

Thermal Conductivity: Reduced State Correlation for Ethylene and Its Application to Gaseous Aliphatic Hydrocarbons and Their Derivatives at Moderate Pressures

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By means of a procedure similar to that used for the inert gases (19) and methane (20) a reduced thermal conductivity correlation was developed for ethylene from experimental data available in the literature (2, 3, 4, 9, 13). The resulting correlation permits the prediction of thermal conductivities for gaseous and liquid ethylene in the temperature range $T_R = 0.4$ to $T_R = 6.0$ and for pressures up to $P_R = 50$. For pressures below $P_R = 0.5$ this correlation was found to apply to gaseous aliphatic hydrocarbons and their derivatives but not to cyclic compounds. For these aliphatic hydrocarbons and their derivatives the relation between thermal conductivity at atmospheric pressure and temperature is $k^*/k_c^* = 0.364 T_R^{1.796}$.

Experimental thermal conductivities of ethylene in the liquid state and dense-phase region were compared with values predicted by the reduced-state correlation. The average deviation for thirty-six experimental points was 1.8%. Gaseous-state data at atmospheric pressure of alkanes, alkenes, alkynes, alcohols, ethers, halogenated derivatives, esters, aldehydes, ketones, amines, nitriles, and other aliphatic compounds were also compared with values predicted by this correlation. For 414 experimental points the average deviation was 1.63%.

Considerable experimental thermal conductivity data for organic compounds is presented in the literature. However few attempts have been made (5, 21, 22) to compile and correlate this information in a manner that would prove practical and useful for engineering purposes. In this study the thermal conductivity data for ethylene in the gaseous and liquid states have been used to develop a reduced-state correlation which predicts thermal conductivities in regions where no experimental data are available for this substance. In addition this correlation has been found to apply to gaseous aliphatic hydrocarbons and their derivatives at moderate pressures but not to cyclic compounds such as naphthenes and aromatic hydrocarbons.

DEVELOPMENT OF REDUCED-STATE CORRELATION

Thermal conductivity values for ethylene (4, 9, 13) at atmospheric pressure are plotted against reduced temperature on log-log coordinates in Figure 1. In addition available k^* values for ethane and propane are also presented in this figure in order to show the similar behavior exhibited by these typical hydrocarbons. Although thermal conductivities are available for other hydrocarbons, ethane and pro-

pane are included in this figure because their data extend over a wide temperature range and include the temperature $T_R = 1.0$.

The relationships presented in Figure 1, although developed from atmospheric pressure data, are applicable to pressures as low as approximately 5 cm. of mercury and as high as 5 to 10 atm. For pressures below 5 cm. of mercury the thermal conductivity of gases decreases with decreasing pressure, whereas for pressures above 10 to 15 atm. this transport property increases with increasing pressure. In the pressure interval 5 cm. of mercury to approximately 10 atm. the thermal conductivity of gases remains essentially unchanged, and therefore, like viscosity, it is independent of pressure. The dependence of thermal conductivity on pressure, at isothermal conditions, suggests the following different classifications of pressure ranges:

Low pressure	$P < 5$ cm. mercury
Moderate pressure	5 cm. mercury (1 atm.) $< P < 10$ atm.
High pressure	$P > 10$ atm.

With these designations the moderate pressure range for gases includes the more common case of atmospheric pressure and consequently the term "moderate pressure" becomes interchangeable with atmospheric pressure.

The straight-line relationships of Figure 1 are essentially parallel to each

other and indicate that ethylene, ethane, and propane follow a corresponding state behavior at atmospheric pressure. This fact can be substantiated analytically from the linear relationship

$$\log k^* = s \log T_R + \log \alpha \quad (1)$$

When one applies the boundary conditions, $k^* = k^*_{T_c}$ at $T_R = 1$, Equation (1) becomes

$$\log \frac{k^*}{k^*_{T_c}} = s \log T_R \quad (2)$$

Equation (2) suggests that a single relationship should result when the ratio $k^*/k^*_{T_c}$ is plotted against T_R on log-log coordinates, if s bears the same functional temperature relationship for the different substances. Figure 2 presents a relationship of $k/k^*_{T_c}$ ratios with reduced temperature for ethylene, ethane, and propane. The resulting straight line indicates that the slope is independent of temperature and that the theorem of corresponding states is applicable to the thermal conductivity of these substances for pressures near 1 atm. The single straight line of Figure 2 permits the extrapolation of the original lines of Figure 1.

The variables of Equation (2) can be expressed conveniently as

$$\frac{k^*}{k^*_{T_c}} = T_R^s \quad (3)$$

The application of a reference state other than $T_R = 1$ and 1 atm. is made possible by associating with Equation (3) the thermal conductivity corresponding to an arbitrarily selected ref-

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erence state. Thus if this state is chosen to be the critical point, it follows that

$$\frac{k^*}{k_c} \frac{k_o}{k^*_{T_c}} = T_R$$

Since the ratio $k_o/k^*_{T_c}$ for a substance is constant, it follows that

$$\frac{k^*_R}{\alpha} = T_R \quad (4)$$

where $\alpha = k^*_{T_c}/k_c$. It is apparent from Equations (3) and (4) that the ratios $k^*/k^*_{T_c}$ and k^*_R/α bear the same functional relationship with temperature. For the case when $T_R = 1$ Equation (4) simplifies to produce

$$k^*_{T_c} = \alpha k_c \quad (5)$$

In this study the true thermal conductivity at the critical point is determined only for ethylene by following the procedure outlined in the study for the inert gases (19).

The liquid and high pressure gaseous state data for ethylene (2, 3, 13) were correlated in Figure 3 by plotting the residual thermal conductivity, $k - k^*$, against the corresponding density values (1, 16, 28). These data produce a single curve which is continuous for both the gaseous and liquid states. From this correlation a critical thermal conductivity value for ethylene, $k_c = 12.05 \times 10^{-5}$ cal./sec. cm. °K., was obtained by the use of the critical density, $\rho_c = 0.227$ g./cc. and a value of $k^*_{T_c} = 4.40 \times 10^{-5}$ cal./sec. cm. °K.

Reduced thermal conductivities, k/k_c , for ethylene were calculated from the available data (2, 3, 4, 9, 13) to produce the correlation presented in Figure 4. It is apparent that these data are fragmentary and restricted to specific regions of temperature and pressure.

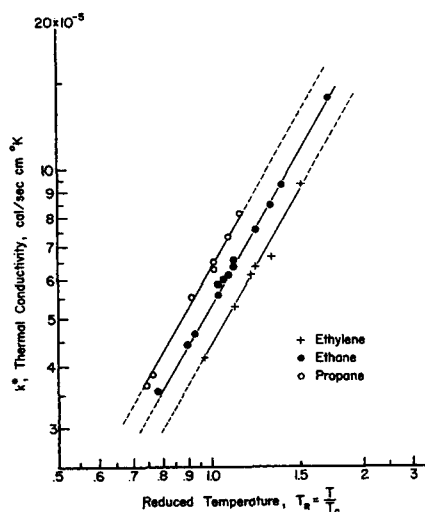


Fig. 1. Thermal conductivity-temperature relationships for ethylene, ethane, and propane at atmospheric pressure.

The construction of a complete reduced-state correlation for ethylene requires that the k^* data presented in Figure 1 be extended over a wider temperature range. Since no experimental data are available above $T_R = 1.71$, the k^* curve for ethylene has been extrapolated on a linear basis up to $T_R = 6.4$. It is felt that this extrapolation is reasonably valid, since the experimental k^* vs. T_R curves in Figure 1 are linear over the temperature range $T_R = 0.75$ to $T_R = 1.71$.

In order to develop the final thermal conductivity plot it was necessary to obtain density values for ethylene covering the required range of temperature and pressure. Experimental density values of Amagat (1), Michels and Geldermans (16), and York and White (28) were used. In the region where no experimental data were available, the compressibility factors of Nelson and Obert (18) were used to extend the temperature range of the experimental density values. In the liquid region saturated liquid densities were corrected for the effect of pressure by the use of the ω -factors of Watson (27).

Figure 5 presents the final reduced-state correlation for ethylene. The moderate pressure isobar, $P_R \approx 0$, was obtained directly from Figure 1 and the high temperature extrapolation to $T_R = 6.4$. At higher pressures thermal conductivities were calculated with Figure 3, the extrapolated k^* data of Figure 1, and the available density data for ethylene.

Each isobar was constructed by first selecting for a fixed pressure a number of density values covering the temperature range. Residual thermal conductivities, $k - k^*$, corresponding to each were obtained from Figure 3. With the k^* values at the same temperature, thermal conductivities were then calculated for this fixed pressure and corresponding temperatures. Reduced thermal conductivities were then calculated from these values and plotted in Figure 5. Isobars constructed in this manner extend up to a reduced pressure of $P_R = 50$ and cover the reduced temperature range $T_R = 0.5$ to $T_R = 6.4$. In order to establish liquid-state isobars at pressures above $P_R = 5.0$ it was necessary to extrapolate the gaseous-state curves into this region.

DISCUSSION OF RESULTS FOR ETHYLENE

The available experimental data for ethylene have been compared with thermal conductivity values calculated from an enlarged plot of Figure 5. The results of these comparisons are tabulated below:

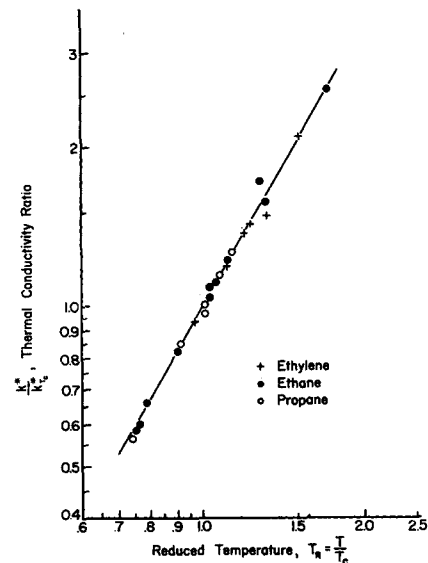


Fig. 2. Correlation of thermal conductivity ratios for ethylene, ethane, and propane at atmospheric pressure.

	Number of points	Average deviation, %
Moderate pressure ($P_R \approx 0$)	6	2.0
High pressure ($P_R > 0$)	23	1.8
Liquid state	7	2.0

For the thirty-six experimental points the over-all deviation is 1.87% with a maximum deviation of 8.8% for ethylene near the critical point. The deviations tabulated above represent percentage differences between values calculated from a large plot of Figure 5 and the experimental thermal conductivities used to develop this correlation. These deviations are only significant in the comparison between values read from Figure 5 and the corresponding experimental values used to develop this correlation. No attempt has been made to assess the experimental data used. The comparisons given above show that the reduced-state correlation for ethylene reproduces experimental values very closely over a wide range of conditions. Therefore it is felt that Figure 5 is reliable for predicting thermal conductivity values for ethylene over the entire range of temperatures and pressures presented.

The enlarged plot of Figure 5 has also been used to calculate thermal conductivities for the binary systems of ethylene with nitrogen and ethylene with carbon dioxide (7). Critical constants for these mixtures were calculated with the pseudocritical concept

$$\% \text{ Deviation} = \frac{|\text{experimental-calculated}|}{\text{experimental}} \times 100.$$

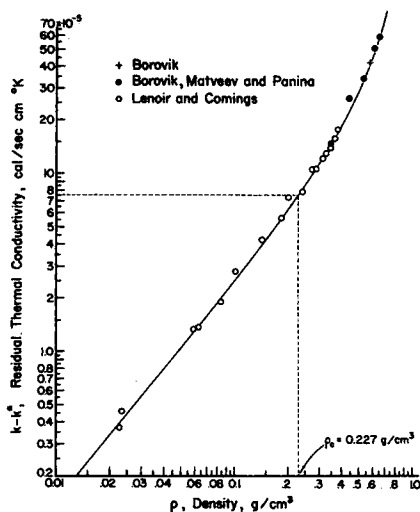


Fig. 3. Residual thermal conductivity-density relationship for ethylene in the gaseous and liquid states.

of Kay (8). The required quasicritical thermal conductivities for nitrogen and carbon dioxide were obtained from experimental k^* values and the corresponding k^*_R values obtained from Figure 5. The calculation of these fictitious critical thermal conductivities is presented later and is outlined in Examples 2 and 3.

Thermal conductivities calculated from Figure 5 have been compared with the data of Junk and Comings (7) for these mixtures for the single temperature of 41°C. and pressures up to 200 atm. The results of these comparisons are presented in Table 1. From these results it appears that Figure 5 can be used to calculate reliable thermal conductivities at high pressures for mixtures of ethylene with nitrogen and ethylene with carbon dioxide. These results indicate that this figure may apply to other multicomponent systems containing ethylene. In the absence of reliable experimental data Figure 5 can be used to obtain reasonable thermal conductivity values for mixtures of ethylene and other nonassociating substances such as the monatomic, diatomic, triatomic, and hydrocarbon gases. However it is doubtful that this correlation is capable of predicting reliable thermal conductivities for mixtures of ethylene with hydrogen, ammonia, or other gases having an unusual corre-

sponding state behavior or possessing polarity effects.

GENERAL APPLICATION TO OTHER ORGANIC COMPOUNDS

Thermal conductivity data for a large number of hydrocarbons and their derivatives have been obtained from the literature in order to test the generality of Figure 5. Thermal conductivities calculated for organic liquids other than ethylene did not agree with the experimental data. Large deviations were found to occur even for molecularly similar substances, such as ethane, propane, and other normal paraffins. Therefore Figure 5 is not applicable to

Figure 6 presents a comparison of the k^*/k_c ratios obtained from experimental data with corresponding k^*_R values for the homologous series of aliphatic hydrocarbons, alcohols, ethers, halogenated hydrocarbons, aldehydes, esters, ketones, amines, nitriles, cyclic hydrocarbons and other miscellaneous compounds. These k^*/k_c ratios fall on the $P_R \approx 0$ curve of Figure 5 in all cases with the exception of the cyclic hydrocarbons. The behavior of the cyclic compounds is presented in Figure 7. The agreement between experimental and predicted thermal conductivity ratios for these substances is presented below:

	Number of points	Temperature range, T_R	Average deviation, %
Aliphatic hydrocarbons	62	0.61-1.71	1.7
Alcohols	143	0.53-0.85	0.9
Ethers	75	0.56-1.04	1.3
Halogenated hydrocarbons	50	0.60-1.17	2.2
Aldehydes	28	0.60-0.87	1.1
Esters	20	0.67-0.87	1.8
Ketones	12	0.63-0.90	1.5
Amines	9	0.69-0.85	1.2
Nitriles	6	0.62-0.79	1.6
Cyclic hydrocarbons	44	0.44-0.90	3.2
Miscellaneous	9	0.64-0.78	1.4

the calculation of thermal conductivities for liquids other than ethylene.

Thermal conductivity data at atmospheric pressure for organic compounds (4, 6, 9, 10, 11, 12, 14, 15, 17, 23, 25, 26) in the gaseous state were segregated into homologous series to determine if Figure 5 applies to each family of substances. Quasicritical thermal conductivities for each substance were calculated by dividing k^*_R values from Figure 5 into available experimental k^* values. It should be emphasized that the quasicritical thermal conductivities obtained in this manner do not necessarily represent the true thermal conductivities at the critical point. They are undoubtedly closely related to the actual critical thermal conductivity, but until further evidence is presented they should be interpreted merely as correlating parameters and therefore should be used only with Figure 5. Quasicritical thermal conductivities for all substances considered in this study are summarized in Table 2 along with their respective critical temperatures.

These results indicate that the moderate pressure isobar, $P_R \approx 0$, of Figure 5 is generally applicable to the aliphatic hydrocarbons and their derivatives with the exception of cyclic compounds. These compounds as shown in Figure 7 tend to follow a trend which is different than that exhibited for the aliphatic hydrocarbons and their derivatives. Since the thermal conductivity-temperature relationship at atmospheric pressure for aliphatic hydrocarbons and their derivatives is linear when plotted on logarithmic coordinates, it can be expressed conveniently as

$$\frac{k^*}{k_c} = 0.364 T_R^{1.798} \quad (6)$$

Equation (6) can be used to calculate the thermal conductivities of other aliphatic derivatives not included in this study. In order to apply Equation (6) it is necessary to have a single experimental thermal conductivity measurement at atmospheric pressure in order to produce a quasicritical thermal conductivity for the substance. If an experimental value is not available, then k_c can be estimated from the following equation:

$$k_c = 62.2 \times 10^{-5} \frac{\sqrt{M P_c^{2/3}}}{T_c^{1/3}} \quad (7)$$

Quasicritical thermal conductivity values calculated with Equation (7) produced an average deviation of 8.5% when compared with the values listed in Table 2. This comparison included

TABLE 1. COMPARISON OF CALCULATED AND EXPERIMENTAL THERMAL CONDUCTIVITIES FOR BINARY ETHYLENE MIXTURES

	Number of points	Ethylene mole %	Pressure, atm.	Deviation, %
Nitrogen-ethylene (41°C.)	15	20.0	1.0-206.5	4.5
	16	38.8	1.0-197.8	4.0
	15	67.5	1.0-196.9	3.3
	17	79.2	1.0-197.3	1.4
Carbon dioxide-ethylene (41°C.)	21	55.5	1.0-199.9	6.2
	21	79.8	1.0-198.1	4.8

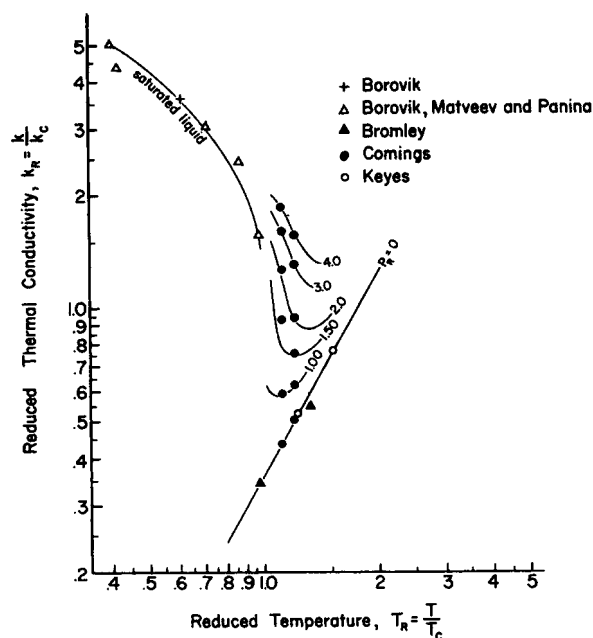


Fig. 4. Reduced-state plot of experimental thermal-conductivity data for ethylene.

over thirty different hydrocarbon derivatives other than halogenated hydrocarbons. For halogenated hydrocarbons a value of 24.4×10^{-5} should be used with Equation (7) in place of the constant 62.2×10^{-5} . The following examples illustrate the use of Figure 5 and Equation (6):

Example 1

Calculate the thermal conductivity of ethylene at 106°F . and 164.1 atm. The critical constants for ethylene are $T_c = 508.3^\circ\text{R}$. and $P_c = 50$ atm. The reduced temperature and pressure corresponding to these conditions are:

$$T_r = \frac{406 + 106}{508.3} = 1.11$$

$$P_r = \frac{164.1}{50.0} = 3.28$$

A reduced thermal conductivity value, $k_r = 1.66$, corresponding to $T_r = 1.11$ and $P_r = 3.28$ is obtained from Figure 5. The thermal conductivity at these conditions then becomes $k = 1.66 (12.05 \times 10^{-5}) = 20.0 \times 10^{-5}$ cal./sec. cm. $^\circ\text{K}$. or in engineering units $k = 241.9 (20.0 \times 10^{-5}) = 0.0484$ B.t.u./hr. ft. $^\circ\text{R}$.

Lenoir and Comings (13) report an experimental value of $k = 0.0491$ B.t.u./hr. ft. $^\circ\text{F}$. at these conditions.

Example 2

Determine the thermal conductivity of a mixture containing 0.612 mole fraction nitrogen and 0.388 mole fraction ethylene at 108°F . and 89.3 atm. The thermal conductivity of nitrogen at 108°F . and atmospheric pressure is found to be 6.46×10^{-5} cal./sec. cm.

$^\circ\text{K}$. from the work of Lenoir and Comings (13):

	$T_c, ^\circ\text{R}$	P_c, atm
Nitrogen	227	33.5
Ethylene	508	50.0

The quasicritical thermal conductivity of nitrogen is calculated from the value $k^* = 6.46 \times 10^{-5}$ cal./sec. cm. $^\circ\text{K}$. as follows:

$$T_r = \frac{460 + 108}{227} = 2.50$$

$$P_r = \frac{1}{33.5} = 0.03$$

From Figure 5 $k_r^* = 1.87$; therefore $k^* = 6.46/1.87 = 3.45$ cal./sec. cm. $^\circ\text{K}$.

Pseudocritical Constants

$$T_r^* = 0.612 (227) + 0.388 (508) = 336^\circ\text{R}$$

$$P_r^* = 0.612 (33.5) + 0.388 (50.0) = 39.9 \text{ atm}$$

$$k_r^* = 0.612 (3.45 \times 10^{-5}) + 0.388$$

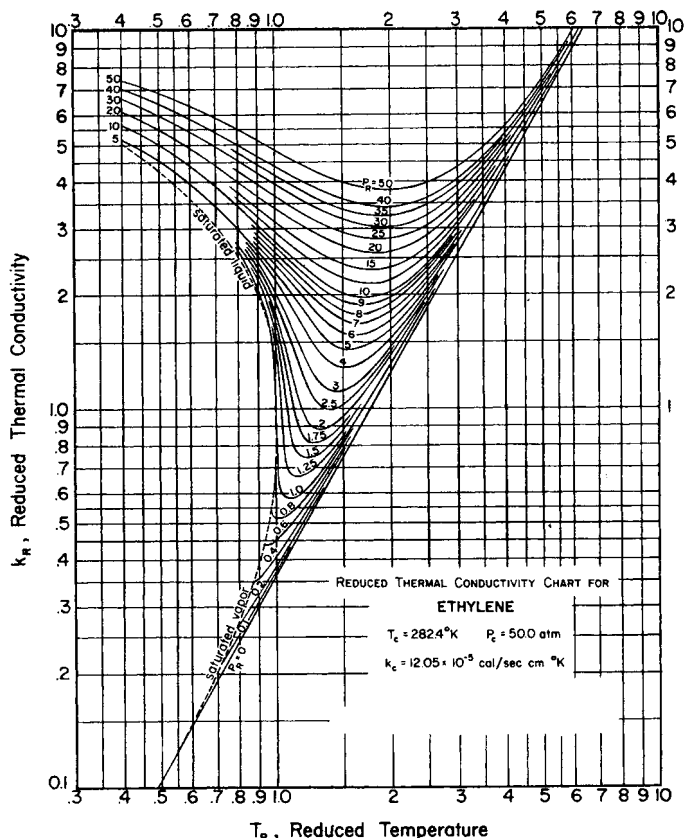


Fig. 5. Reduced thermal-conductivity chart for ethylene.

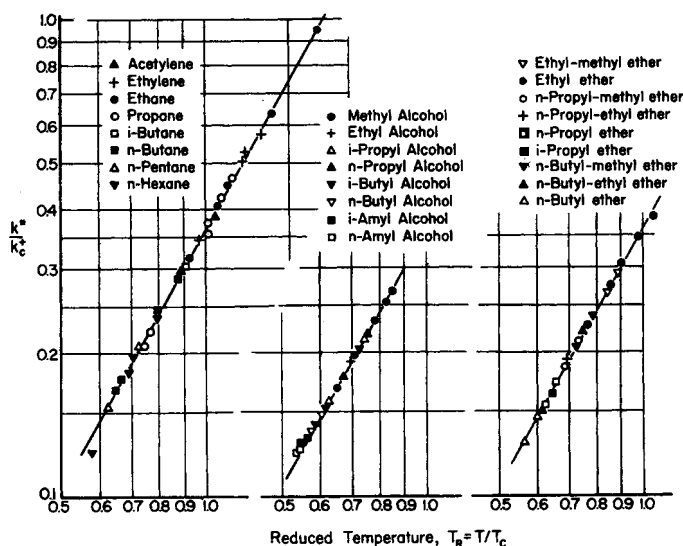


Fig. 6. Thermal conductivity-temperature relationships for aliphatic hydrocarbons, alcohols, and ethers in the gaseous state and atmospheric pressure.

TABLE 2. QUASICRITICAL THERMAL CONDUCTIVITIES OF ORGANIC COMPOUNDS*

	$T_c, ^\circ\text{K.}$	$k^*, \text{cal./sec. cm. } ^\circ\text{K.}$		$T_c, ^\circ\text{K.}$	$k^*, \text{cal./sec. cm. } ^\circ\text{K.}$
Alkanes			Ethers		
Ethane	305.5	14.6×10^{-5}	Ethyl-methyl ether	437.9	21.4×10^{-5}
Propane	370.0	17.42	Ethyl ether	467	21.8
<i>i</i> -Butane	408.1	18.8	<i>n</i> -Propyl-methyl ether	475.3	22.5
<i>n</i> -Butane	425.2	19.6	<i>n</i> -Propyl-ethyl ether	500.6	23.1
<i>n</i> -Pentane	469.8	21.1	<i>n</i> -Propyl ether	529.2	23.5
<i>n</i> -Hexane	507.9	23.0	<i>i</i> -Propyl ether	505.4	22.6
Alkenes			<i>n</i> -Butyl-methyl ether	511.1	24.0
Ethylene	282.4	12.05	<i>n</i> -Butyl-ethyl ether	529.8	24.2
Alkynes			<i>n</i> -Butyl ether	581.0	24.0
Acetylene	309	15.1	Halogenated hydrocarbons		
Alcohols			Methyl bromide	464	11.2
Methanol	513.2	25.5	Methyl chloride	416.3	12.6
Ethanol	516	25.8	Methyl iodide	528	10.0
<i>i</i> -Propanol	508.8	25.0	Dichloromethane	583	10.3
<i>n</i> -Propanol	537	25.8	Ethyl chloride	460.4	16.2
<i>i</i> -Butanol	545.9	26.2	1,1-Dichloroethane	523	15.7
<i>n</i> -Butanol	555.2	26.4	1,2-Dichloroethane	561	17.5
<i>i</i> -Pentanol	570.1	28.2	Carbon tetrachloride	556.4	10.6
<i>n</i> -Pentanol	574.0	27.1	Chloroform	536.6	12.8
Esters			Aldehydes		
Methyl acetate	506.9	20.2	Acetaldehyde	461	16.6
Ethyl acetate	523.3	21.4	Ketones		
Ethyl formate	508.5	21.1	Acetone	508.7	20.0
Amines			Nitriles		
Diethylamine	496	23.9	Acetonitrile	547.9	18.0
Triethylamine	532	24.2	Miscellaneous		
			Dioxane	585	24.9
			Ethyl nitrate	538.6	20.4
			Nitromethane	588	19.0

* The reported quasicritical thermal conductivities are not necessarily true critical thermal conductivities, and therefore their use should be limited with Figure 5.

$$(12.05 \times 10^{-5}) = 6.79 \times 10^{-5} \text{ cal./sec. cm. } ^\circ\text{K.}$$

$$T'_R = \frac{460 + 108}{336} = 1.69$$

$$P'_R = \frac{89.3}{39.9} = 2.24$$

For this mixture a value of $k'_R = 1.12$ is obtained from Figure 5 for $T'_R = 1.69$ and $P'_R = 2.24$. The thermal conductivity for the mixture then becomes $k' = 1.12 (6.79 \times 10^{-5}) = 7.60 \times 10^{-5}$ cal./sec. cm. $^\circ\text{K.}$, or in engineering units $k' = 241.9 (7.60 \times 10^{-5}) = 0.0184$ B.t.u./hr. ft. $^\circ\text{R.}$

Junk and Comings (7) report for this mixture at these conditions an experimental value of $k = 0.0184$ B.t.u./hr. ft. $^\circ\text{F.}$

Example 3

Determine the thermal conductivity of gaseous diethyl ether at atmospheric pressure and 415°F. The thermal conductivity of this substance at atmospheric pressure and 211°F. is reported by Vines and Bennett (26) to be 5.30×10^{-5} cal./sec. cm. $^\circ\text{K.}$ The critical temperature of diethyl ether is 381°F.

This experimental value is used to determine the quasicritical thermal conductivity from Equation (6):

for $t = 211^\circ\text{F.}$

$$T_R = \frac{460 + 211}{460 + 381} = \frac{671}{841} = 0.798$$

$$\frac{k^*}{k'_c} = 0.364 (0.798)^{1.786} = 0.243$$

$$k^*_c = \frac{5.30 \times 10^{-5}}{0.243} = 21.8 \times 10^{-5} \text{ cal./sec. cm. } ^\circ\text{K.}$$

for $t = 415^\circ\text{F.}$

$$T_R = \frac{460 + 415}{460 + 381} = \frac{875}{841} = 1.04$$

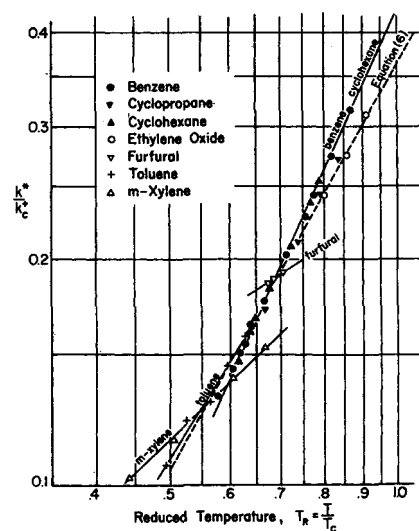


Fig. 7. Thermal conductivity-temperature relationships for cyclic compounds at atmospheric pressure.

$$\frac{k^*}{k'_c} = 0.364 (1.04)^{1.786} = 0.390$$

$$k^* = 0.390 (21.8 \times 10^{-5}) = 8.50 \times 10^{-5} \text{ cal./sec. cm. } ^\circ\text{K.}$$

Vines and Bennett (26) report for diethyl ether at 415°F. a value of $k^* = 8.55 \times 10^{-5}$ cal./sec. cm. $^\circ\text{K.}$

Thermal conductivity values for ethane and propane at pressures up to 200 atm. were calculated with an enlarged plot of Figure 5 and were compared with experimental values (9, 12, 14) presented in the literature. Data for these hydrocarbons agreed closely with calculated values for reduced pressures up to $P_R \approx 0.5$. In this range average deviations were generally less than 2.0%. However for reduced pressures $0.5 \leq P_R \leq 1.0$ the average deviation increased to 5.2%. For reduced pressures $P_R > 1.0$, the experimental data of Leng and Comings (12) for ethane and Lenoir, Junk, and

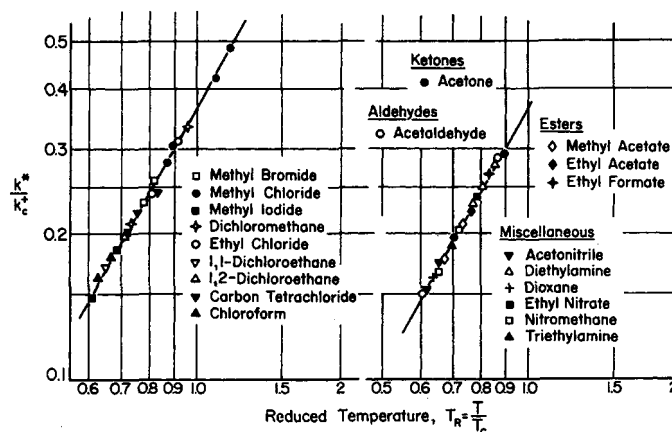


Fig. 8. Thermal conductivity-temperature relationships for halogenated hydrocarbons, esters, aldehydes, ketones, and miscellaneous aliphatic derivatives in the gaseous state and atmospheric pressure.

Comings (14) for propane did not agree with values predicted with Figure 5. Deviations above $P_R = 1.0$ were generally greater than 20%.

These results suggest that Figure 5 may be used for pressures up to $P_R \approx 0.5$ for hydrocarbons other than ethylene. The failure of the theorem of corresponding states to apply adequately at elevated pressures for these substances may be the result of increased rotational and vibrational energy contributions present in the larger hydrocarbon molecules. However it is interesting to note that no such discrepancies were found to exist at atmospheric pressure for a large number of aliphatic hydrocarbons and related derivatives over a wide temperature range covered in Figures 6 and 8. As a result no firm conclusions can be drawn with regard to the validity of Figure 5 in the high-pressure region of gases and liquids other than ethylene. Therefore until more high pressure experimental values become available, Figure 5 should be used to calculate thermal conductivities for other aliphatic hydrocarbons for pressures up to $P_R = 0.5$. However in the absence of such experimental data this correlation can be used to calculate tentative thermal conductivity values for aliphatic hydrocarbons in their gaseous state and for pressures below $P_R = 0.5$.

LIMITATIONS OF REDUCED-STATE CORRELATIONS

Reduced-state correlations are based on the classical theory of corresponding states as first proposed by van der Waals (24). It is well known that this theory is not rigorous for all substances but is dependent on the molecular configuration and intermolecular force relationships of the molecules of a given substance. Therefore a single reduced state thermal conductivity correlation cannot apply to all substances over a wide range of temperatures and pressures. This is clearly illustrated by a comparison of the reduced thermal conductivity relationships at moderate pressures for the inert gases (19), methane (20), and the present work concerned with the aliphatic hydrocarbons. It should be pointed out that these thermal conductivity relationships do not follow a similar behavior. In this investigation the slope of the moderate pressure isobar, $\log k^*/\log T_R$ is constant. For the inert gases (19) this ratio decreases with an increase in temperature, while for methane (20) an opposite behavior has been reported. In view of these results it is reasonable to expect that each family of molecularly similar substances will follow a corresponding states behavior and therefore should correlate

on a single reduced-state plot. Previous correlations for the inert gases (19) and methane (20) and the present correlation for the aliphatic hydrocarbons support this conclusion. In the future it is felt that this approach should be utilized for other families of substances in order to provide a comprehensive summary of transport properties in general.

CONCLUSIONS

The reduced-state correlation of Figure 5 gives reliable results for ethylene for the gaseous and liquid states at all conditions of temperature and pressure. This correlation can also be used to calculate reliable thermal conductivities at moderate pressures (1 atm.) for gaseous alkanes, alkenes, alkynes, alcohols, ethers, halogenated hydrocarbons, aldehydes, esters, ketones, amines, nitriles, and other aliphatic derivatives but is not applicable to cyclic hydrocarbons, such as naphthenes and aromatics. In the absence of experimental data this correlation may be used to predict tentative thermal conductivity values for noncyclic substances at higher pressures. However the correlation fails to produce reliable results for any organic liquid other than ethylene.

In addition Figure 5 applies to ethylene mixtures provided a quasical critical thermal conductivity is used for the other components. In this treatment the pseudocritical concept of Kay (8) has been found to apply.

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NOTATION

k	= thermal conductivity, cal./sec. cm. °K.
k^*	= thermal conductivity at $P_R \approx 0$ (approximately 1 atm.), cal./sec. cm. °K.
k_c	= critical thermal conductivity, cal./sec. cm. °K.
k^*	= quasical critical thermal conductivity, cal./sec. cm. °K.
k_R	= reduced thermal conductivity, k/k_c .
k^*_R	= reduced thermal conductivity at moderate pressures, k^*/k_c .
$k^*_{T_c}$	= thermal conductivity at the critical temperature and atmospheric pressure, cal./sec. cm. °K.
M	= molecular weight
P	= pressure, atm.
P_c	= critical pressure, atm.
P_R	= reduced pressure, P/P_c .
s	= slope or exponent, $\phi(T_R)$
T	= absolute temperature, °K.

T_c = critical temperature, °K.
 T_R = reduced temperature, T/T_c .

Greek Letters

α = constant
 ρ = density, g/cc.
 ρ_c = critical density, g./cc.

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