Physical Properties of Hydrocarbons

Part 9—Thermal Conductivity of C_1 to C_4 Hydrocarbons

Robert W. Gallant
The Dow Chemical Co., Plaquemine, La.

THIS ARTICLE PRESENTS thermal conductivity data for the C_1 to C_4 straight chain hydrocarbons covered in Parts 1-4 of this series of physical properties. The importance of thermal conductivity in heat transfer calculations has resulted in extensive experimental work by many investigators over the years. However, the difficulty of obtaining steady state conditions and minimizing radiation losses has presented a formidable task for these investigators, and only in recent years have they been able to design equipment which gives reliable and reproducible results at high temperatures. Much of the data available in the standard handbooks is of questionable value, because it is based on data gathered before 1940.

For those interested in an in-depth review of thermal conductivity, McLaughlin[1] has presented an excellent review of both the present status of the theory, and also an analysis of the problems involved in experimentally measuring thermal conductivity. Coates and Sakiadis have also been active in this area and have numerous publications on experimental apparatus,[2,3] literature surveys of available data on liquid thermal conductivity,[4,5] and estimation methods.[6,7] The past 15 years have seen major progress made in all areas of thermal conductivity research but there remain major gaps in high temperature and high pressure thermal conductivity measurement.

Because of the limited amount of experimental data over wide temperature ranges, it has been necessary to use estimation methods extensively. In past articles reference has been made to several good reviews on estimation methods[8,9] and no attempt has been made to explain the methods in depth. However, both these reviews were published before 1960 and do not include the newer estimation methods developed in the early 1960s by Thodos[10,11,12] for vapor thermal conductivity and by Robbins and Kingrea[13] for liquid thermal conductivity. While the reader is referred to the original articles for the thorough explanation of the methods and their derivation, the methods will be discussed here to illustrate their use and limitations.

Liquid Thermal Conductivity. There is almost no data available on the liquid thermal conductivities of the C_1-C_4 hydrocarbons. Hence, Figures 9-1, 9-2, 9-3 and 9-4, which present the liquid thermal conductivities of the hydrocarbons from —200° C to just below their critical point, were all derived by using the estimation method of Robbins and Kingrea. For the C_1-C_4 straight chain hydrocarbons,

$$k = A \frac{C_p \, (d)^{\,4/3}}{T}$$

where

k = thermal conductivity at temperature T, in Btu/hr-ft-°F
A = a calculated constant for each hydrocarbon
C_p = liquid heat capacity at temperature T, in Btu/lb° F
T = temperature, in degrees Rankine

It is obvious that the accuracy of the calculated thermal conductivity is directly dependent upon the accuracy of the liquid heat capacity and density. The data on these properties were presented in Parts 1-4 of this series. Densities are accurate to ± 1 percent, whether determined experimentally or by estimation methods. Liquid heat capacities were largely estimated by the method of Schiff, which gives an error of 5-10 percent. The constant A is evaluated from the equation

$$A = \frac{0.0473 \, T_c}{(S)(M)^{1/3}}$$

where

T_c = critical temperature, in degrees Rankine
S = a calculated constant for each hydrocarbon
M = molecular weight
$S = \dfrac{H_v}{T_b} + 4.56 \, log \, \dfrac{492}{T_b}$

where

H_v = heat of vaporization at the normal boiling point, in Btu/lb-mole
T_b = normal boiling point, in degrees Rankine

Since the critical temperature, boiling point, and heat of vaporization are accurately known for these hydrocarbons, the error will be largely dependent upon the accuracy of the liquid heat capacity. Thus, the calculated results should be accurate to ±10 percent. In the mod-
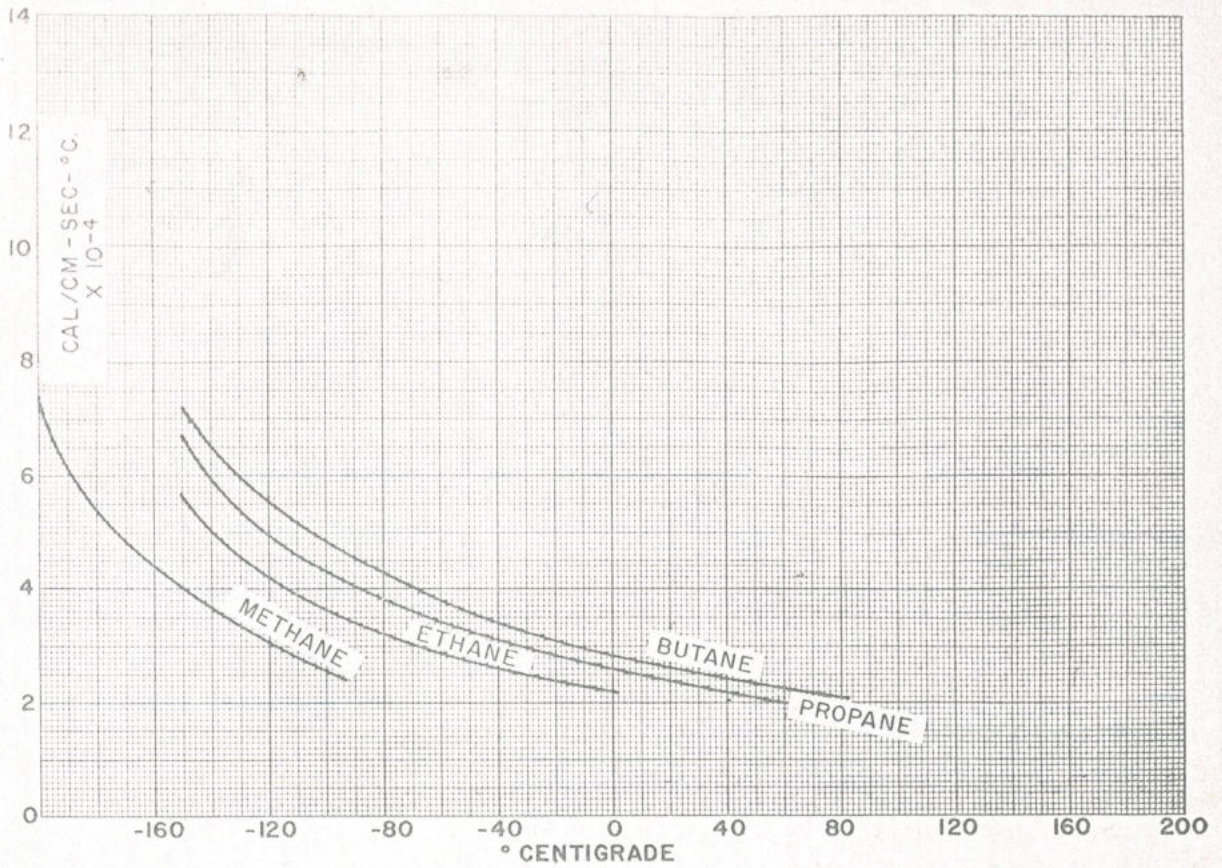
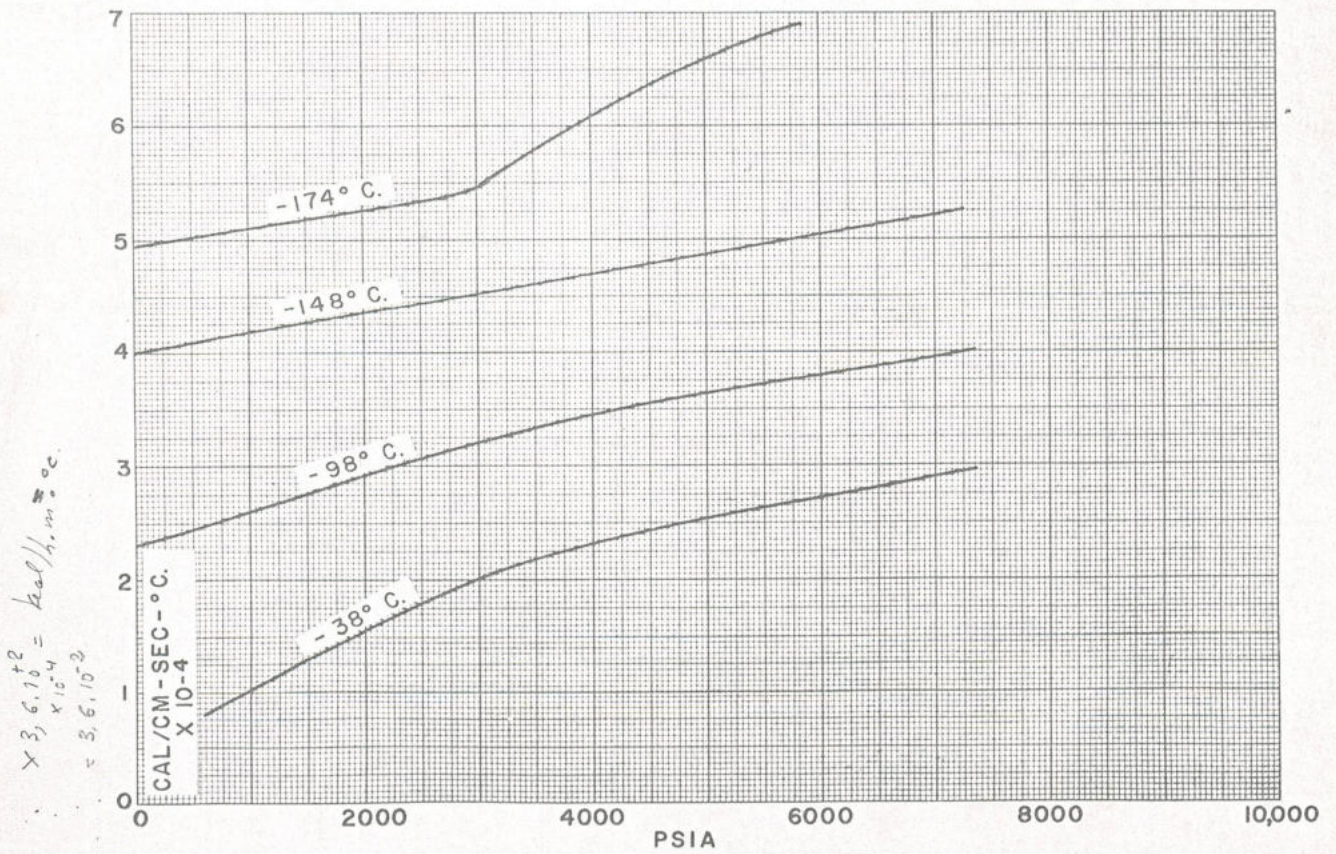Fig. 9-1—Gives liquid thermal conductivity for C_1-C_4 alkanes.

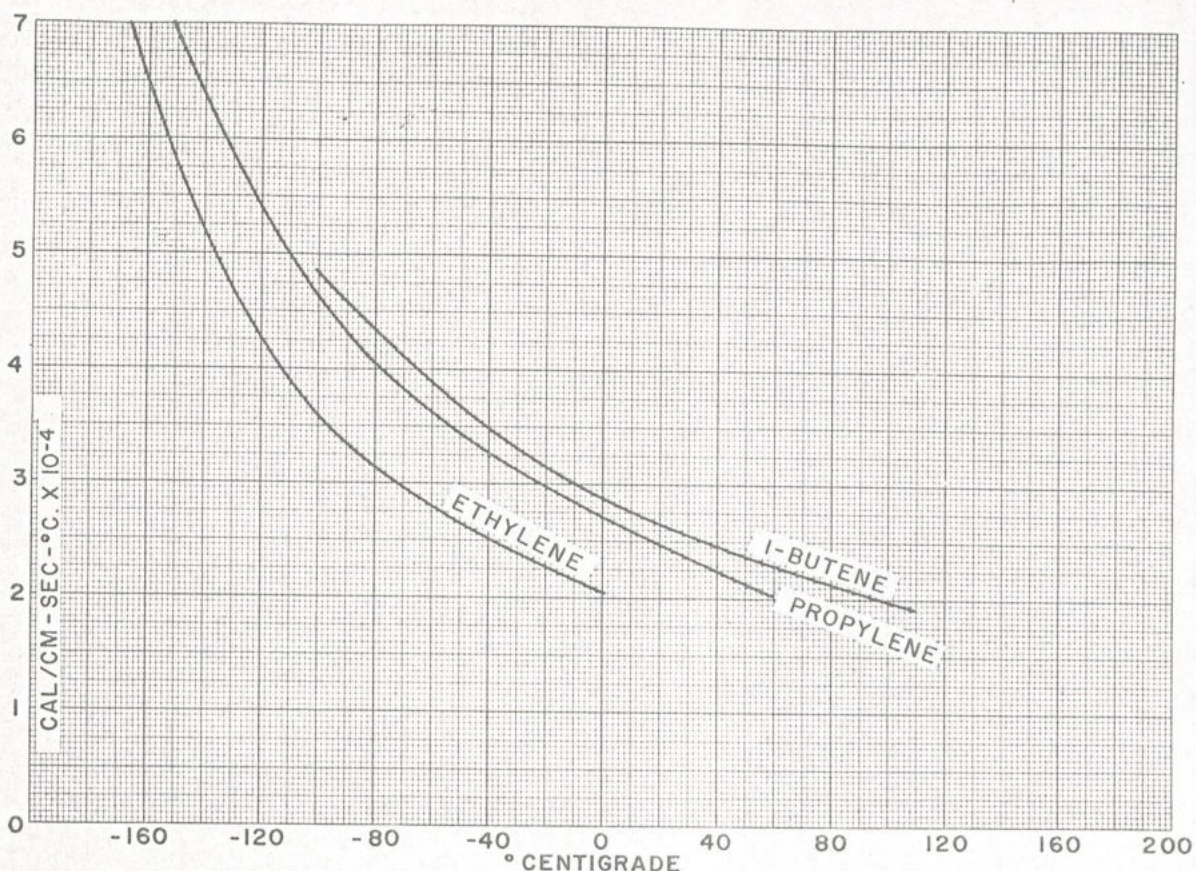Fig. 9-1A—Shows pressure effect on liquid thermal conductivity of methane.

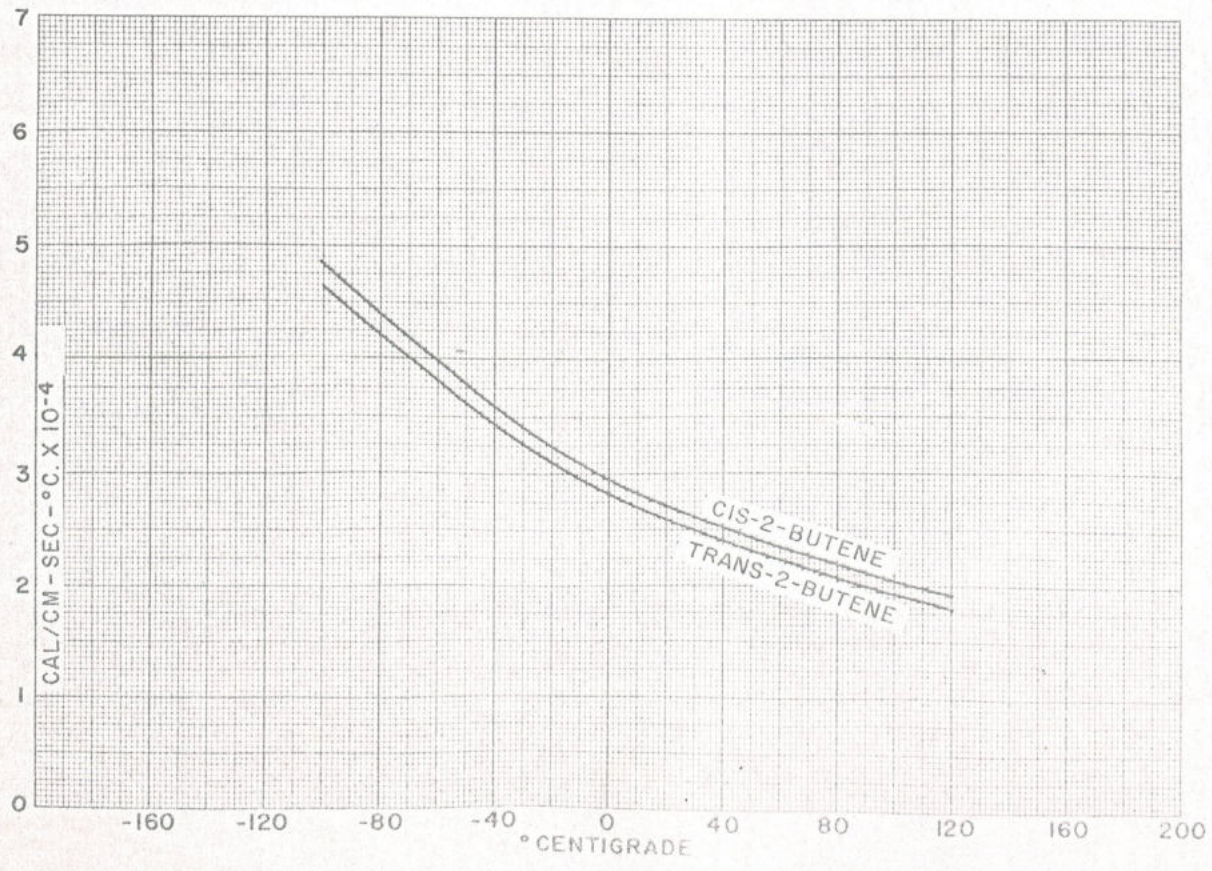Fig. 9-2—Gives liquid thermal conductivity of C_2-C_4 olefins.

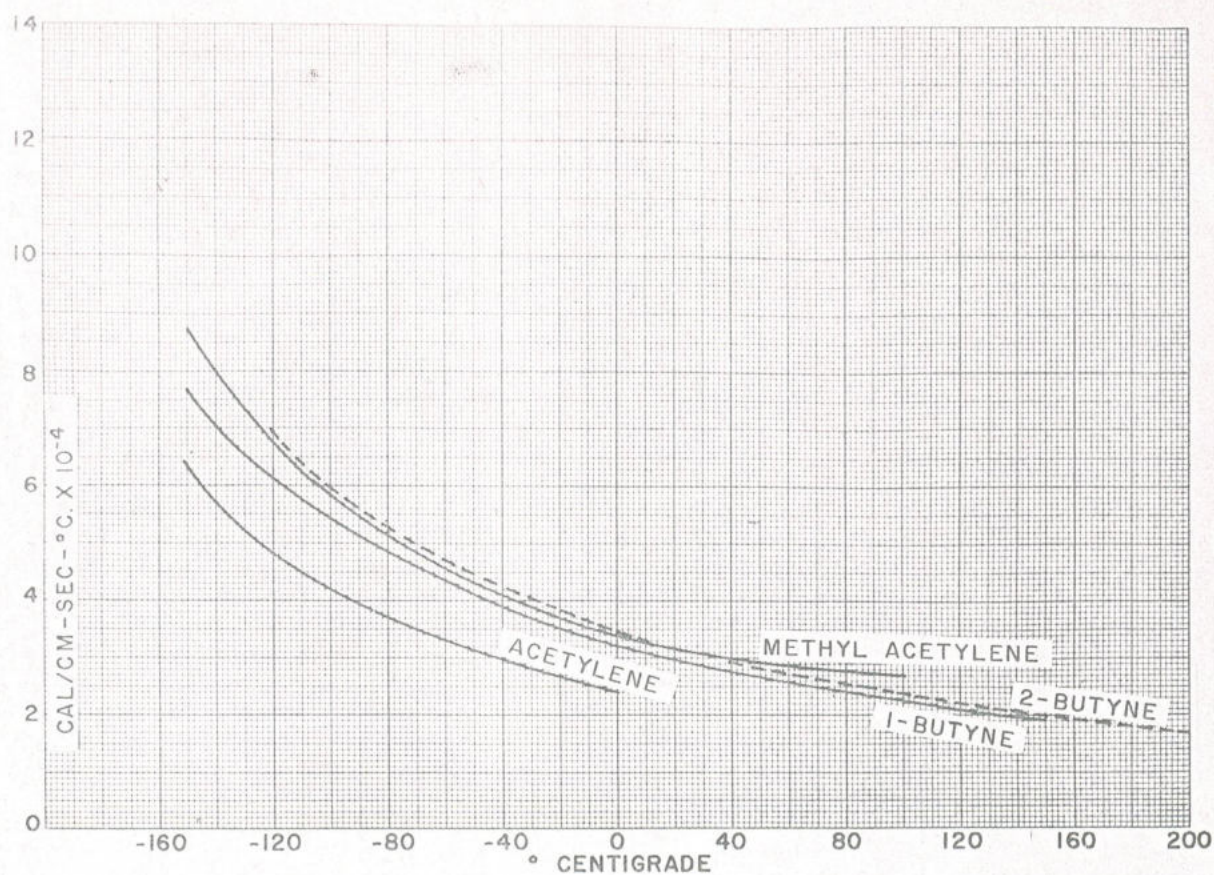Fig. 9-2A—Gives liquid thermal conductivity of 2-butenes.

Fig. 9-3—Gives liquid thermal conductivity of C_2-C_4 alkynes.
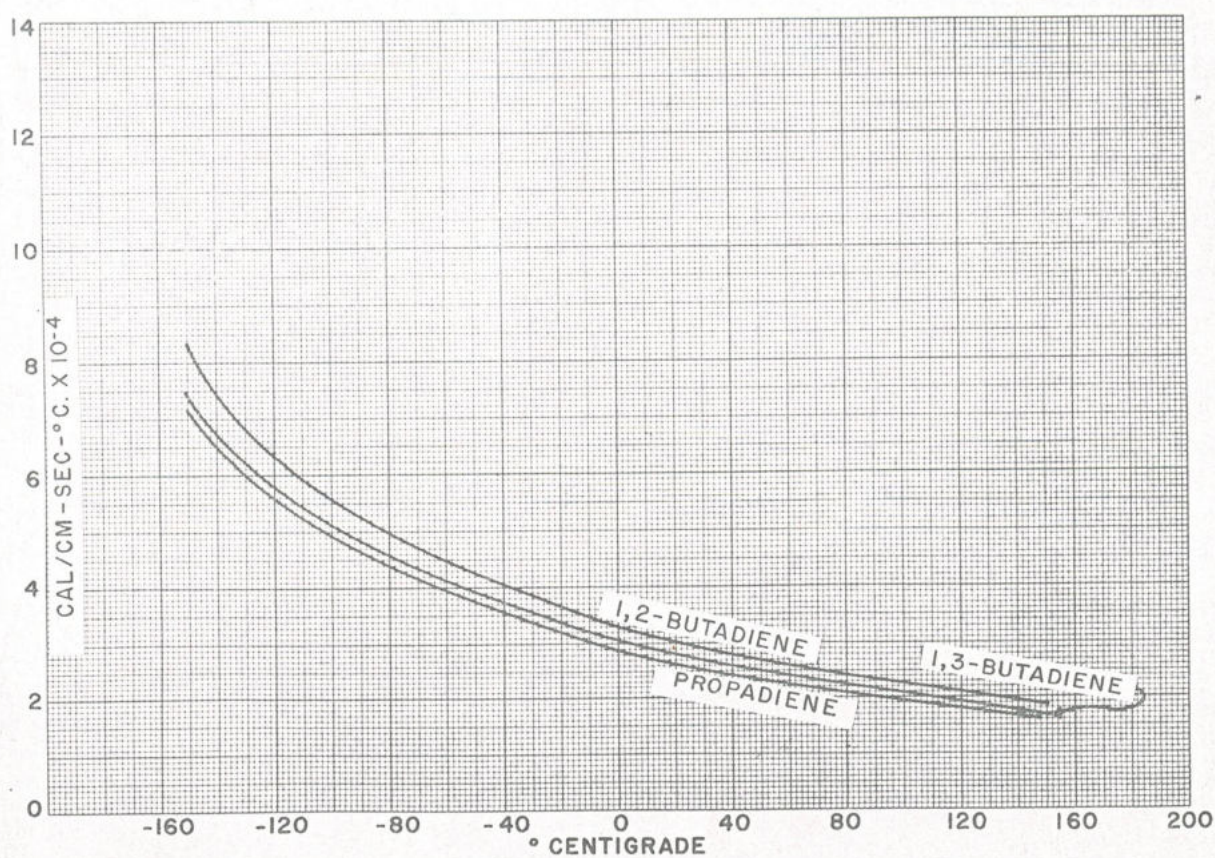

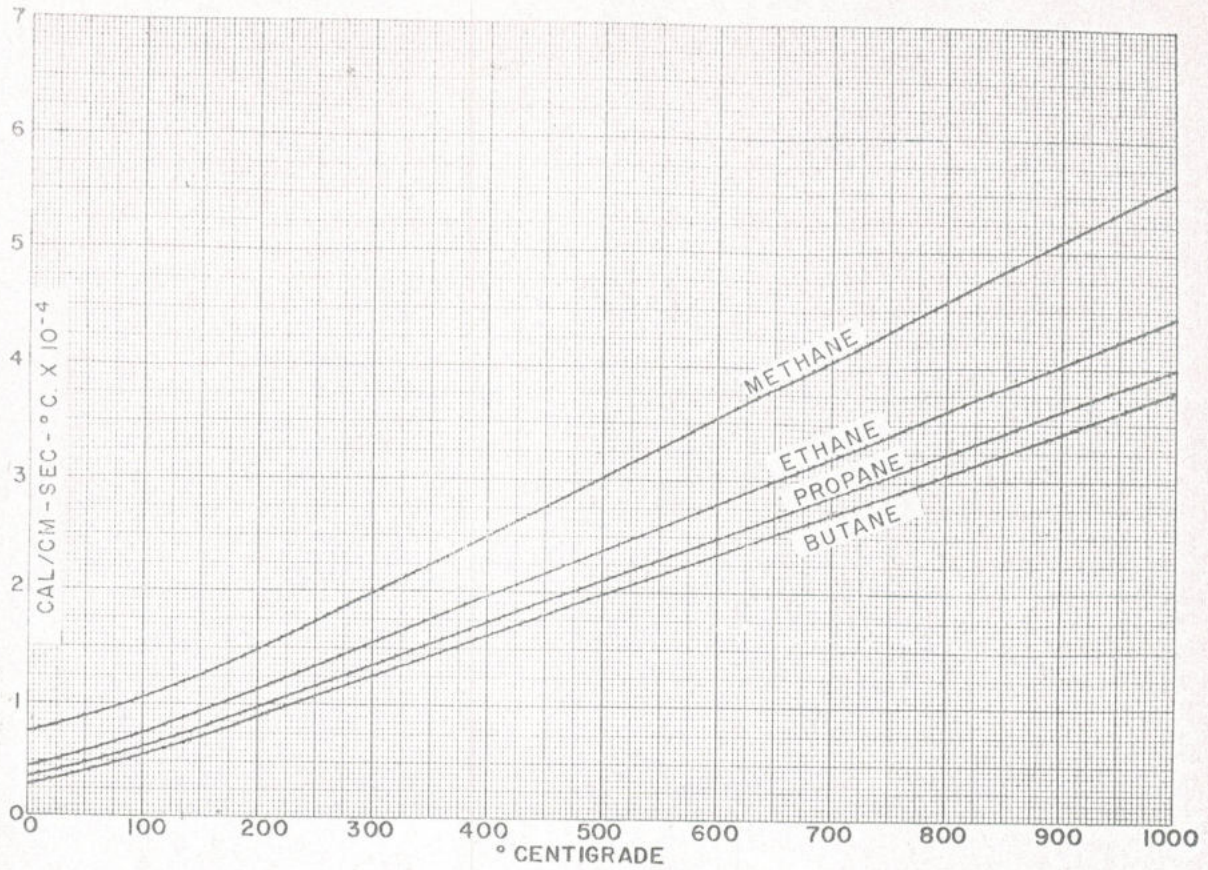Fig. 9-4—Gives liquid thermal conductivity of propadiene and butadienes.

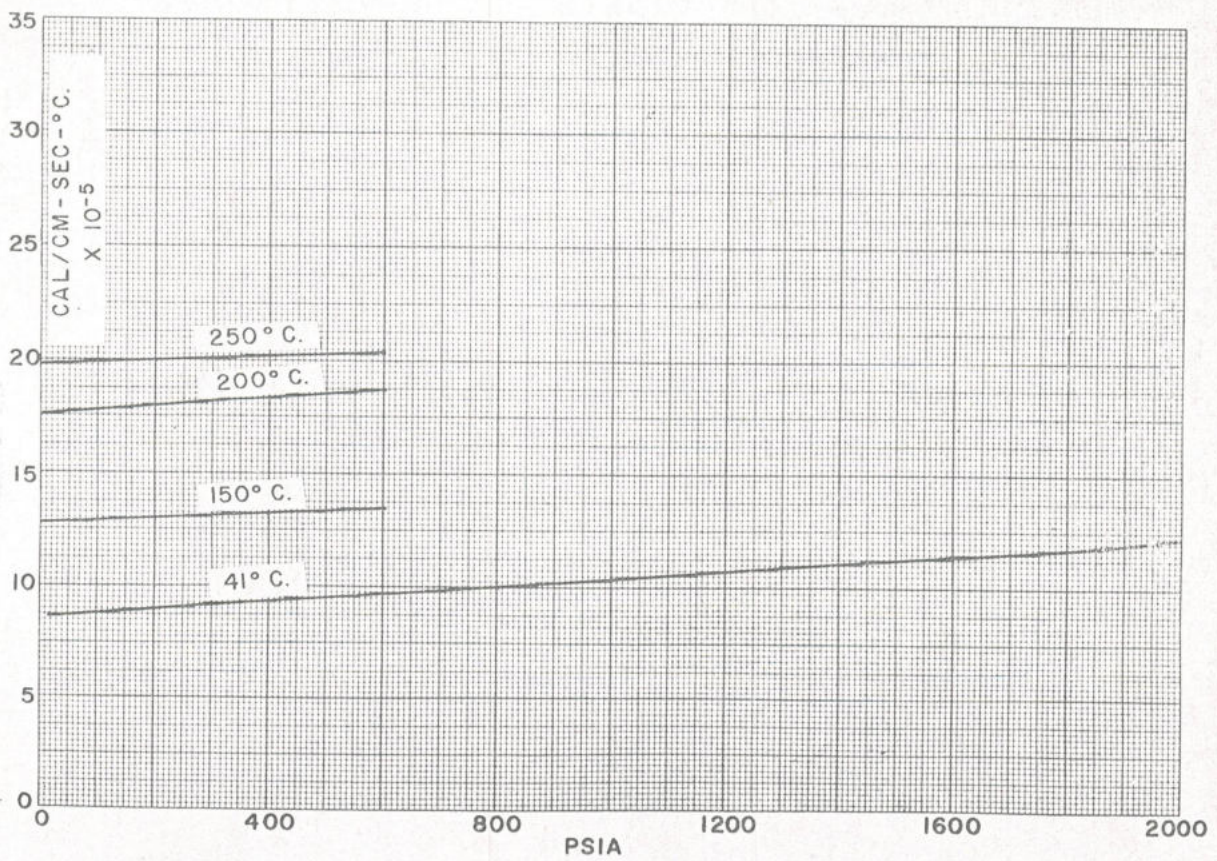Fig. 9-5—Gives vapor thermal conductivity of C₁-C₄ alkanes at 14.7 psia.

Fig. 9-5A—Shows pressure effect on vapor thermal conductivity of methane.
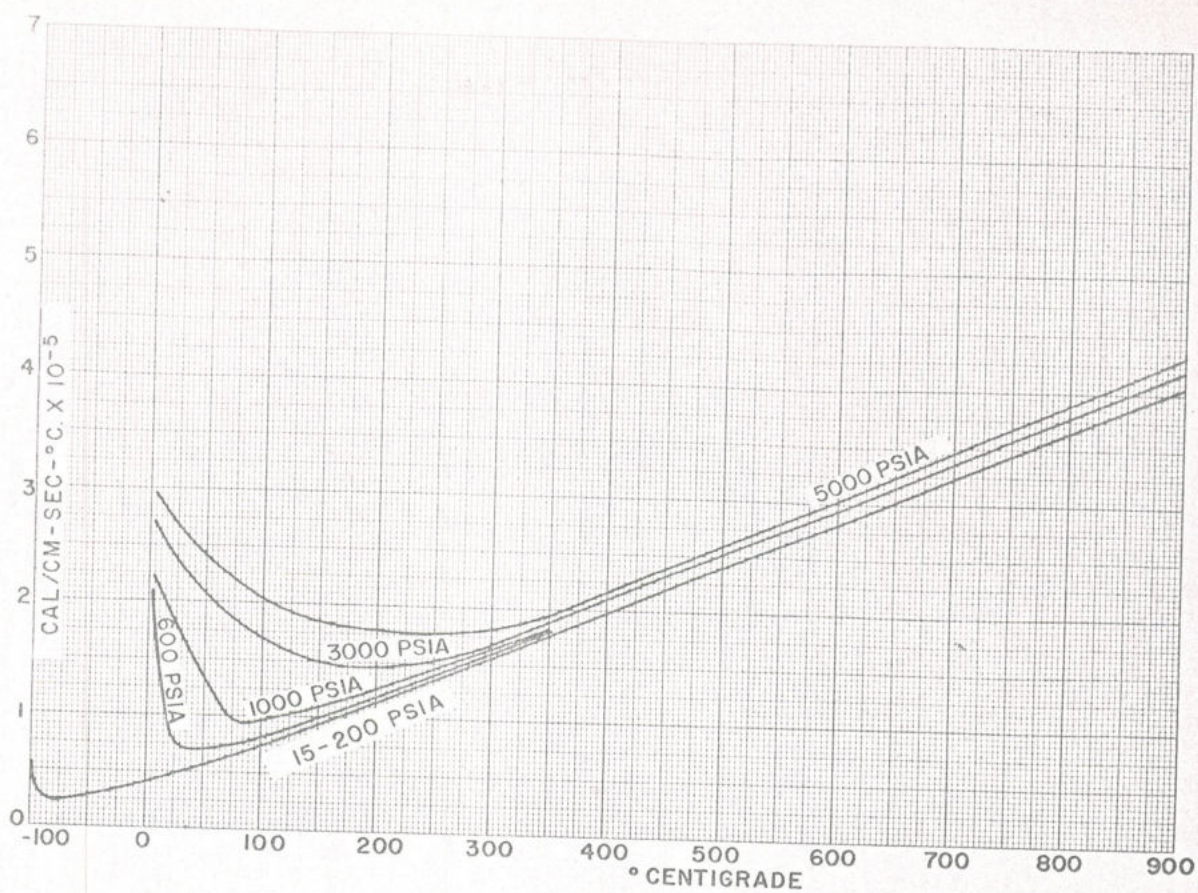
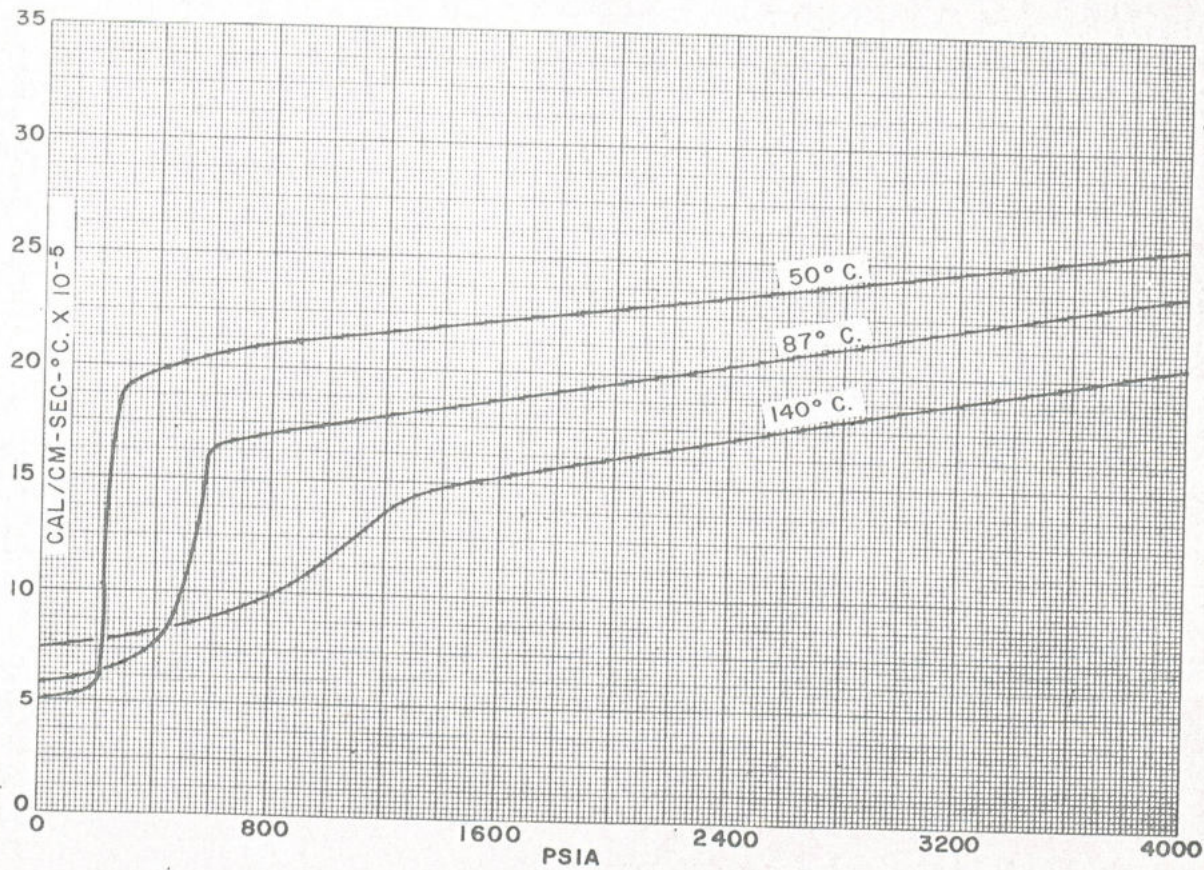Fig. 9-5B—Shows pressure effect on vapor thermal conductivity of ethane.

Fig. 9-5C—Shows pressure effect on vapor thermal conductivity of propane.
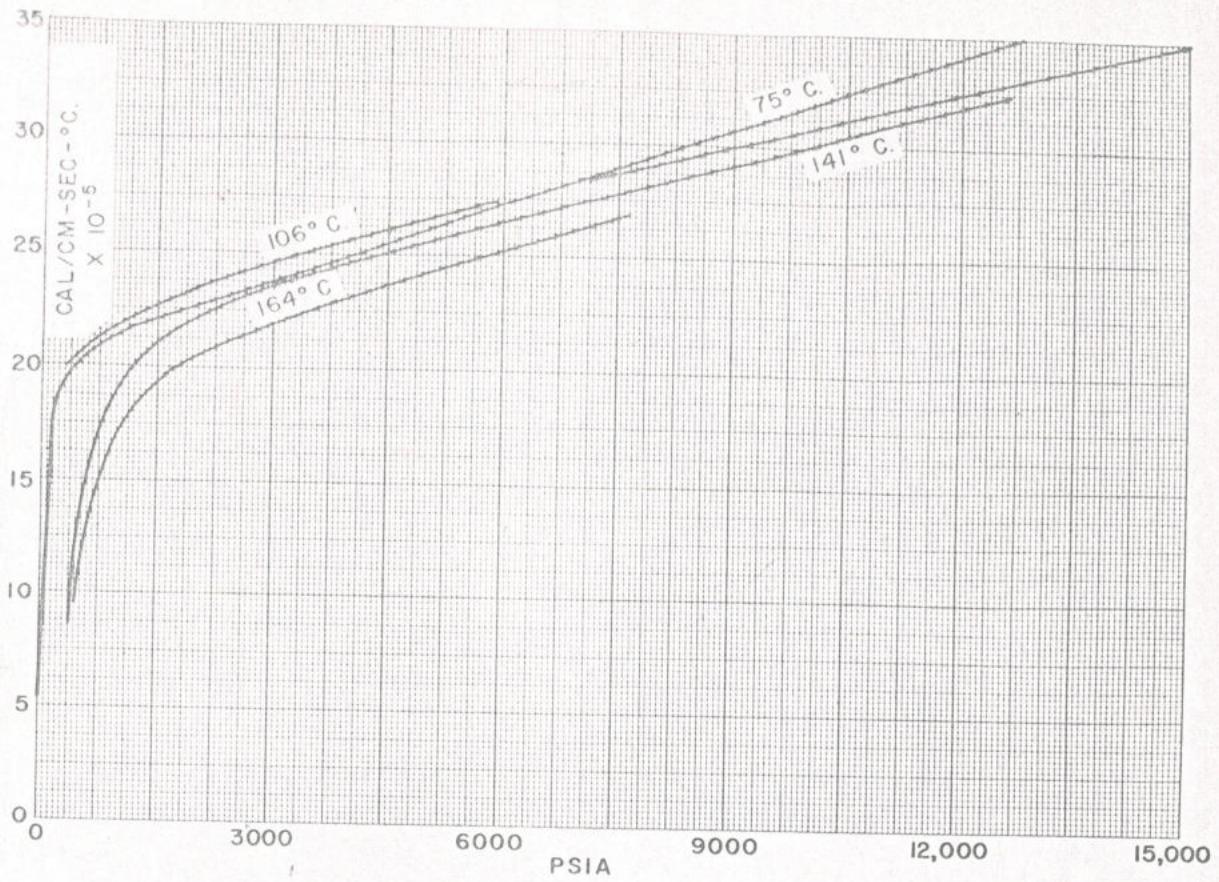
Fig. 9-5D—Shows pressure effect on vapor thermal conductivity of butane.

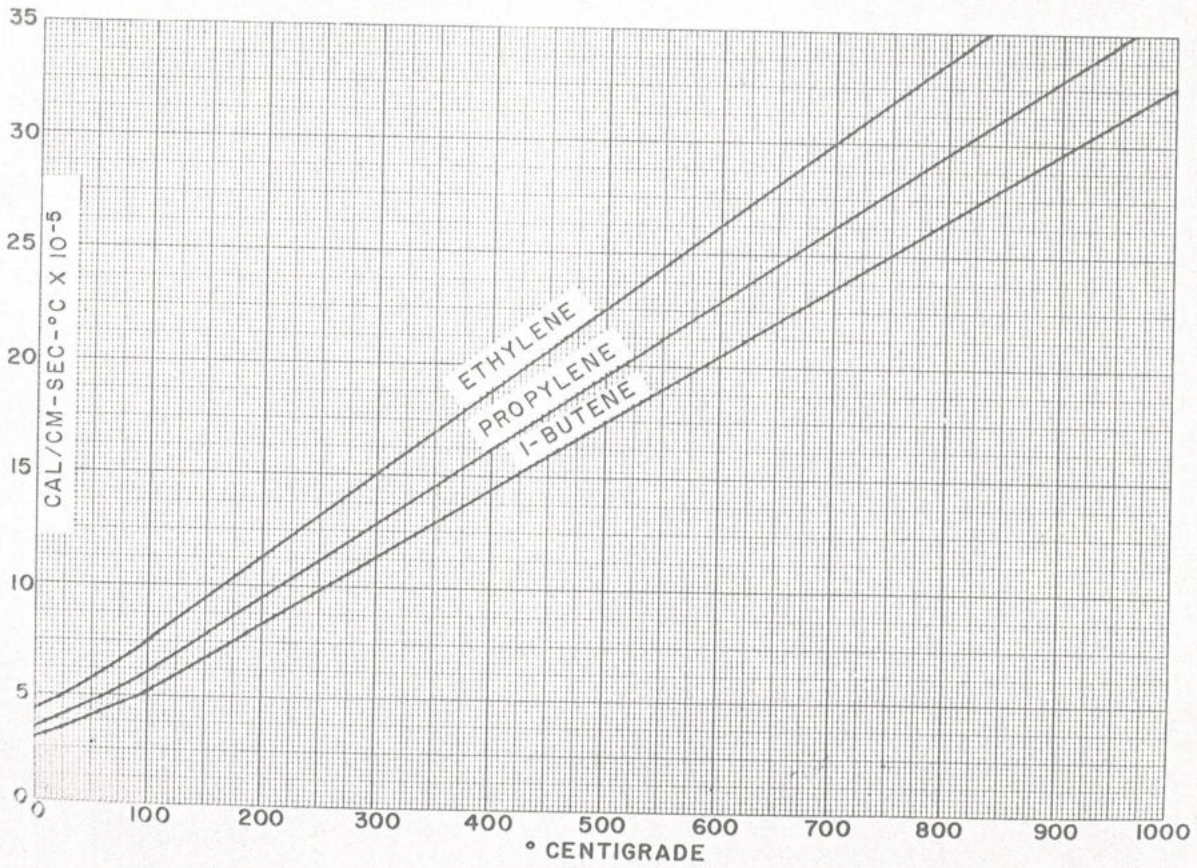Fig. 9-6—Gives vapor thermal conductivity of C₂-C₄ olefins at 14.7 psia.
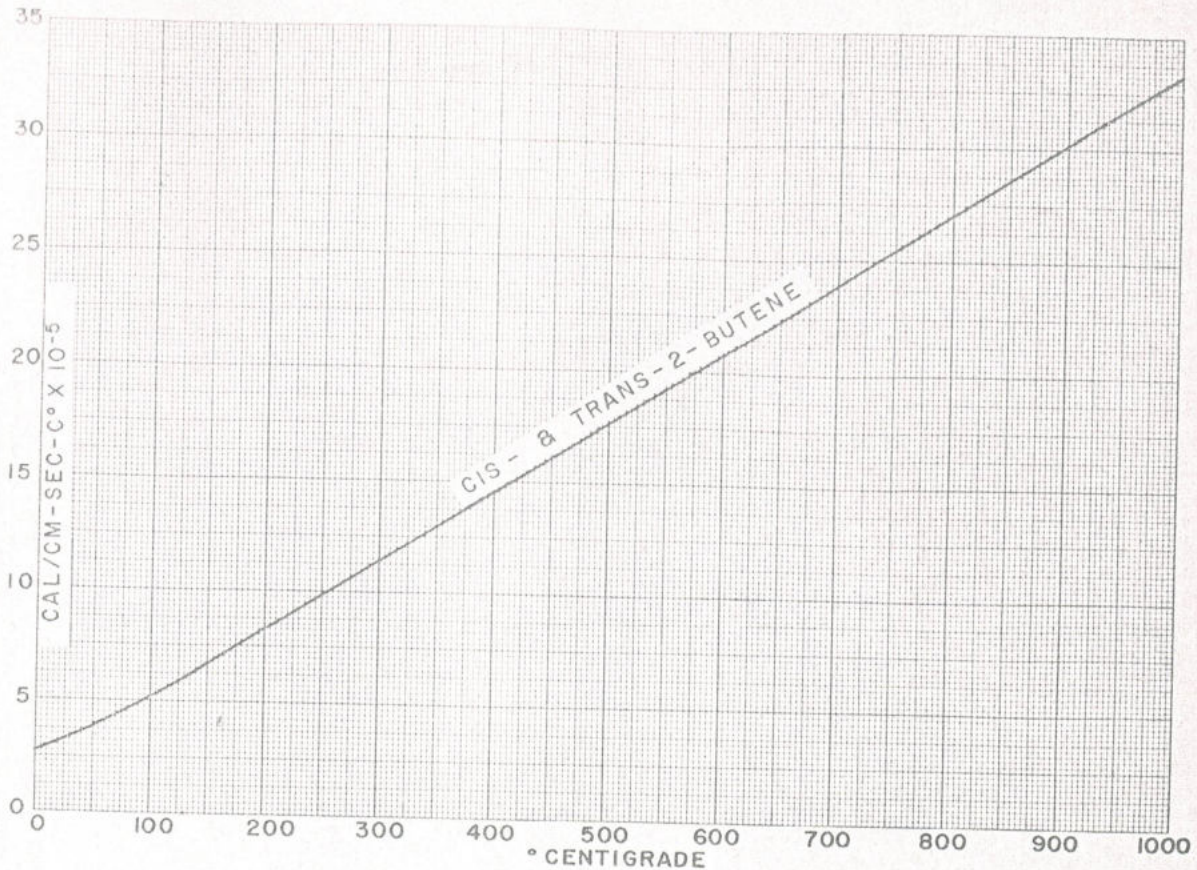
PHYSICAL PROPERTIES OF HYDROCARBONS

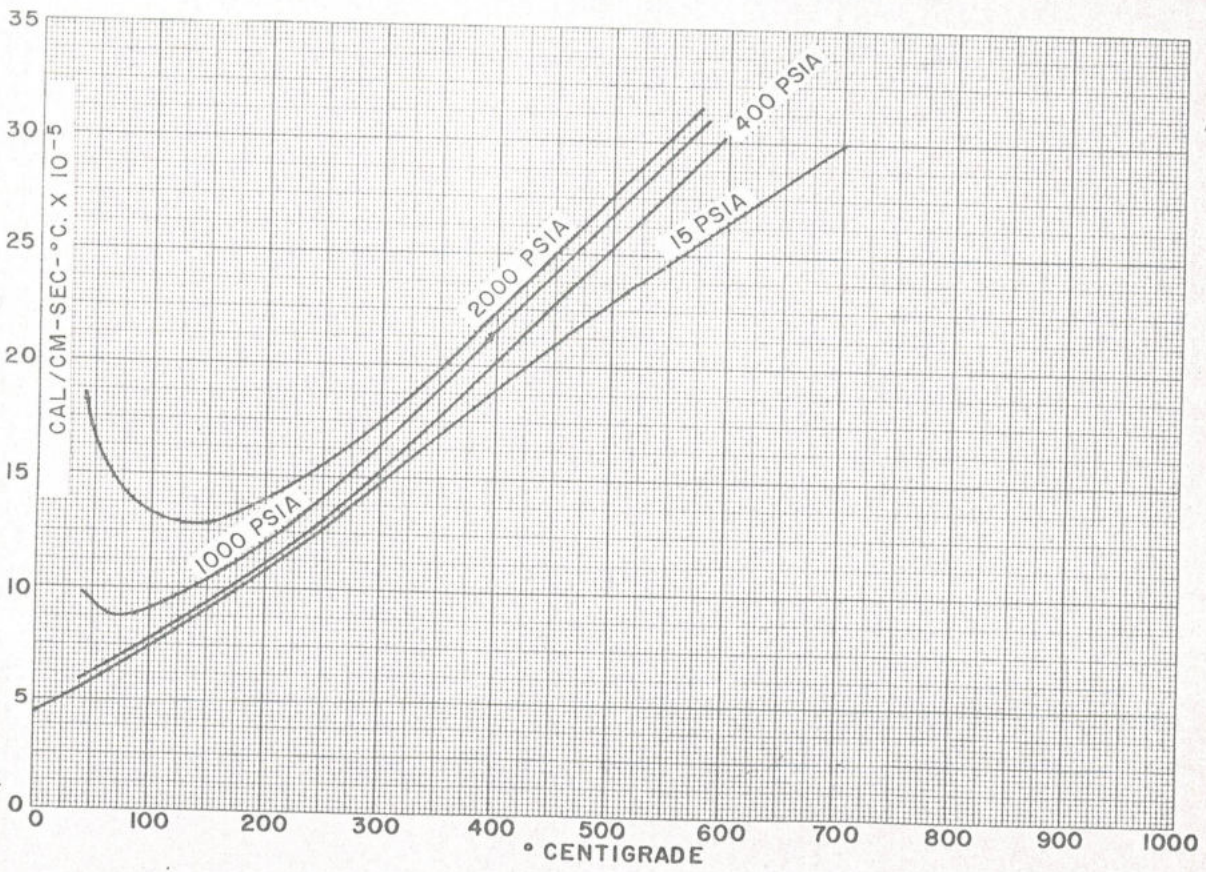Fig. 9-6A—Gives vapor thermal conductivity of 2-butenes at 14.7 psia.

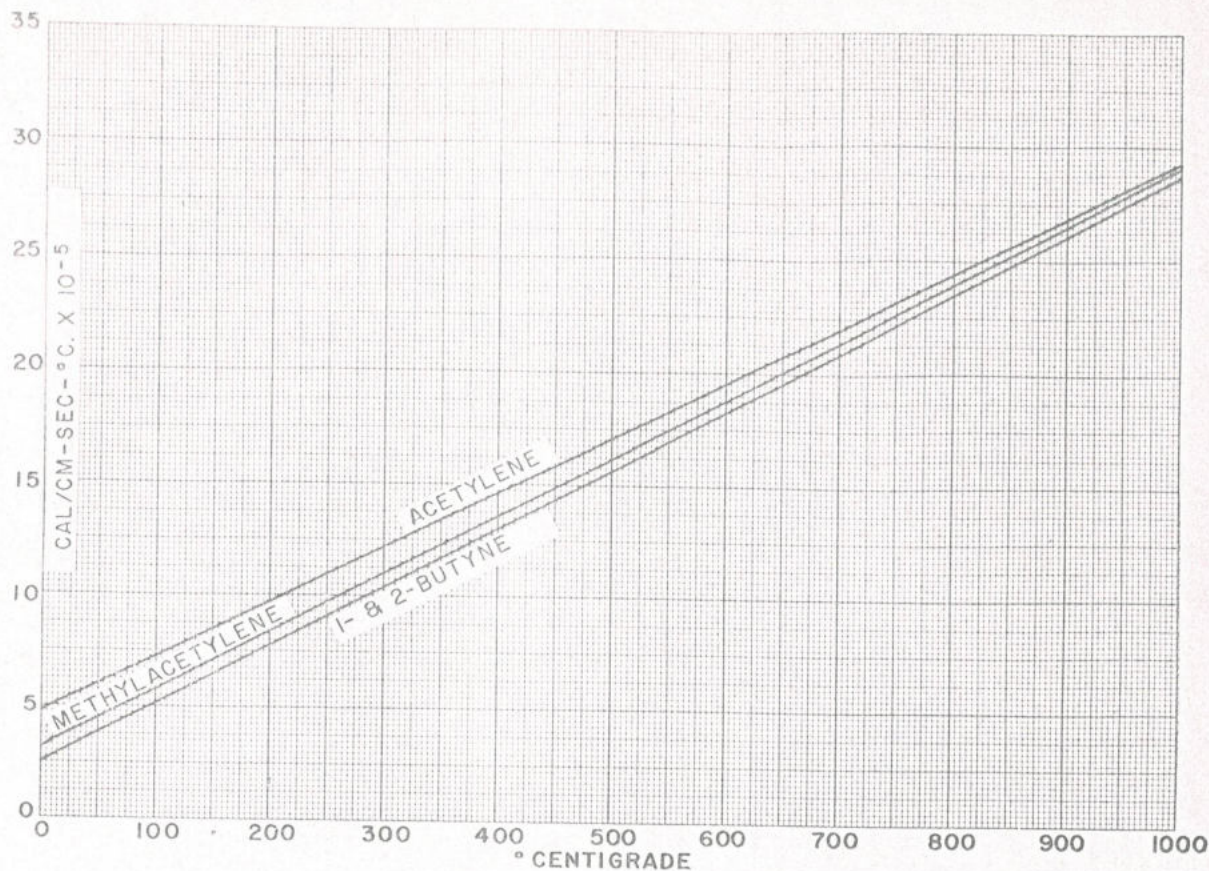Fig. 9-6B—Shows pressure effect on vapor thermal conductivity of ethylene.

Fig. 9-7—Gives vapor thermal conductivity of C₂-C₄ alkynes at 14.7 psia.

erate temperature range where liquid heat capacity is well known, Robbins and Kingrea report an average error of 2.7 percent, and a maximum error of 5.0 percent, for 25 experimental points for straight chain hydrocarbons. The author compared the calculated values with experimental methane data and found the following results:

°C	Experimental	Estimated	Error
—98	23.0	25.0	8.0%
—148	39.8	39.0	2.0%
—174	49.5	50.0	1.0%

The agreement is excellent except in the critical temperature range. Robbins and Kingrea also found poor results near the critical point and recommend the method only for the reduced temperature range of 0.4-0.9.

Graph 9-1A shows the effect of pressure on the liquid thermal conductivity of methane.[14] For practical purposes, the effect of pressure can be ignored up to 500 psia, since it only increases the thermal conductivity a few percent.

Owens and Thodos have developed reduced thermal conductivity charts for methane[15] and ethylene.[10] While these are designed predominantly for determining the vapor thermal conductivity at various temperatures and pressures, the charts do include a saturated liquid thermal conductivity plot.

Vapor Thermal Conductivity. Extensive experimental work has been done on the vapor thermal conductivities

of hydrocarbons. However, the temperature range has generally been 0-200°C. Consequently, Figures 9-5, 9-6, 9-6A, 9-7 and 9-8, which present the thermal conductivity at atmospheric pressure, have been largely determined by the estimation method proposed by Misic and Thodos. For all straight chain hydrocarbons (except methane, which is treated separately),

$$k = \frac{C_p \times 10^{-6} \, (14.52 \, T_r - 5.14)^{2/3}}{\lambda}$$

where

$k =$ vapor thermal conductivity, in cal/sec-cm-°C
$C_p =$ vapor heat capacity, cal/g-mole-°C
$\lambda =$ a calculated constant for each hydrocarbon
$\quad = \dfrac{(M)^{1/2} \, (T_c)^{1/6}}{(P_c)^{2/3}}$
$M =$ molecular weight
$T_c =$ critical temperature, in degrees Kelvin
$P_c =$ critical pressure, in atmospheres

The accuracy of the equation depends on the reliability of the vapor heat capacities and the critical constants. For these hydrocarbons, the vapor heat capacities can be estimated within 2 percent. The critical properties are also known to within a few percent. Thus, we would expect the accuracy for the calculated vapor thermal conductivities to be ±3 percent. Misic and Thodos report an average error of 2.4 percent for 154 experimental points. The author found an average error of 1.7 percent, and a maximum error of 5.2 percent for 23 experimental points for eight of the hydrocarbons.
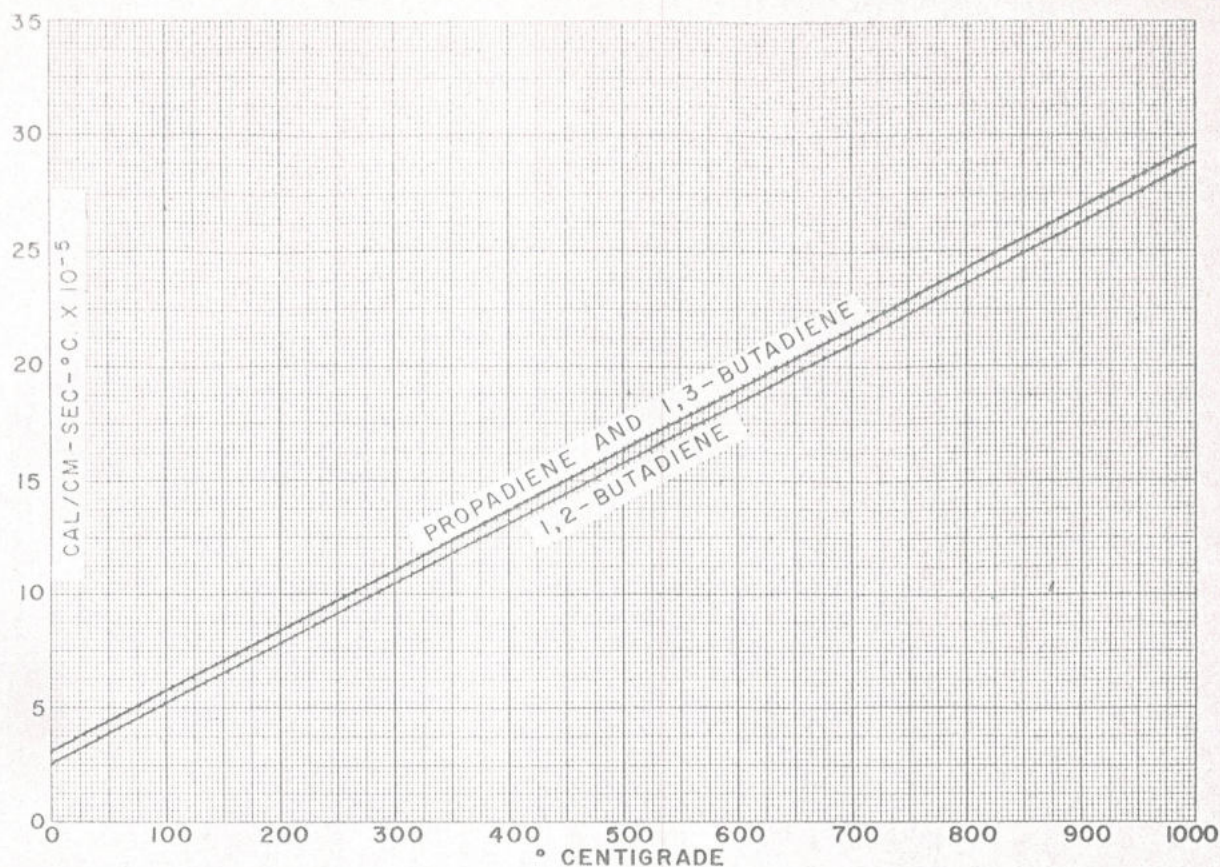
Fig. 9-8—Gives vapor thermal conductivity of propadiene-butadiene at 14.7 psia.

With its excellent accuracy and wide temperature range (the method is recommended for use over a reduced temperature range of 0.6-3.0), this estimation method will almost always yield better data than a literature search.

The method does have one major limitation. It is applicable only to low pressure systems. For vapor thermal conductivity, there is very little change in thermal conductivity up to 200 psia. Many attempts have been made to correlate the change in thermal conductivity with such properties as reduced pressure, but the results have generally been disappointing. Consequently, experimental data are the only reliable source for high pressure systems.

Figures 9-5A, 9-5B, 9-5C and 9-5D present experimental data for methane,[15, 16, 17] ethane,[18] propane,[19] and butane[20] at high pressures. The sudden changes in the slopes of the curves can be attributed to the transition from the vapor state to the liquid state. The source of the propane data also includes the thermal conductivity of the saturated liquid from 50° to 100°C.

The data for Figure 9-6B were taken largely from the reduced thermal conductivity-reduced temperature-reduced pressure chart prepared by Owens and Thodos.[10] The data were supplemented by the experimental data of Lenoir[17] and Keyes.[16]

While not used directly in plotting the graphs, the experimental data of Lambert[21] for eight of the hydrocarbons at 66°C were used to compare results with the estimation method of Owens and Thodos. Likewise, other experimenters have covered methane,[22] and methane,

propane, and butane[23] over a narrow temperature range. It is also the author's understanding that Svehla[24] has authored a government report on the high temperature gaseous thermal conductivity of over 100 organic and inorganic compounds.

LITERATURE CITED

[1] McLaughlin, E., *Chemical Reviews* 64, pp. 389-428 (1964).
[2] Sakiadis, B. C., and Coates, Jr., Louisiana State University Engineering Experiment Station, *Bulletin 35* (1963).
[3] Ibid, Bulletin 45 (1954).
[4] Ibid, Bulletin 34 (1952).
[5] Ibid, Bulletin 48 (1954).
[6] Sakiadis, B. C., and Coates, Jr., *AIChE J.* 1 (3), pp. 275-288 (September 1955).
[7] Ibid, 3 (1), pp. 121-126 (March, 1957).
[8] Gambrill, W. R., *Chemical Engineering*, Reprint No. 94.
[9] Reid, R. C., and Sherwood, T. K., The Properties of Gases and Liquids, McGraw-Hill Publishing Co., New York (1959).
[10] Owens, E. J., and Thodos, G., *AIChE J.* 6 (4), pp. 676-681 (December 1960).
[11] Misic, D., and Thodos, G., *AIChE J.* 7, (2), pp. 264-267 (June 1961).
[12] Mathur, G. P., and Thodos, G., *AIChE J.* 11 (1), pp. 164-167 (January 1965).
[13] Robbins, L. A., and Kingrea, C. L., American Petroleum Institute, Division of Refining 42 (III), pp. 52-61 (1962).
[14] Ikenberry, L. D., *Journal Chemical Physics* 39 (6), pp. 1561-1571 (1963).
[15] Owens, E. J., and Thodos, G., Proceedings of Conference on Thermodynamic and Transport Properties of Fluids, London 1957, pp. 163-8 (1957).
[16] Keyes, F. G., Transactions of the ASME, pp. 809-16 (July 1954).
[17] Lenoir, J. M., and Comings, E. W., *Chemical Engineering Progress* 47, (5), pp. 223-31 (May 1951).
[18] Carmichael, L. T., *Journal of Chemical and Engineering Data* 8 (3). pp. 281-5 (1963).
[19] Leng, D. E., and Comings, E. W., *Industrial Engineering Chemistry* 49, 2042-5 (1957).
[20] Kramer, F. R., *Journal of Chemical and Engineering Data* 5, pp. 462-7 (1960).
[21] Lambert, J. D., Proceedings of the Royal Society (London) A231, pp. 280-290 (1955).
[22] Johnson, H. L., *Journal Chemical Physics* 14, pp. 233-8 (1946).
[23] Smith, W. J., *Journal of Chemical and Engineering Data* 5, pp. 316-21 (1960).
[24] Svehla, R. A., NASA Technical Report R132, 140 pages (1962).

See Parts 1-8 for additional bibliography.

Part 10 will appear in an early issue.