

Thermal conductivity was measured in this equipment

A, high pressure nitrogen. B, low pressure nitrogen. C, thermal conductivity cell, 30 X 6 inches. D<sub>1</sub>, D<sub>2</sub>, sample gas compressor. E, sample gas supply. F, reference gas supply. G, vacuum pump. H, J, K, L, pressure gages. M, rupture disk. N, mercury U-tube. P, vents. R, higher temperature constant temperature bath. S, lower temperature constant temperature bath. T, centrifugal pumps. U, agitators, 1/4 hp. V, thermocouples in cell



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## Thermal Conductivity of Propane

New experimental measurements show behavior which differs considerably from that previously measured, and indicate how methods of prediction now in the literature may be corrected

A GENERALIZED correlation for the thermal conductivity of gases, based on experimental data for simple gases, has been proposed by Lenoir, Junk, and Comings (12). However, experimental values for ethane did not agree with those predicted by the correlation, and irregularities were observed in the critical region.

Internal degrees of freedom are important in the conduction of thermal energy. Propane has a more complex molecular structure than ethane and consequently more degrees of freedom for internal vibration and rotation. Thus, its thermal conductivity was studied to determine whether the generalized correlation would be valid for gases of greater molecular complexity.

The thermal conductivity of propane was measured in both gas and liquid regions at temperatures and pressures above and below the critical point. Five isotherms at 122°, 154°, 189°, 222°, and 284° F. and at pressures from 1 to 282 atm. were measured. One isotherm at 154° F. was measured for ethane and one at 122° F. for nitrogen.

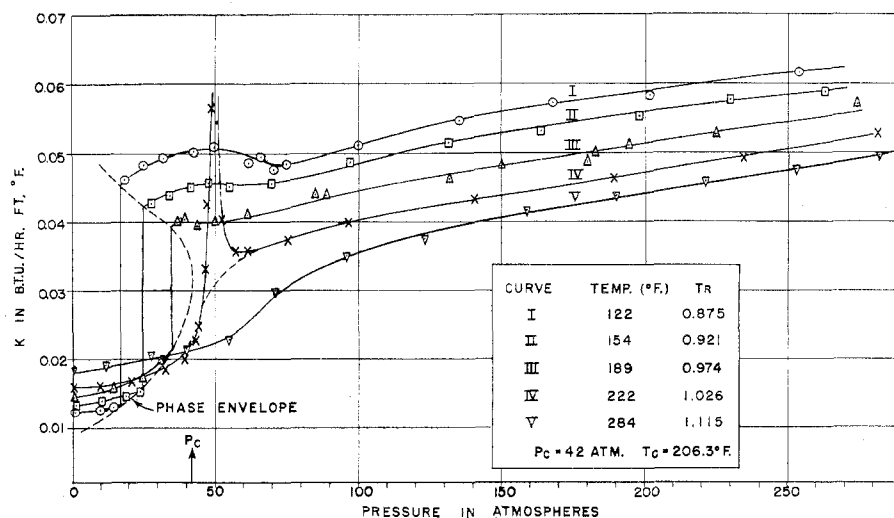
### Apparatus and Procedure

The thermal conductivity cell of Lenoir and Comings (17) was modified for this investigation. Two thermostatically

### Thermal Conductivity Measurements at High Pressure

A	Michels, Botzen, Friedman, Sengers (15)
N	Michels, Botzen (13)
	Borovik (2)
N, A	Uhlir (19)
H, N, air, CH <sub>4</sub> , CO <sub>2</sub>	Stoliarov, Ipatiev, Teodorovitch (18)
C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> H <sub>4</sub>	Abas-Sadje (1)
N, H <sub>2</sub> O	Vargaftik (20)
A, N, CO <sub>2</sub> , CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , H, C <sub>2</sub> H <sub>4</sub>	Lenoir, Comings (11)
	Lenoir, Junk, Comings (12)
H <sub>2</sub> O, N, CO <sub>2</sub>	Keyes (6, 7)
	Keyes, Sandell (8)

controlled oil circulating systems were used, in place of water circulating systems, to raise the temperature level beyond the critical temperature of propane. Heat is supplied by hot oil circulating through an outer jacket and is removed by oil passing through a central tube in the cell at about 15° F. lower. Thus, heat flowed radially inward across two concentric annular layers of gas. The inner annulus was 0.008 inch thick and contained the gas to be measured; the outer annulus contained helium as a reference gas.



THERMAL CONDUCTIVITY OF PROPANE AS A FUNCTION OF PRESSURE

Figure 1. Thermal conductivity of propane

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Leaks in both gas layers at the ends of the concentric cylinders occurred as a result of thermal stresses set up by the hot oil. The leaks in the reference (low pressure) gas layer were corrected by modifying the ends of the cell with flanges and gaskets. The high pressure gap was sealed with annealed copper gaskets. Many other gasket materials proved unsatisfactory. Other minor modifications of the cell were required before reliable measurements were made.

The sample gas was introduced from cylinder *E* into *D*<sub>2</sub> and compressed by high pressure nitrogen gas admitted over the mercury in *D*<sub>1</sub>. The reference gas was introduced from *F* into the outer annulus of the cell at 20 pounds per square inch gage. Both annuli were evacuated during filling by *G*. The oil at the higher temperature was circulated from *S* by *T*<sub>1</sub>, and the lower temperature oil was circulated from *R* by *T*<sub>2</sub>. These reservoirs were regulated to  $\pm 0.02^\circ$  F. The temperature difference between them,  $8^\circ$  to  $16^\circ$  F., provided a temperature difference across the sample gas layer of from  $5^\circ$  to  $10^\circ$  F. About 20 to 30 gallons per minute were circulated by each of two 1-hp. centrifugal

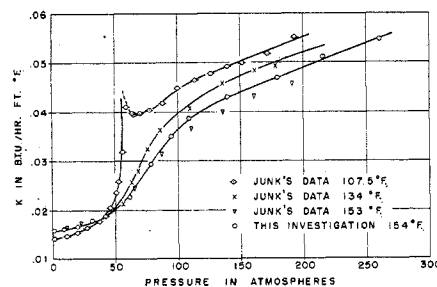


Figure 2. Thermal conductivity of ethane

pumps. A turbine oil, Shell Tellus 27, was satisfactory up to  $220^\circ$  F.

Propeller-type stirrers driven by  $1/4$ -hp. motors, *U*, maintained a uniform temperature in the reservoirs. The pressure was measured by two Heise Bourdon gages, *K* (0 to 3000 pounds per square inch gage) and *L* (0 to 5000 pounds per square inch gage), connected to the high pressure system through *N*.

Five copper-constantan thermocouples were located at *V*. Three of these, aligned radially at the middle of the cell, provided the measurements used

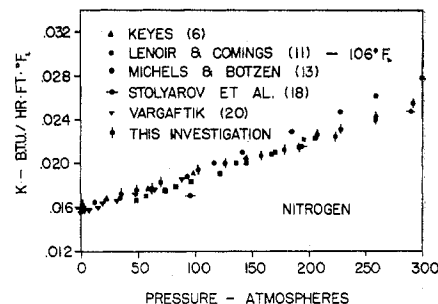


Figure 3. Thermal conductivity of nitrogen

in calculating thermal conductivity. Two thermocouples were located at the ends of the cell to detect longitudinal temperature gradients. These gradients were minimized by adjustment of heaters at each end of the bomb (not shown).

The cell was calibrated at atmospheric pressure, using helium, nitrogen, carbon dioxide, and methane in the test gas annulus. The thermal conductivities of these gases (5) were related to the measured temperature differences by

$$\frac{\Delta_z}{\Delta_N} = \bar{R} = \frac{\beta}{K} + \gamma \quad (1)$$

A calibration curve of  $\bar{R}$  vs.  $1/K$  was prepared for each temperature level at which measurements were made. The gases used were obtained from commercial sources and were not further purified. The reported purities were: carbon dioxide, 99.9; helium, 99.9; methane, 99; nitrogen, 99.6; propane, 99.9%; and ethane, 99 mole %.

## Experimental Results

The thermal conductivity of propane was measured at five temperatures (Table I);  $222^\circ$  and  $284^\circ$  F. were chosen to compare the thermal conductivity of propane with existing measurements for other gases at the same reduced temperatures. At  $122^\circ$ ,  $154^\circ$ , and  $189^\circ$  F., measurements were made for both the gas and liquid states.

In Figure 1 the three vertical lines represent saturation pressures. The curves joining their lower ends are for the gas phase and those joining the upper ends are for the liquid phase. A parabolic dotted line joining the locus points formed by the intersection of the experimental and vertical lines represents the phase envelope. No data were taken in the envelope region, as boiling phenomena would lead to erroneous results.

Table II lists the thermal conductivity of the saturated phases of propane obtained by extrapolation.

The thermal conductivity of ethane was measured at  $154^\circ$  F. at pressures up to 261 atm. (Table III). Figure 2 compares the data for ethane obtained in this investigation with those of Lenoir, Junk, and Comings (12).

Table I. Thermal Conductivity of Propane

Temp., ° F.	Pressure, Atm.	Thermal Conductivity, B.t.u./Hr. $\times$ Ft. $\times$ ° F.	Temp., ° F.	Pressure, Atm.	Thermal Conductivity, B.t.u./Hr. $\times$ Ft. $\times$ ° F.
122	1	0.0124	189	61.0	0.0411
	10.7	0.0136		85.0	0.0441
	14.1	0.0139		88.9	0.0440
	18.5	0.0456		131.8	0.0466
	25.2	0.0485		149.6	0.0484
	31.8	0.0497		180.3	0.0490
	42.7	0.0503		182.0	0.0501
	49.6	0.0510		194.5	0.0514
	61.3	0.0488		225.0	0.0529
	65.9	0.0496		274.0	0.0574
	70.5	0.0478	222	1.0	0.0158
	74.7	0.0488		10.1	0.0161
	100.5	0.0514		21.1	0.0169
	135.8	0.0549		32.5	0.0188
	168.3	0.0575		39.3	0.0204
	202.5	0.0586		43.3	0.0230
	254.0	0.0618		44.4	0.0249
154	1.0	0.0131		46.4	0.0334
	10.2	0.0137		47.1	0.0428
	18.5	0.0146		48.9	0.0565
	23.6	0.0155		52.4	0.0404
	27.5	0.0430		56.9	0.0359
	33.9	0.0442		61.4	0.0360
	41.1	0.0453		75.5	0.0377
	47.6	0.0461		96.7	0.0402
	54.6	0.0456		140.9	0.0435
	69.5	0.0462		189.5	0.0467
	96.7	0.0490		235.0	0.0494
	131.5	0.0518		282.0	0.0527
	164.0	0.0536	284	1.0	0.0184
	197.5	0.0562		12.1	0.0191
	230.0	0.0580		27.8	0.0204
	263.0	0.0592		40.0	0.0212
189	1.0	0.0148		54.5	0.0235
	14.4	0.0158		70.8	0.0297
	24.5	0.0174		95.3	0.0353
	30.8	0.0200		123.0	0.0376
	36.7	0.0400		159.2	0.0419
	39.1	0.0403		190.0	0.0439
	43.5	0.0399		220.8	0.0459
	49.8	0.0402		252.8	0.0479
				282.0	0.0498

Data obtained for nitrogen at 122° F. are compared in Figure 3 with data of other investigators (7, 11, 13, 18, 20) as an indication of the reliability of the measurements with present equipment.

## Discussion

The thermal conductivity-pressure isotherms for propane at 122°, 154°, and 189° F. (Figure 1) have "humps" above their saturation pressures, the magnitude decreasing as temperature increases. An analogous phenomenon appears as a slight change in slope in the viscosity-pressure isotherms for propane reported by Smith and Brown (77) at corresponding pressures. This change also decreases with increasing temperature, becoming scarcely detectable at 104° F. Three possible causes are: circulation, molecular rearrangement, and convection.

Table II. Thermal Conductivity of Propane in Coexisting Phases

Temp., ° F.	Vapor Pressure, Atm.	Thermal Conductivity, B.t.u./Hr. × Ft. × ° F.	
		Satd. liq.	Satd. vap.
122	16.7	0.0452	0.0132
154	24.3	0.0422	0.0156
189	35.5	0.0394	0.0216
120	16.3	(0.0456) <sup>a</sup>	(0.0130)
140	20.9	(0.0438)	(0.0144)
160	26.1	(0.0419)	(0.0164)
180	31.2	(0.0404)	(0.0190)
200	39.5	(0.0366)	(0.0260)
206	42.0	(0.0320) <sup>b</sup>	(0.0320) <sup>b</sup>

<sup>a</sup> Figures in parentheses represent interpolated values, determined from Figure 1.

<sup>b</sup> Estimated value at critical point.

Table III. Thermal Conductivity of Ethane at 154° F.

Pressure, Atm.	Thermal Conductivity, B.t.u./Hr. × Ft. × ° F.
1.0	0.0159
9.5	0.0162
20.4	0.0166
32.0	0.0178
43.1	0.0186
61.5	0.0225
78.5	0.0292
95.3	0.0350
109.0	0.0387
140.2	0.0431
180.3	0.0469
216.0	0.0514
261.0	0.0548

Table IV. Effect of Changing  $\Delta T_x$  on Apparent Thermal Conductivity of Propane at 222° F.

$\Delta T_x = 8.4^\circ \text{F.}$		$\Delta T_x = 4.2^\circ \text{F.}$	
Pres- sure, atm.	Thermal cond., B.t.u./hr. × ft. × ° F.	Pres- sure, atm.	Thermal cond., B.t.u./Hr. × ft. × ° F.
47.1	0.0428	47.1	0.0310
48.9	0.0565	48.9	0.0436
52.4	0.0404	52.5	0.0330

Waelbroeck, Lafleur, and Prigogine (27) have suggested that, in the presence of a temperature gradient, gases exhibit a circulation effect resulting from the migration of small clusters and single molecules to cool regions and of large clusters to warm regions, where they associate and dissociate, accompanied by absorption or liberation of the heat of cluster formation. This leads to an increase in the thermal conductivity for a given temperature gradient. As the pressure is increased, migration of the clusters is impaired, and thermal conductivity decreases. The effects of circulation decrease with increasing temperature and become negligible at the Boyle temperature. This is consistent with the trend noted here for the thermal conductivity of propane.

Moore, Gibbs, and Eyring (76) have pointed out that many liquids have several recognizable transitions in addition to those of solid-liquid-gas, such as from cubic rotation to hexagonal rotation to nonrotation of the molecules. Considering the propane molecule to be bounded by sides of 4.0, 4.9, and 6.5 Å., the authors calculated the volumes occupied by these models when rotation occurs in the 4.9 Å. dimension. In a cubic arrangement each molecule requires a volume of  $6.5 \times 4.9 \times 4.9 \text{ Å.}^3$ . In a hexagonal arrangement the last dimension is 4.3; if the molecules do not rotate, it is 4.0. These volumes are 157, 136, and 128 Å.<sup>3</sup> per molecule, respectively. At 122° F., the volumes available per molecule, as shown by PVT measurements of Sage and Lacey at 16.7, 47.6, and 75.0 atm., are 162, 159, and 154 Å.<sup>3</sup> It is thus possible that a transition from cubic rotation to hexagonal rotation of the molecules occurs for propane when the pressure is increased from 47 to 75 atm. at this temperature. This is the

range of the observed hump. The implication is that the hump is due to a change in the arrangement of the molecules in the liquid. Calculations for 154° and 189° F. predict similar transitions in the neighborhood of 119 and 204 atm., respectively. However, no corresponding hump is observed in the thermal conductivity measurements.

A third possible explanation of the hump is convection, which is likely to occur if the product  $N_{Gr} \times N_{Pr}$  exceeds 600 (9). The factor contributing most to an increase in  $N_{Gr}$  as a function of pressure is  $\beta$ , defined as  $\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$ . At 100° F.,  $\beta$  remains essentially constant at pressures where the hump occurs and, as seen in Figure 4,  $N_{Gr} \times N_{Pr}$  is well below 600 in this region. These two facts indicate that convection is improbable at this temperature. (These calculations were based on a temperature difference of 10° F. across the high pressure gas layer, which is close to that maintained during experimental observations.) If convection were responsible for the hump phenomenon, the magnitude of the hump should increase rather than decrease as the temperature is raised to the critical.

The isotherm at 222° F. shows a sharp peak in the neighborhood of 50 atm., believed to be due to convection, as  $N_{Gr} \times N_{Pr}$  values at 220° F. (Figure 4) are considerably over 600 at these pressures. To find further evidence that convection was responsible for this peak, the thermal conductivity of propane was determined with temperature differences of 8.4° and 4.2° F. across the high pressure gas layer. The values obtained (Table IV) reveal that the apparent thermal conductivity decreases appreciably with a decrease in the temperature difference across the gas layer. Probable values of the thermal conductivity of

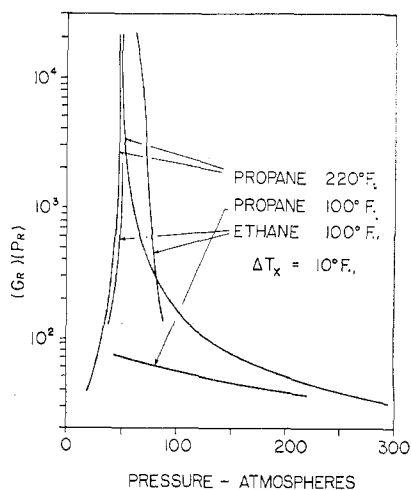


Figure 4. Tendency for convection for propane at 100° and 220° F. and ethane at 100° F. as shown by product of Prandtl and Grashof numbers

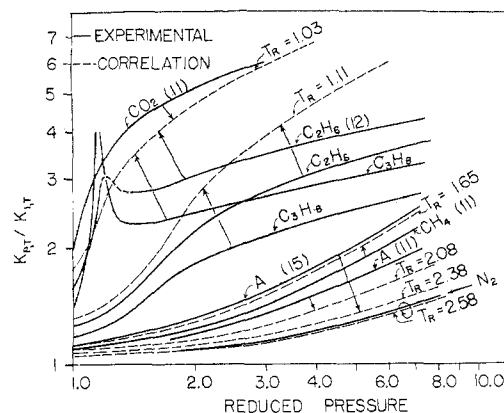


Figure 5. Comings and Nathan correlation of thermal conductivity ratio, showing deviations of measured values

propane at 222° F. over the convection region are shown by a dotted line in Figure 1.

Kreglewski (10) has reported the co-existence of two distinct densities for propane in a region extending several degrees above the critical temperature, which he attributes to clustered and non-clustered molecules. Similar observations have been reported for propylene and methyl ether (22). Convection probably occurs in this region due to bulk movement of these molecular species. If two densities exist at a given temperature and pressure, then  $(\frac{\partial V}{\partial T})_P$  and therefore  $\beta$  must be infinite and convection is predicted.

At low pressures, values for the thermal conductivity of ethane at 154° F. agree with those reported by Lenoir, Junk, and Comings (12), but show a gradual deviation as the pressure is increased, amounting to 7.5% at 191 atm. The apparatus was recalibrated and results were again verified. In the ethane isotherm at 107.5° F. there is an irregularity, probably due to convection (Figure 4), in spite of the statement (12) that no variation in conductivity was found with a change in the temperature difference across the gas layer. It is believed that insufficient measurements were made in the region where convection is most probable.

The thermal conductivity ratios ( $K_{P,T}/K_{1,T}$ ) for propane and ethane are compared at reduced temperatures of 1.03 and 1.11° in Figure 5 with a correlation based on calculated values (4). Both isotherms are much lower than predicted values, propane showing an even greater deviation than ethane. Experimental values for the thermal conductivity ratio of ethane have been shown to be lower than values predicted from an experimental correlation proposed by Lenoir, Junk, and Comings (12) based on data for nitrogen, argon, methane, ethylene, and carbon dioxide. The experimental correlation predicts values of  $K_{P,T}/K_{1,T}$  comparable to those from the correlation based on calculated values except in the critical region, where it predicts higher values.

The Chapman and Enskog equations (3) for the thermal conductivity and viscosity of an idealized gas, consisting of hard spheres having only repulsive forces, were used as a basis for the Comings and Nathan correlation. The quantity  $b$  is evaluated from known viscosity data. Although  $b$  is defined as a constant ( $2\pi D^3 N/3$ ), values determined from viscosity data vary considerably with pressure for a number of substances (4). The viscosity of argon does not behave according to the Chapman and Enskog equation. This is attributed by Michels (14) to neglecting the attractive forces between molecules in these equations.

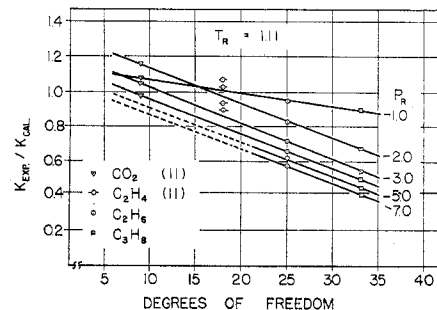
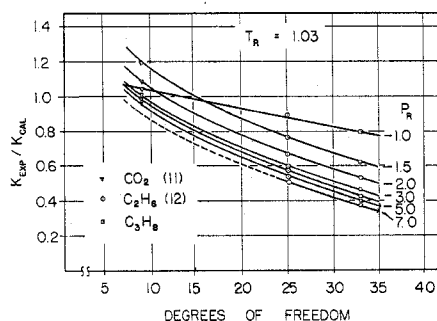


Figure 6. Deviations from Comings and Nathan correlation as a function of number of degrees of vibrational freedom in a molecule

## Correlation

Both the magnitude and the sign of the deviations of experimental curves from curves predicted by the Comings and Nathan correlation (Figure 5) suggest a function that relates these deviations to the molecular complexity of the gas. Deviations from the correlation (represented by  $K_{\text{exptl.}}/K_{\text{calcd.}}$ ) are shown as a function of the number of degrees of freedom for several gases, with reduced pressure as the parameter, at reduced temperatures of 1.03° and 1.11° in Figure 6. More data for simple gases at low temperatures and for complex gases at high temperatures are needed. If the validity of this correlation can be established, this, in conjunction with the correlation of Comings and Nathan, permits calculation of the thermal conductivity of any gas at high pressures, requiring only a knowledge of the thermal conductivity of that gas at 1 atm. at the desired temperature, its molecular formula, and its critical temperature and critical pressure.

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## Nomenclature

- $b$  = actual volume of molecules ( $2\pi D^3 N/3$ )
- $D$  = molecular diameter
- $K_{P,T}$  = thermal conductivity at pressure  $P$  and temperature  $T$
- $K_{1,T}$  = thermal conductivity at 1 atm. and temperature  $T$
- $M$  = molecular weight
- $N$  = number of molecules per unit weight
- $N_{Gr}$  = Grashof number
- $N_{Pr}$  = Prandtl number
- $P$  = pressure, atm.
- $P_r$  = reduced pressure
- $\bar{R}$  = ratio of inner to outer layer e.m.f. differences
- $T$  = temperature ° F. or ° F. abs.
- $T_r$  = reduced temperature
- $\beta$  = constant; also coefficient of thermal expansion
- $\delta$  = constant
- $\Delta T_x$  = temperature difference across inner or sample gas layer

- $\Delta_V$  = e.m.f. difference between outer pair of thermocouples
- $\Delta_i$  = e.m.f. difference between inner pair of thermocouples

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