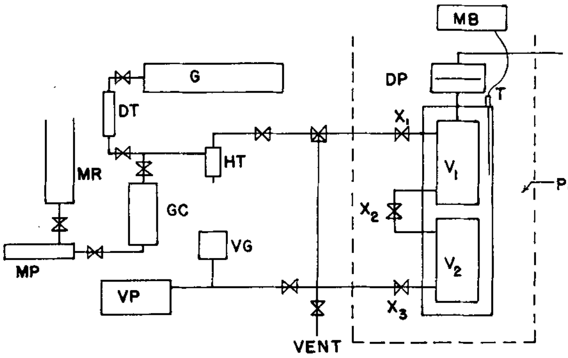

Fig. 1. Charge and expansion sections.

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