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THERMAL CONDUCTIVITY OF BINARY MIXTURES OF CARBON DIOXIDE, NITROGEN AND ETHANE AT HIGH PRESSURES: COMPARISON WITH CORRELATION AND THEORY

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The transport properties of dense gas mixtures have received little attention either by experimentalists or theoreticians because of the difficulty in obtaining accurate data at high pressures and the complexity of the theoretical analysis of dense mixtures of real gases. However, commercial chemical processes deal almost exclusively with mixtures. For this reason, it is important to characterize the transport behavior of mixtures under these conditions.

Keyes (12) measured the conductivity of nitrogen-carbon dioxide mixtures at normal temperatures and at pressures of a few hundred psi, and attempted to correlate behavior on the basis of the Enskog pure gas theory. Junk and Comings (11) made measurements on ethylene-nitrogen and ethylene-carbon dioxide mixtures to 200 atm. and compared their values with those predicted by their own pure compound reduced state correlation and Kay's rule. Reid and Sherwood (25) compared the Junk and Comings' data with dense gas values calculated by the Lindsay-Bromley dilute gas correlation.

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When determining dense gas thermal conductivities, there are advantages to using a secondary cell. Such a cell may be of simple design; when calibrated against gases of known thermal conductivity, it can be used to make measurements at a fairly rapid rate. It should be possible with such a cell to obtain an accuracy of 2%, as compared to 1% obtained by investigators using primary cells. The cell suggested by Comings, Lee and Kramer (3) is of this type. It was used by Kramer (14) and others (6, 18) to measure dense gas thermal conductivities. In this investigation the cell used by Kramer was modified to increase the accuracy, decrease the measurement time, and simplify the calibration. It was then used to measure the thermal conductivity of binary mixtures of the three gases carbon dioxide, nitrogen and ethane at 75°C to 3,000 atm. with an estimated accuracy of 3%. The values of carbon dioxide and argon measured by Sengers (22, 23) were used for calibration. Measurements were also made on pure ethane and pure nitrogen.

EXPERIMENTAL APPARATUS

The thermal conductivity cell is shown in Figure 1. It is a modification of the Kramer-Comings cell (14) consisting of two horizontal concentric cylinders totally immersed in the sample fluid, and with a nominal gap of 0.006 inches. The cell, which has a total length of 6-1/4 inches, is made of copper. The center cylinder or emitter is 2-1/2 inches long with a diameter

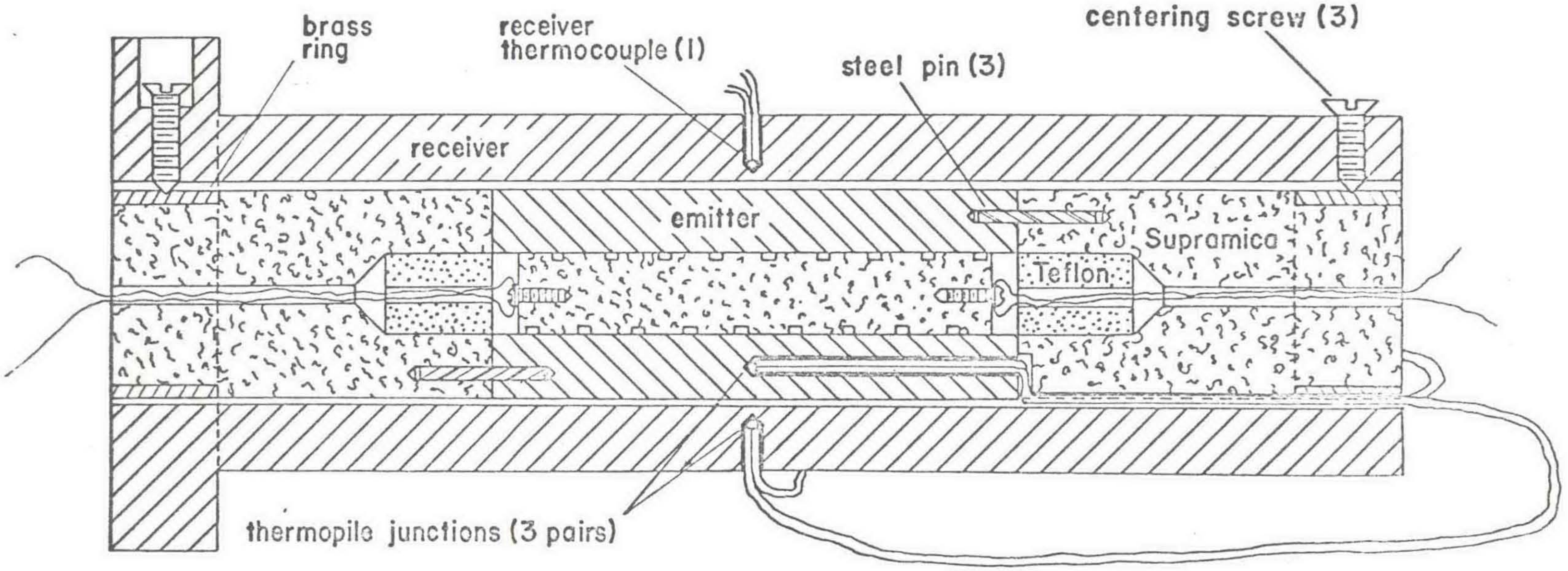

Figure I. THE THERMAL CONDUCTIVITY CELL

of 1.015 inches and is drilled axially with a 3/8 inch hole to accept a Supramica core. The Supramica core is slightly shorter than the emitter and is spirally grooved for a 1/32 x 0.00275 inch, 10 ohm, chromel-2A resistance ribbon. The emitter is drilled to a depth of 1-5/16 inches with three equally spaced #42 holes for the three thermocouple junctions. One inch diameter by 1-7/8 inch long Supramica end insulators minimize end losses.

The outer cylinder, or receiver, has an inside diameter of 1.027 inches and an outside diameter of 1-3/4 inches. At one end there is a 2-7/16 inch diameter collar which is bolted to the pressure vessel closure. At each end of the receiver, there are three equally spaced centering screws. There are four #42 holes drilled radially to within 1/16 inch of the inner surface at the longitudinal center of the receiver, three of which are spaced 120° apart, while the fourth is halfway between two of the equally spaced holes. The equally spaced holes contain the three copper-constantan thermocouple junctions used in a thermopile, while the fourth contains a single thermocouple used to measure the absolute temperature of the receiver and permit calculation of the average temperature of the gas in the gap. The thermocouples were cemented in place with a copper oxide cement. This cement combines the properties of high electrical resistance and high thermal conductivity.

The cell was contained in a specially constructed high pressure bomb which had an i.d. of 2-1/2 inches. Pressures were generated with a Harwood 200,000 psi intensifier system. Separation of the hydraulic fluid and the sample gas was accomplished with a mercury U-tube arrangement consisting of two 1-1/2 liter, 47,500 psi reaction vessels connected with 1/16 inch i.d. tubing at their bottom outlets.

Three Heise gages with the ranges 0-5000 psi, with 5 psi subdivisions, 0-10,000 psi, with 10 psi subdivisions, and 0-50,000 psi, with 50 psi subdivisions were used. The gages were calibrated against a Harwood controlled clearance precision dead weight tester and corrections of the gage pressure were made where necessary. The corrected pressures were accurate to 0.1% of the full scale value.

Electrical measurements were made with a Leeds and Northrup Type K-3 potentiometer. The bomb was mounted in an agitated hot oil bath, the temperature control of which was sufficiently sensitive that variations could not be detected within the bomb.

EXPERIMENTAL ERRORS

The errors introduced by convection within the gap have been discussed by numerous authors (7). In a horizontal cylindrical cell convection is present as long as there is a temperature difference; however, below a critical value of the

Rayleigh number, the error introduced by laminar convection is relatively small. To determine the ΔT at which turbulent convection begins, measurements were made at varying ΔT's with carbon dioxide in the cell and at the pressure corresponding to its critical density. It is at this density that turbulent convection most easily occurs. The results of these measurements are shown in Figure 2 and indicate that in this worst case, convection will have a serious effect above a ΔT of 0.75°C. At temperature differences less than 0.75°C convection will not affect the measurement more than a small fraction of a percent. Therefore, measurements away from the critical density were made with temperature differences less than 1.0°C, while close to the critical density, the temperature differences were maintained less than about 0.6°C for CO_2. This procedure was also followed for ethane and all mixtures.

Related to convection is the effect of thermal diffusion. With mixtures of gases and a temperature gradient it is possible that some separation of components may occur. The effect of ordinary radial diffusion can be shown to be quite negligible; however, when circulation occurs, the cell becomes essentially a Clusius-Dickel column, and there is the possibility that considerable separation could occur at the higher densities. During his measurements on the conductivity of carbon dioxide-nitrogen mixtures, Keyes (12) noticed that his cell thermocouple

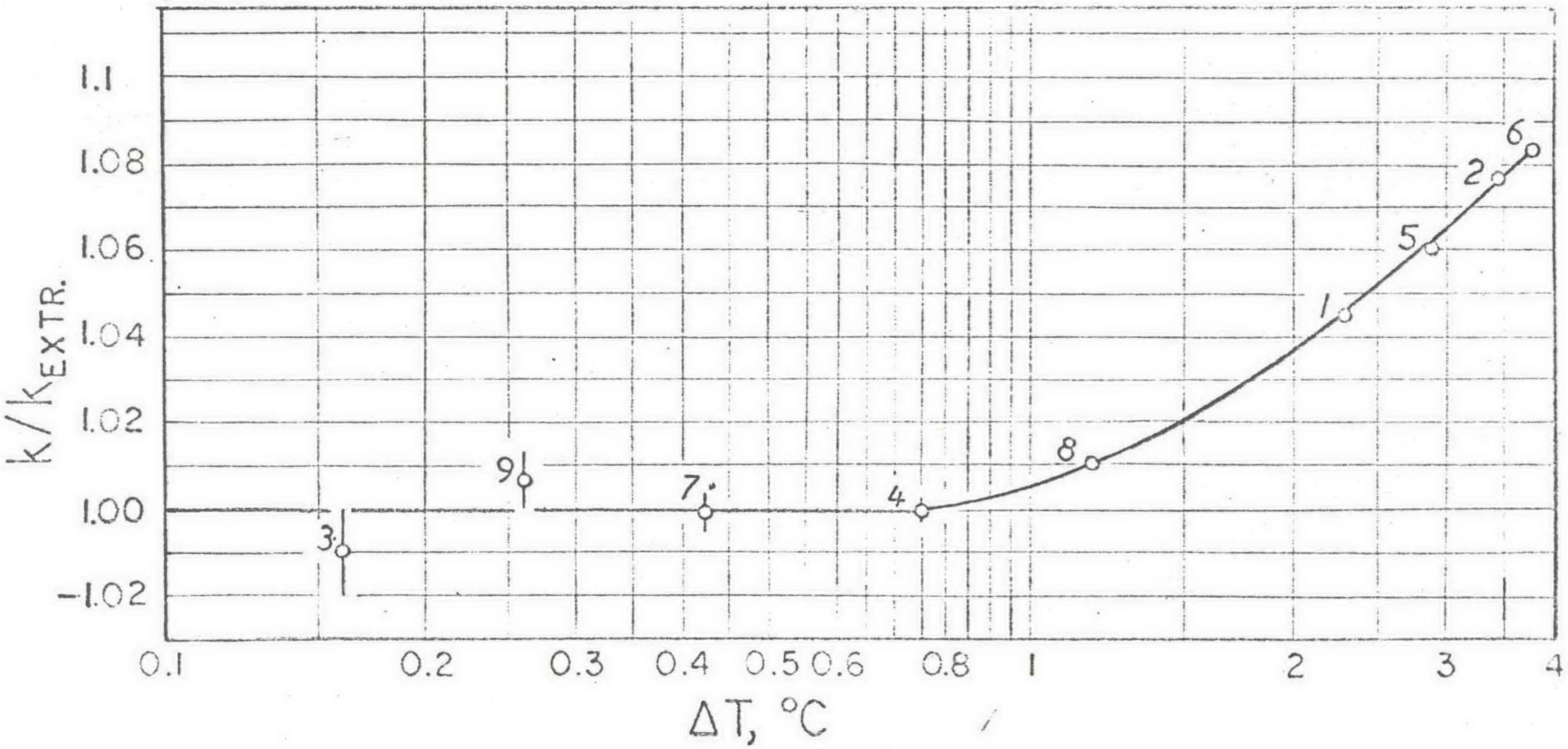

FIGURE 2. CONVECTION EFFECT FOR CO_2 AT ρ_c

potentials never reached a steady state during the higher pressure determinations, but instead oscillated with extremely small amplitude about a mean. He attributed this to separation of the gases by thermal diffusion with the result that the rate of circulation varied with time. Keyes' cell consisted of vertical concentric cylinders with a relatively large annulus, and would closely approximate a Clusius-Dickel column.

The present cell is horizontal and the degree of convection and the degree of separation will be much smaller. An analysis (7) following that of Jones and Fury (10), indicates the effect of thermal diffusion to be undiscernible. Experimentally, no diffusion effect could be detected with the cell, i.e. the measured value of the conductivity had no time dependence.

The effect of <u>thermal radiation</u> as a source of heat transfer parallel to that by conduction is taken into account accurately by the calibration equation (1). However, at higher pressures, carbon dioxide and ethane both absorb radiation in the far infrared changing the heat load and temperature profile from that obtained from the Fourier equation. The effect of the absorption of radiation is discussed by Leidenfrost (15) who demonstrates that even if information were available on spectral absorptivity and index of refraction of the gases as a function of pressure, exact corrections would be very difficult to make. "Diffusion" approximations have been made by some authors;

however, it is necessary to take into consideration the effect of the walls if the gap is narrow (4, 24, 26). Leidenfrost demonstrates that correcting data in this manner can lead to serious over-correction and errors of the same magnitude as the original, but in the opposite direction. Even though the necessary information is not available to make a correction in the case of the present work, it can be demonstrated that the error caused by absorption of radiation is small (7).

Pressure has a negligible effect on cell dimensions (7). For example, the error introduced in the measured conductivity by increasing the pressure from 1 atm. to 3,000 atm. is approximately 0.05%.

Cell Model

It is easily demonstrated (7) that the cell may be characterized to a good approximation by the infinite summation:

$$\frac{\Delta T}{q} = A\left[1 + B\left(1 - \frac{k_r}{k} + \left(\frac{k_r}{k}\right)^2 - \cdots\right)\right] \tag{1}$$

A and B are constants at a particular temperature and are determined by the cell geometry and the physical properties of the materials of construction. $k_r \times \Delta T/t$ is the radiant heat flux across the gap, where k_r is defined by

$$k_r = \left[4\sigma\left(\frac{\epsilon}{2-\epsilon}\right)T^3\right]\left[t \ln\left(\frac{r_o}{r_i}\right)\right] \tag{2}$$

k_r remains constant at a particular temperature if the emissivities and cell dimensions remain constant.

Calibration

The quantity k_r/k is the ratio of the "radiation conductivity" to the gas conductivity, and has a value of 0.03 or less. Therefore, (1) converges rapidly. Since k_r is a constant at a particular temperature, (1) may be rewritten

$$\frac{\Delta T}{q} = \sum_{i=0}^{\infty} c_i k^{-i}, \tag{3}$$

where the c_i are constants.

In order to calibrate the cell, the quantity $\Delta T/q$ is measured for gases of known thermal conductivity. By regression analysis, the coefficients are obtained up to the eighth order, and the order is chosen which has the lowest percentage standard error of estimate, S, as defined by

$$S = \left[\sum_{i=1}^{n} \left(\frac{\left(\frac{\Delta T}{q}\right)_{ci} - \left(\frac{\Delta T}{q}\right)_i}{\left(\frac{\Delta T}{q}\right)_i} \right)^2 \Big/ (N - n - 1) \right]^{1/2} \times 100 \tag{4}$$

Since the relative precision of the measurements was approximately constant, the data was weighted by the factor $(q/\Delta T)^2$.

With the constants for equation (3) known, values of $\Delta T/q$ for gases of unknown thermal conductivity may be measured, and equation (3) solved by an iterative technique to yield the thermal conductivity of the sample. These calculations were easily performed on a digital computer.

This calibration technique may be used with several gases of accurately known thermal conductivity (permissively at atmospheric pressure). In particular, a gas of high thermal conductivity, such as helium, is required. However, it was demonstrated that the use of helium at atmospheric pressure was severely limited in this cell because of temperature discontinuities at the gas-copper interfaces (7). To avoid this error the cell was calibrated under pressure using the measured values obtained by Sengers, et al. (22) for carbon dioxide at 75°C. It is judged that these values away from the critical conditions have an error of less than 1%.

Using a single calibrating gas at many pressures provides values more evenly distributed over the range of values to be measured, thus reducing interpolation errors and making the regression analysis more accurate. In addition, argon was used for some of the calibrations based on the data of Michels, et al (23). However, the conductivity of argon at the highest pressures was not as great as that of carbon dioxide, thus limiting the maximum conductivity which could be measured.

Conditions of Measurement and Results

Determinations were made on the two pure gases nitrogen and ethane, and on twelve binary mixtures of approximately 20, 40, 60, and 80 mole per cent, nitrogen, ethane, and carbon dioxide at 75°C. Sengers' (22) data on carbon dioxide was used to complete the system. All gases were purchased from the Matheson Company and the mixtures were made and analyzed by them. The minimum purities of the gases were specified by the Matheson Company as follows:

Nitrogen, Prepurified Grade	99.996%
Ethane, C. P. Grade	99.0%
Carbon Dioxide (in mixtures), Bone Dry Grade	99.8%
Carbon Dioxide (for calibration), Coleman Grade	99.99%
Argon	99.998%

The compositions of the mixtures were specified to 0.1%, and were accepted without further analysis.

The experimental data, smoothed and interpolated, are presented in Table I. Smoothing and interpolation were accomplished by fitting polynomials in density or pressure over one or two ranges of conductivity (7). The percentage standard error of estimate,

$$S = \left[\sum_{i=0}^{n} \left(\frac{k_{ci} - k_i}{k_i} \right)^2 \Big/ (N - n - 1) \right]^{1/2} \times 100 \qquad (5)$$

for each of the ranges is presented with the data.

TABLE I. SMOOTHED VALUES OF THERMAL CONDUCTIVITY FOR PURE GASES AND MIXTURES AT 75 C

		P, ATM.	DENSITY, G-MOLES/L	k X 10^4, CAL/CM SEC °C
GAS NO. 1, .194 M/F CARBON DIOXIDE, .806 M/F NITROGEN				
	1- 1	1.	3.50E-02	.657
	1- 2	25.	8.81E-01	.684
	1- 3	50.	1.77E-00	.713
	1- 4	60.	2.12E-00	.725
	1- 5	70.	2.48E-00	.737
	1- 6	80.	2.84E-00	.750
	1- 7	90.	3.19E-00	.762
	1- 8	100.	3.54E-00	.776
	1- 9	125.	4.41E-00	.810
	1-10	150.	5.26E-00	.846
	1-11	175.	6.08E-00	.883
	1-12	200.	6.88E-00	.921
	1-13	250.	8.36E-00	.998
	1-14	300.	9.70E-00	1.08
	1-15	400.	1.20E+01	1.23
	1-16	500.	1.38E+01	1.38
	1-17	750.	1.70E+01	1.73
	1-18	1000.	1.91E+01	2.05
	1-19	1500.	2.18E+01	2.62
	1-20	2000.	2.38E+01	3.12
	1-21	3000.	2.66E+01	3.99

S = .218, $1 \leqq P \leqq 3000$

		P, ATM.	DENSITY, G-MOLES/L	k X 10^4, CAL/CM SEC °C
GAS NO. 2, .367 M/F CARBON DIOXIDE, .633 M/F NITROGEN				
	2- 1	1.	3.50E-02	.602
	2- 2	25.	8.91E-01	.636
	2- 3	50.	1.81E-00	.669
	2- 4	60.	2.18E-00	.683
	2- 5	70.	2.56E-00	.697
	2- 6	80.	2.94E-00	.712
	2- 7	90.	3.32E-00	.727
	2- 8	100.	3.70E-00	.743
	2- 9	125.	4.66E-00	.786
	2-10	150.	5.60E-00	.834
	2-11	175.	6.52E-00	.885
	2-12	200.	7.41E-00	.938
	2-13	250.	9.07E-00	1.04
	2-14	300.	1.05E+01	1.15
	2-15	400.	1.29E+01	1.33
	2-16	500.	1.48E+01	1.49
	2-17	750.	1.76E+01	1.89
	2-18	1000.	1.91E+01	2.25
	2-19	1500.	2.08E+01	2.86
	2-20	2000.	2.19E+01	3.37
	2-21	3000.	2.31E+01	4.22

S = .392, $1 \leqq P \leqq 3000$

TABLE I CONTINUED

	P ATM.	DENSITY, G-MOLES/L	$k \times 10^4$, CAL/CM SEC °C
GAS NO. 3, .634 M/F CARBON DIOXIDE, .366 M/F NITROGEN			
3- 1	1.	3.54E-02	.550
3- 2	25.	9.13E-01	.581
3- 3	50.	1.89E-00	.621
3- 4	60.	2.31E-00	.639
3- 5	70.	2.74E-00	.659
3- 6	80.	3.18E-00	.681
3- 7	90.	3.64E-00	.705
3- 8	100.	4.11E-00	.730
3- 9	125.	5.31E-00	.800
3-10	150.	6.52E-00	.880
3-11	175.	7.70E-00	.964
3-12	200.	8.82E-00	1.05
3-13	250.	1.08E+01	1.21
3-14	300.	1.25E+01	1.36
3-15	400.	1.50E+01	1.59
3-16	500.	1.67E+01	1.82
3-17	750.	1.85E+01	2.26
3-18	1000.	1.92E+01	2.64
3-19	1500.	2.00E+01	3.26
3-20	2000.	2.05E+01	3.78
3-21	3000.	2.12E+01	4.64
S = .339, $1 \leqq P \leqq 637$; S = .214, $497 \leqq P \leqq 3000$			
GAS NO. 4, .762 M/F CARBON DIOXIDE, .238 M/F NITROGEN			
4- 1	1.	3.52E-02	.531
4- 2	25.	9.23E-01	.570
4- 3	50.	1.95E-00	.616
4- 4	60.	2.40E-00	.637
4- 5	70.	2.86E-00	.661
4- 6	80.	3.36E-00	.687
4- 7	90.	3.88E-00	.715
4- 8	100.	4.42E-00	.747
4- 9	125.	5.85E-00	.840
4-10	150.	7.32E-00	.949
4-11	175.	8.73E-00	1.06
4-12	200.	1.00E+01	1.17
4-13	250.	1.21E+01	1.36
4-14	300.	1.38E+01	1.53
4-15	400.	1.63E+01	1.81
4-16	500.	1.78E+01	2.04
4-17	750.	2.01E+01	2.51
4-18	1000.	2.14E+01	2.90
4-19	1500.	2.30E+01	3.54
4-20	2000.	2.40E+01	4.06
4-21	3000.	2.55E+01	4.93
S = .243, $1 \leqq P \leqq 627$; S = .230, $498 \leqq P \leqq 3000$			

TABLE I CONTINUED

	P, ATM.	DENSITY, G-MOLES/L	k X 10^4, CAL/CM SEC °C
GAS NO. 5, .187 M/F CARBON DIOXIDE, .813 M/F ETHANE			
5- 1	1.	3.50E-02	.638
5- 2	25.	9.80E-01	.693
5- 3	50.	2.28E-00	.785
5- 4	60.	2.94E-00	.839
5- 5	70.	3.73E-00	.908
5- 6	80.	4.68E-00	.995
5- 7	90.	5.75E-00	1.10
5- 8	100.	6.85E-00	1.21
5- 9	125.	8.98E-00	1.42
5-10	150.	1.02E+01	1.56
5-11	175.	1.11E+01	1.68
5-12	200.	1.17E+01	1.78
5-13	250.	1.26E+01	1.94
5-14	300.	1.33E+01	2.09
5-15	400.	1.42E+01	2.33
5-16	500.	1.50E+01	2.53
5-17	750.	*	2.96
5-18	1000.	*	3.32
5-19	1500.	*	3.91
5-20	2000.	*	4.42
5-21	3000.	*	5.28
S = .262, 1 ≦ P ≦ 497; S = .189, 497 ≦ P ≦ 3000			
GAS NO. 6, .385 M/F CARBON DIOXIDE, .615 M/F ETHANE			
6- 1	1.	3.51E-02	.611
6- 2	25.	9.65E-01	.661
6- 3	50.	2.19E-00	.739
6- 4	60.	2.79E-00	.783
6- 5	70.	3.48E-00	.837
6- 6	80.	4.28E-00	.903
6- 7	90.	5.18E-00	.981
6- 8	100.	6.14E-00	1.07
6- 9	125.	8.41E-00	1.27
6-10	150.	1.00E+01	1.43
6-11	175.	1.11E+01	1.56
6-12	200.	1.19E+01	1.67
6-13	250.	1.31E+01	1.84
6-14	300.	1.39E+01	1.99
6-15	400.	1.50E+01	2.24
6-16	500.	1.58E+01	2.45
6-17	750.	*	2.85
6-18	1000.	*	3.21
6-19	1500.	*	3.80
6-20	2000.	*	4.29
6-21	3000.	*	5.09
S = .206, 1 ≦ P ≦ 613; S = .216, 497 ≦ P ≦ 3000			

TABLE I CONTINUED

		P ATM.	DENSITY, G-MOLES/L	k X 10^4, CAL/CM SEC °C
GAS NO. 7, .581 M/F CARBON DIOXIDE, .419 M/F ETHANE				
	7- 1	1.	3.53E-02	.578
	7- 2	25.	9.56E-01	.632
	7- 3	50.	2.13E-00	.701
	7- 4	60.	2.70E-00	.737
	7- 5	70.	3.34E-00	.781
	7- 6	80.	4.06E-00	.834
	7- 7	90.	4.87E-00	.897
	7- 8	100.	5.74E-00	.968
	7- 9	125.	8.02E-00	1.16
	7-10	150.	9.99E-00	1.33
	7-11	175.	1.14E+01	1.46
	7-12	200.	1.23E+01	1.58
	7-13	250.	1.36E+01	1.77
	7-14	300.	1.46E+01	1.93
	7-15	400.	1.58E+01	2.21
	7-16	500.	1.68E+01	2.44
	7-17	750.	*	2.91
	7-18	1000.	*	3.29
	7-19	1500.	*	3.86
	7-20	2000.	*	4.31
	7-21	3000.	*	4.97
S = .250, $1 \leqq P \leqq 601$; S = .091, $384 \leqq P \leqq 3000$				
GAS NO. 8 .795 MF CARBON DIOXIDE, .205 M/F ETHANE				
	8- 1	1.	3.50E-02	.531
	8- 2	25.	9.52E-01	.573
	8- 3	50.	2.10E-00	.636
	8- 4	60.	2.64E-00	.669
	8- 5	70.	3.24E-00	.709
	8- 6	80.	3.92E-00	.756
	8- 7	90.	4.68E-00	.812
	8- 8	100.	5.54E-00	.879
	8- 9	125.	8.00E-00	1.08
	8-10	150.	1.02E+01	1.28
	8-11	175.	1.19E+01	1.43
	8-12	200.	1.31E+01	1.55
	8-13	250.	1.47E+01	1.75
	8-14	300.	1.58E+01	1.91
	8-15	400.	1.72E+01	2.17
	8-16	500.	1.83E+01	2.39
	8-17	750.	*	2.83
	8-18	1000.	*	3.20
	8-19	1500.	*	3.79
	8-20	2000.	*	4.28
	8-21	3000.	*	5.07
S = .191, $1 \leqq P \leqq 607$; S = .078, $490 \leqq P \leqq 3000$				

TABLE I CONTINUED

	P, ATM.	DENSITY, G-MOLES/L	k X 10^4, CAL/CM SEC°C
GAS NO. 9, .192 M/F NITROGEN, .808 M/F ETHANE (ARGON CAL.)			
9- 1	1.	3.49E-02	.675
9- 2	25.	9.41E-01	.725
9- 3	50.	2.04E-00	.803
9- 4	60.	2.54E-00	.844
9- 5	70.	3.06E-00	.891
9- 6	80.	3.63E-00	.944
9- 7	90.	4.21E-00	1.00
9- 8	100.	4.82E-00	1.06
9- 9	125.	6.31E-00	1.22
9-10	150.	7.61E-00	1.35
9-11	175.	8.67E-00	1.46
9-12	200.	9.54E-00	1.55
9-13	250.	1.08E+01	1.71
9-14	300.	1.18E+01	1.84
9-15	400.	1.32E+01	2.08
9-16	500.	1.42E+01	2.29
9-17	750.	*	2.69
S = .348, 1 ≦ P ≦ 600; S = .246, 103 ≦ P ≦ 834			
GAS NO. 10, .368 M/F NITROGEN, .632 M/F ETHANE (ARGON CAL.)			
10- 1	1.	3.49E-02	.675
10- 2	25.	9.29E-01	.719
10- 3	50.	1.98E-00	.779
10- 4	60.	2.45E-00	.808
10- 5	70.	2.93E-00	.839
10- 6	80.	3.44E-00	.873
10- 7	90.	3.96E-00	.910
10- 8	100.	4.49E-00	.949
10- 9	125.	5.82E-00	1.06
10-10	150.	7.05E-00	1.17
10-11	175.	8.13E-00	1.28
10-12	200.	9.05E-00	1.38
10-13	250.	1.05E+01	1.54
10-14	300.	1.16E+01	1.65
10-15	400.	1.32E+01	1.83
10-16	500.	1.42E+01	2.02
10-17	750.	*	2.45
S = .338, 1 ≦ P ≦ 493; S = .260, 381 ≦ P ≦ 3000			

TABLE I CONTINUED

	P, ATM.	DENSITY, G-MOLES/L	k X 10^4, CAL/CM SEC °C
GAS NO. 11, .598 M/F NITROGEN, .402 M/F ETHANE (ARGON CAL.)			
11- 1	1.	3.49E-02	.674
11- 2	25.	8.98E-01	.711
11- 3	50.	1.84E-00	.752
11- 4	60.	2.23E-00	.770
11- 5	70.	2.62E-00	.789
11- 6	80.	3.01E-00	.809
11- 7	90.	3.41E-00	.830
11- 8	100.	3.80E-00	.852
11- 9	125.	4.79E-00	.911
11-10	150.	5.75E-00	.974
11-11	175.	6.67E-00	1.04
11-12	200.	7.54E-00	1.10
11-13	250.	9.06E-00	1.21
11-14	300.	1.03E+01	1.32
11-15	400.	1.23E+01	1.51
11-16	500.	1.37E+01	1.68
11-17	750.	*	2.04
11-18	1000.	*	2.37
S = .202, $1 \leqq P \leqq 493$; S = .338, $379 \leqq P \leqq 3000$			
GAS NO. 12, .787 M/F NITROGEN, .213 M/F ETHANE (ARGON CAL.)			
12- 1	1.	3.49E-02	.695
12- 2	25.	8.89E-01	.730
12- 3	50.	1.80E-00	.763
12- 4	60.	2.16E-00	.775
12- 5	70.	2.53E-00	.789
12- 6	80.	2.90E-00	.802
12- 7	90.	3.26E-00	.817
12- 8	100.	3.63E-00	.832
12- 9	125.	4.52E-00	.871
12-10	150.	5.39E-00	.912
12-11	175.	6.22E-00	.954
12-12	200.	7.01E-00	.996
12-13	250.	8.46E-00	1.08
12-14	300.	9.73E-00	1.16
12-15	400.	1.18E+01	1.33
12-16	500.	1.34E+01	1.48
12-17	750.	*	1.85
12-18	1000.	*	2.18
S = .181, $1 \leqq P \leqq 491$; S = .174, $378 \leqq P \leqq 3000$			

TABLE I CONTINUED

GAS NO. 13, NITROGEN

	P, ATM.	DENSITY, G-MOLES/L	$k \times 10^4$, CAL/CM SEC°C
13- 1	1.	3.50E-02	.685
13- 2	25.	8.72E-01	.710
13- 3	50.	1.73E-00	.736
13- 4	60.	2.07E-00	.746
13- 5	70.	2.41E-00	.757
13- 6	80.	2.74E-00	.767
13- 7	90.	3.07E-00	.778
13- 8	100.	3.40E-00	.789
13- 9	125.	4.21E-00	.817
13-10	150.	4.99E-00	.845
13-11	175.	5.74E-00	.875
13-12	200.	6.46E-00	.905
13-13	250.	7.81E-00	.968
13-14	300.	9.05E-00	1.03
13-15	400.	1.11E+01	1.16
13-16	500.	1.29E+01	1.28
13-17	750.	1.63E+01	1.59
13-18	1000.	1.87E+01	1.88
13-19	1500.	2.20E+01	2.42
13-20	2000.	2.44E+01	2.93
13-21	3000.	2.77E+01	3.83

S = .154, $1 \leqq P \leqq 3000$

GAS NO. 14, ETHANE

	P, ATM.	DENSITY, G-MOLES/L	$k \times 10^4$, CAL/CM SEC°C
14- 1	1.	3.50E-02	.659
14- 2	25.	1.00E-00	.723
14- 3	50.	2.42E-00	.840
14- 4	60.	3.22E-00	.918
14- 5	70.	4.22E-00	1.03
14- 6	80.	5.47E-00	1.16
14- 7	90.	6.81E-00	1.31
14- 8	100.	7.93E-00	1.42
14- 9	125.	9.60E-00	1.61
14-10	150.	1.05E+01	1.74
14-11	175.	1.11E+01	1.85
14-12	200.	1.16E+01	1.94
14-13	250.	1.24E+01	2.11
14-14	300.	1.29E+01	2.25
14-15	400.	1.37E+01	2.49
14-16	500.	1.44E+01	2.70
14-17	750.	*	3.13
14-18	1000.	*	3.50
14-19	1500.	*	4.12
14-20	2000.	*	4.64
14-21	3000.	*	5.50

S = .212, $1 \leqq P \leqq 610$; S = .195, $390 \leqq P \leqq 3000$

TABLE I CONTINUED

	P, ATM.	DENSITY, G-MOLES/L	k X 10^4, CAL/CM SEC °C
GAS NO. 14, ETHANE (ARGON CALIBRATION)			
14- 1	1.	3.50E-02	.663
14- 2	25.	1.00E-00	.726
14- 3	50.	2.42E-00	.845
14- 4	60.	3.22E-00	.928
14- 5	70.	4.22E-00	1.04
14- 6	80.	5.47E-00	1.19
14- 7	90.	6.81E-00	1.34
14- 8	100.	7.93E-00	1.45
14- 9	125.	9.60E-00	1.61
14-10	150.	1.05E+01	1.73
14-11	175.	1.11E+01	1.83
14-12	200.	1.16E+01	1.92
14-13	250.	1.24E+01	2.08
14-14	300.	1.29E+01	2.22
14-15	400.	1.37E+01	2.46
14-16	500.	1.44E+01	2.66

S = .329, $1 \leqq P \leqq 503$, S = .283, $391 \leqq P \leqq 1851$

Discussion of Results

The data are plotted against composition with pressure as a parameter in Figures 3, 4 and 5 and against pressure with composition as a parameter in Figures 6, 7, and 8.

The results for nitrogen are compared with those of Johannin and Vodar (9) up to a pressure of 1000 atm., their maximum, in Figure 9. The agreement is good.

The results for ethane at 75°C are compared with those of Carmichael, Berry, and Sage (1) at 71.1°C in Figure 10. The comparison is not fully satisfactory, especially when one realizes that above about 100 atm., the temperature coefficient of thermal conductivity is negative. This difference in results cannot be explained in terms of convection or absorption of radiation. The purity of the ethane used by Carmichael was 99.93% compared to 99% used in this work. However, impurities in the ethane would most likely cause a lower apparent conductivity, which is not the case. A comparison is also made in this figure of the results for ethane by carbon dioxide calibration with the results using argon calibration.

In Figure 11 a comparison is made between the results for argon using two different carbon dioxide calibrations and Sengers' argon data. Since Sengers' argon data were obtained with the same cell as the carbon dioxide data used to make these calibrations, one would expect the argon data not to vary more

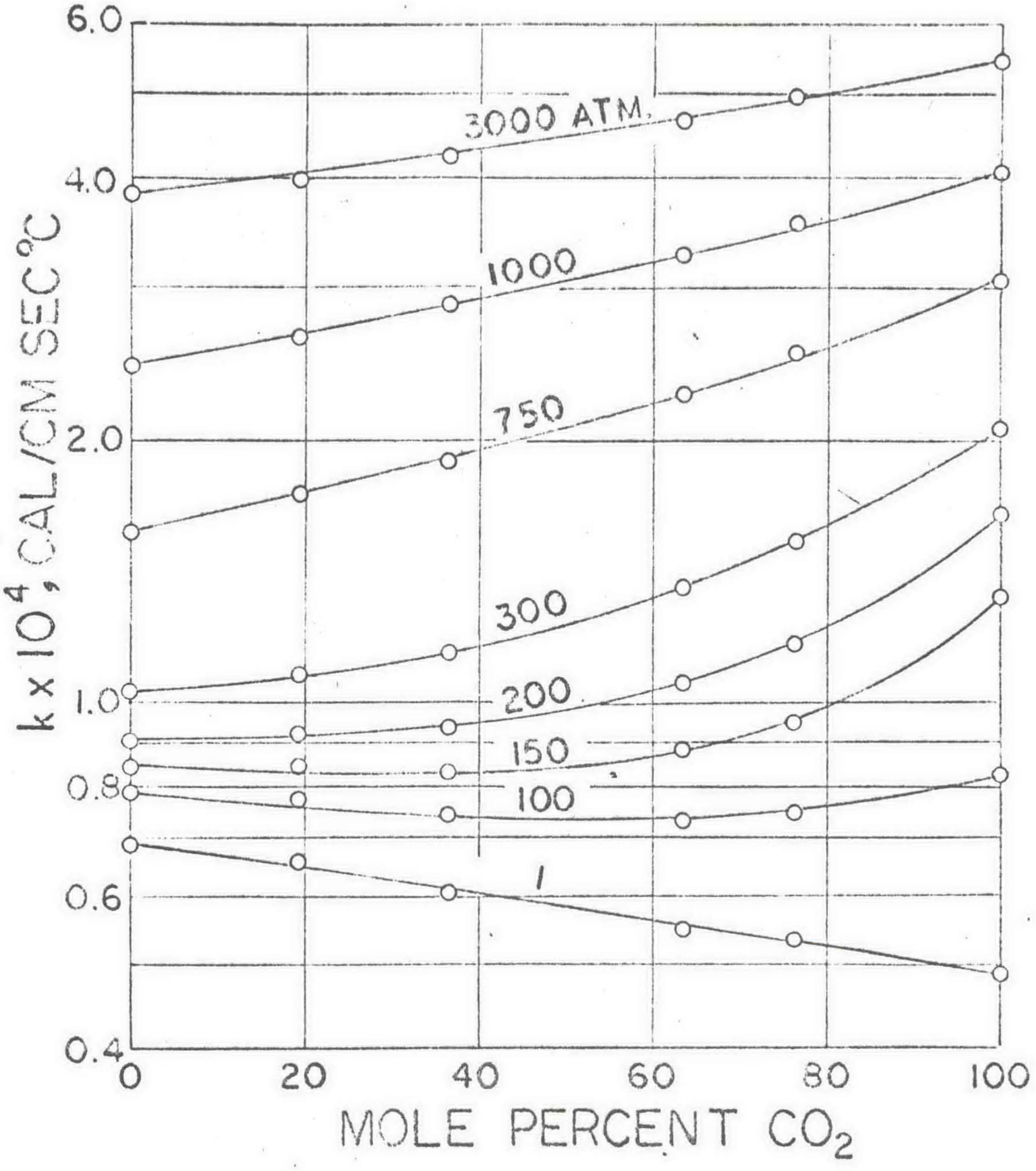

FIGURE 3. THERMAL CONDUCTIVITY OF CO_2-N_2 MIXTURES AT 75°C

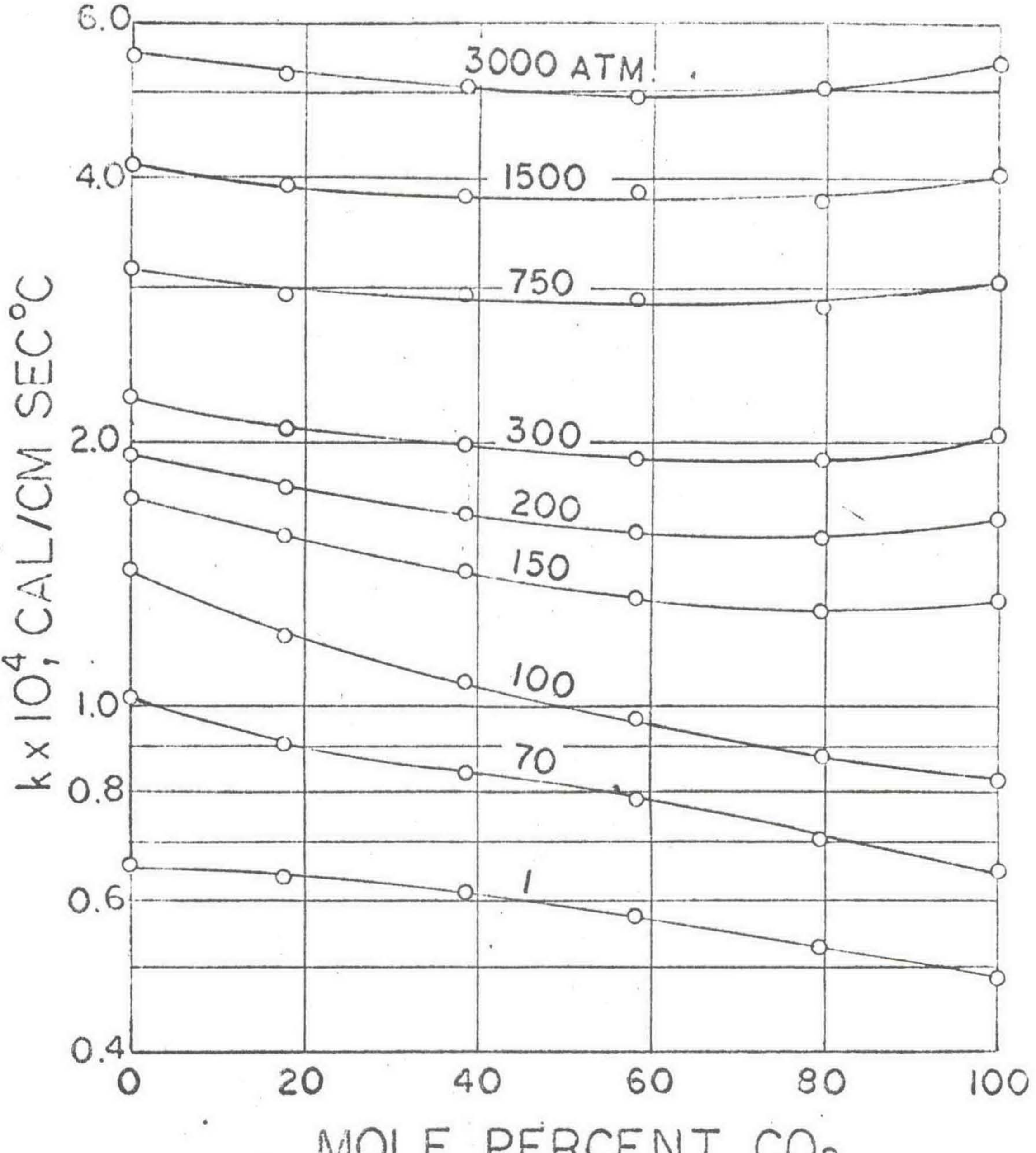

FIGURE 4. THERMAL CONDUCTIVITY OF CO_2-C_2H_6 MIXTURES AT 75°C

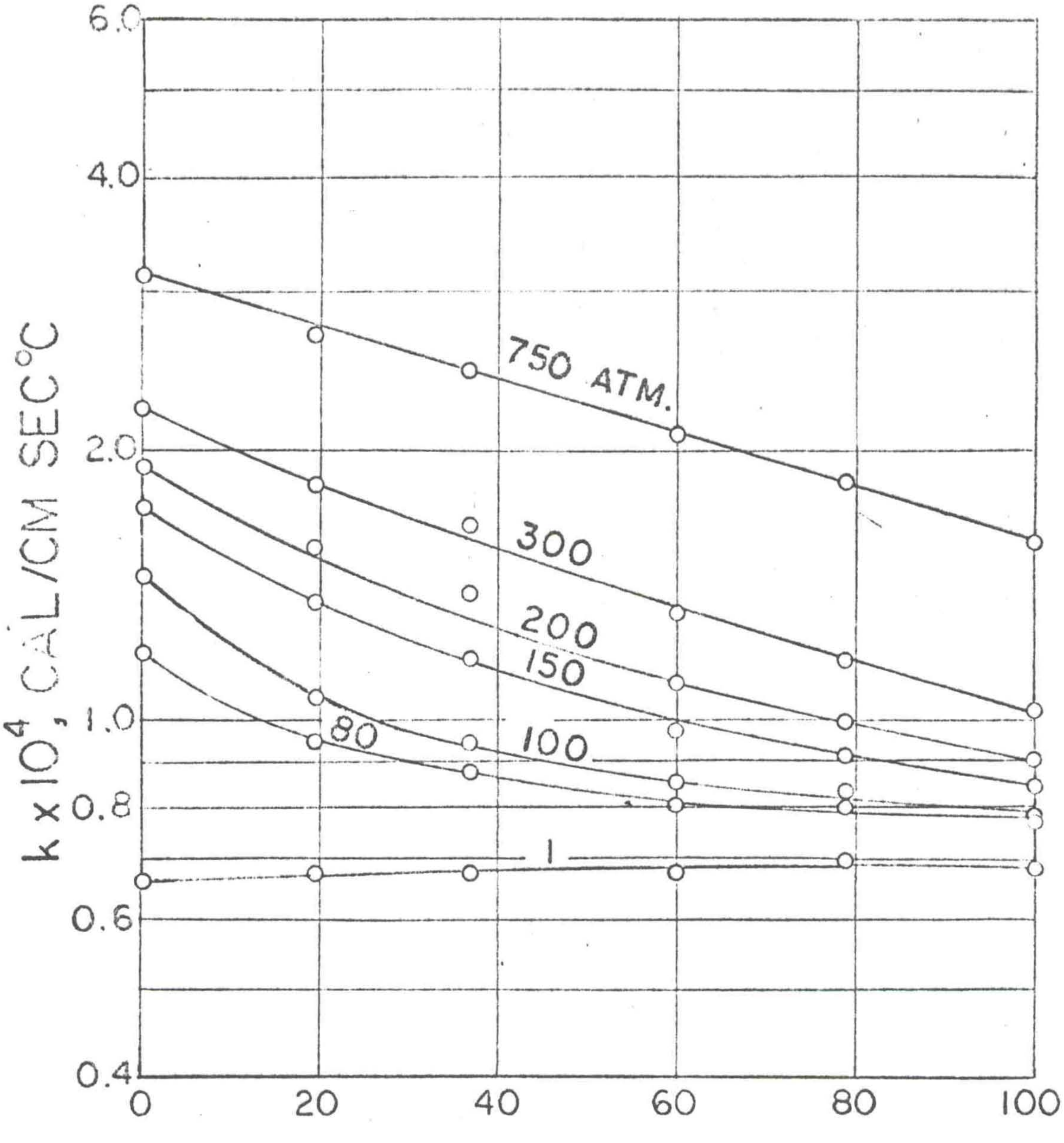

FIGURE 5. THERMAL CONDUCTIVITY OF N_2-C_2H_6 MIXTURES AT 75°C

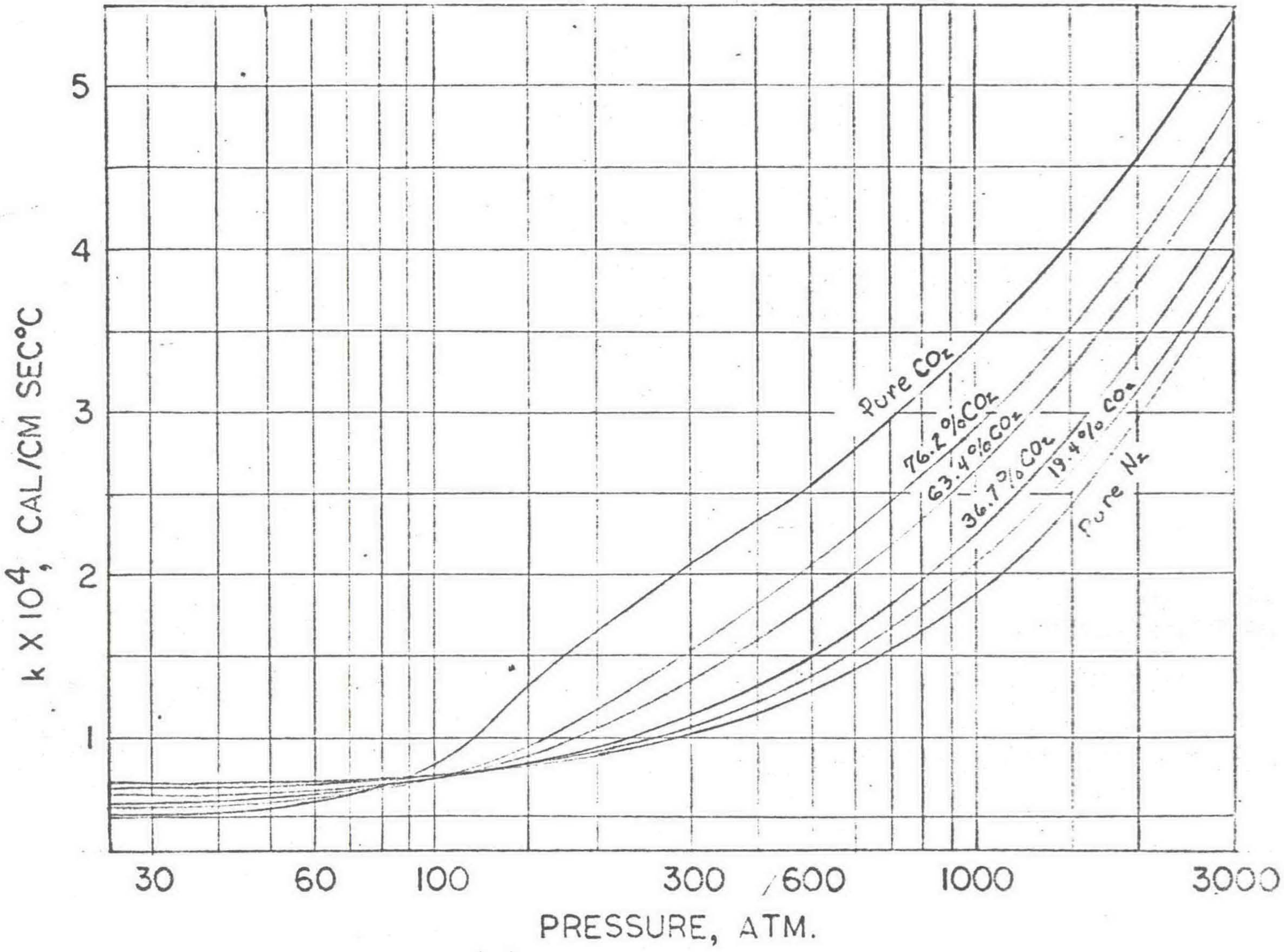

FIGURE 6. THERMAL CONDUCTIVITY OF CO_2-N_2 MIXTURES AT 75°C

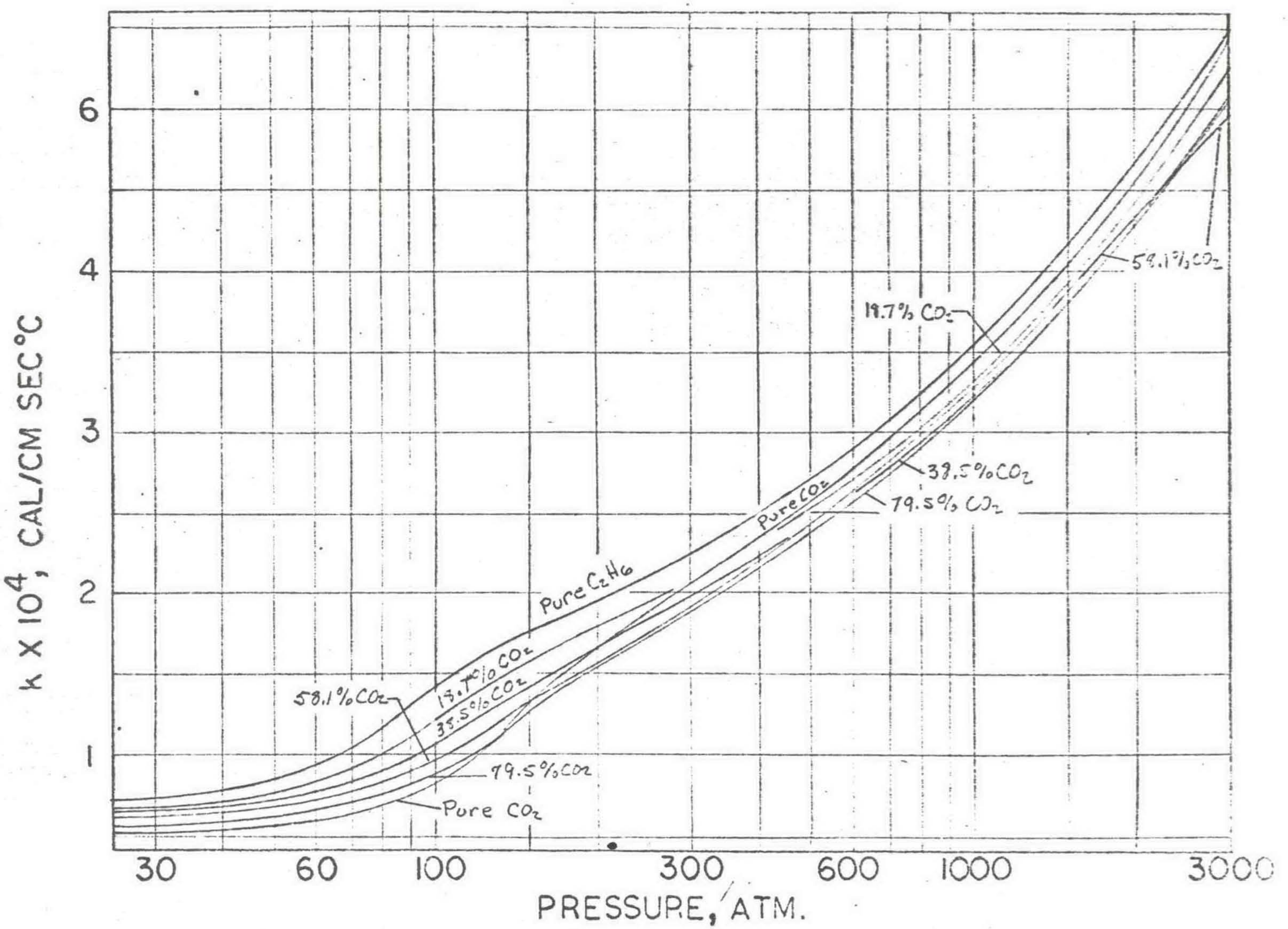

FIGURE 7. THERMAL CONDUCTIVITY OF CO_2-C_2H_6 MIXTURES AT 75°C

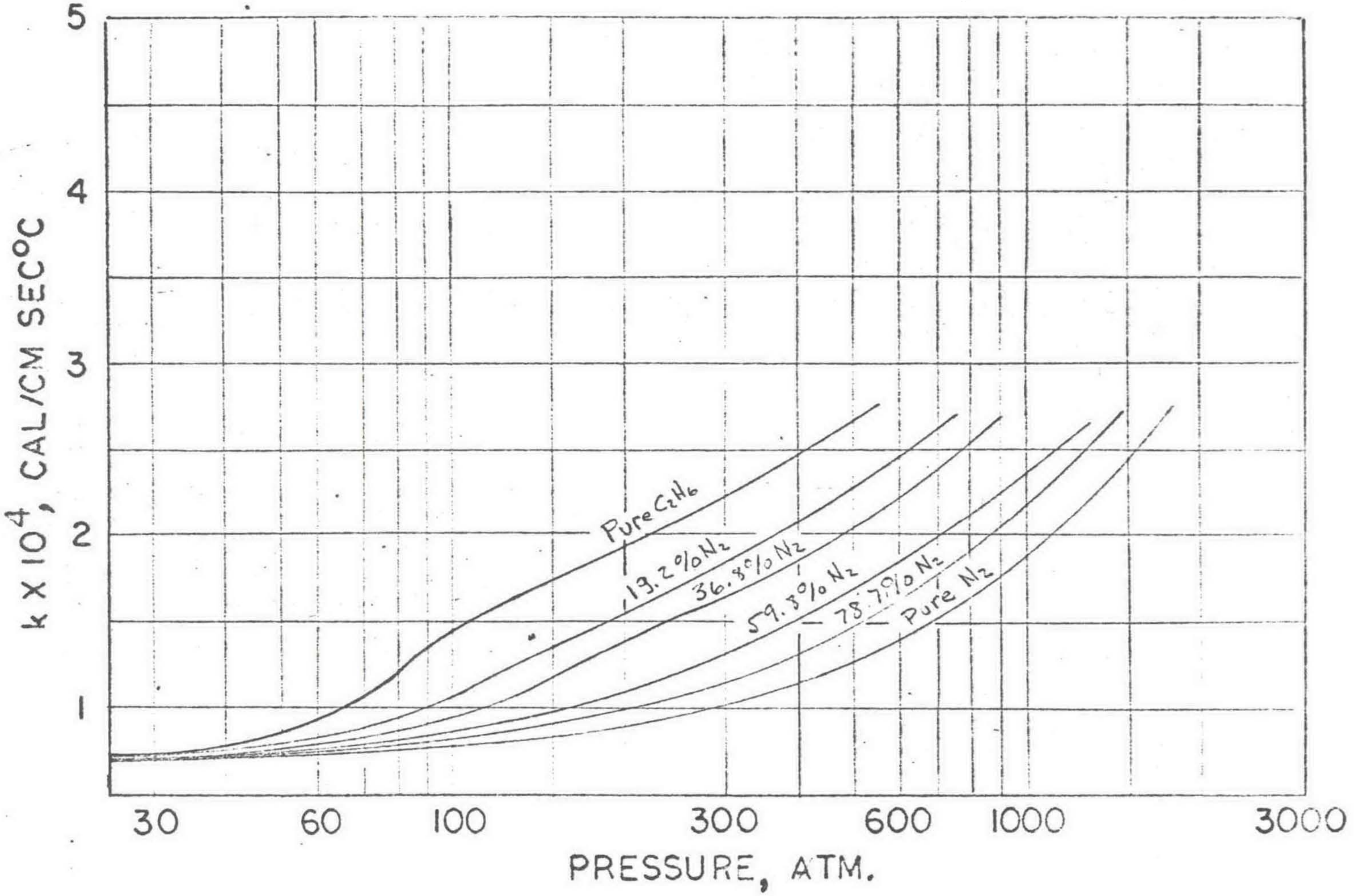

FIGURE 8. THERMAL CONDUCTIVITY OF N_2-C_2H_6 MIXTURES AT 75°C

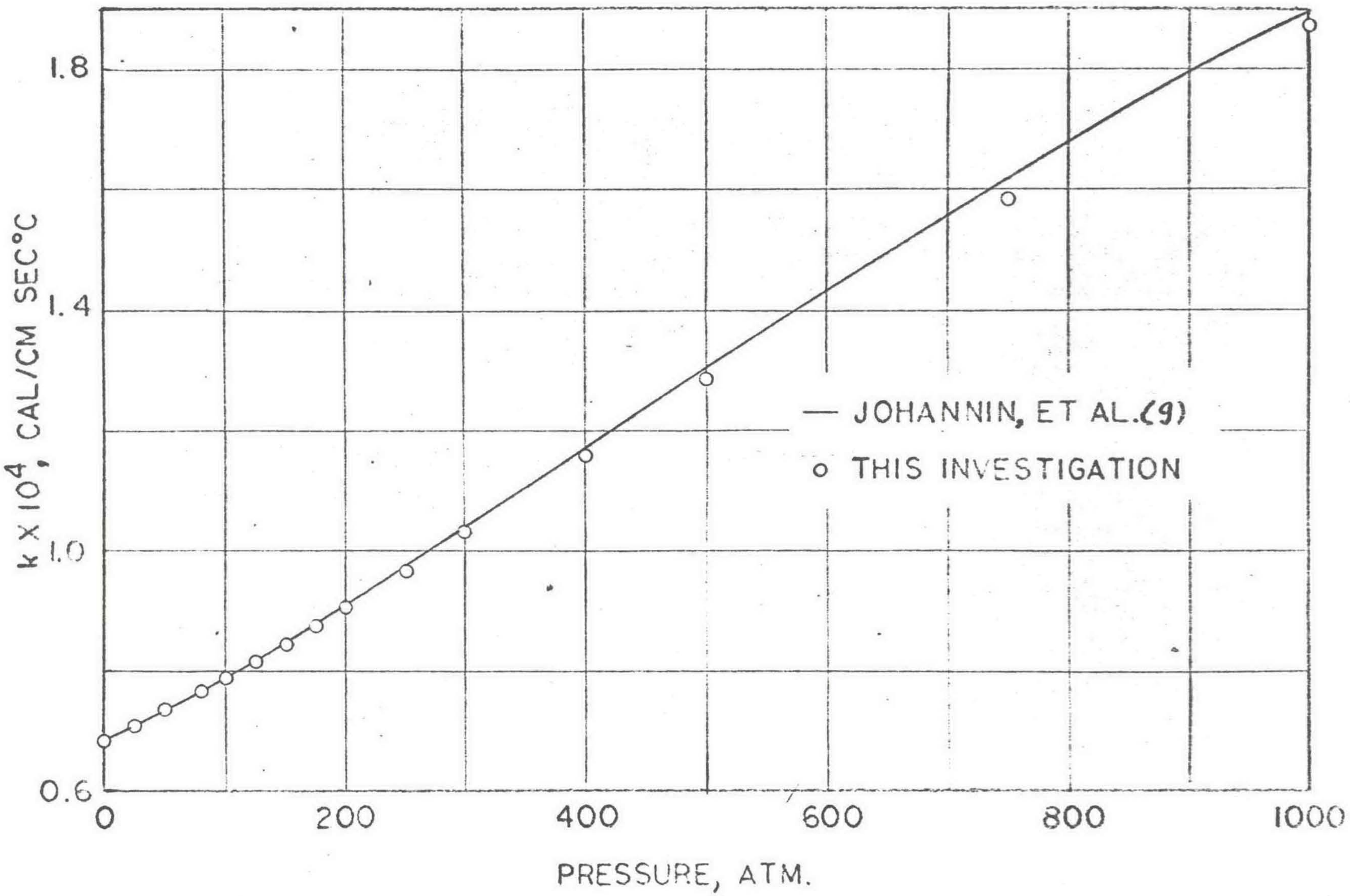

FIGURE 9. COMPARISON WITH THE RESULTS OF OTHER INVESTIGATORS: NITROGEN AT 75°C

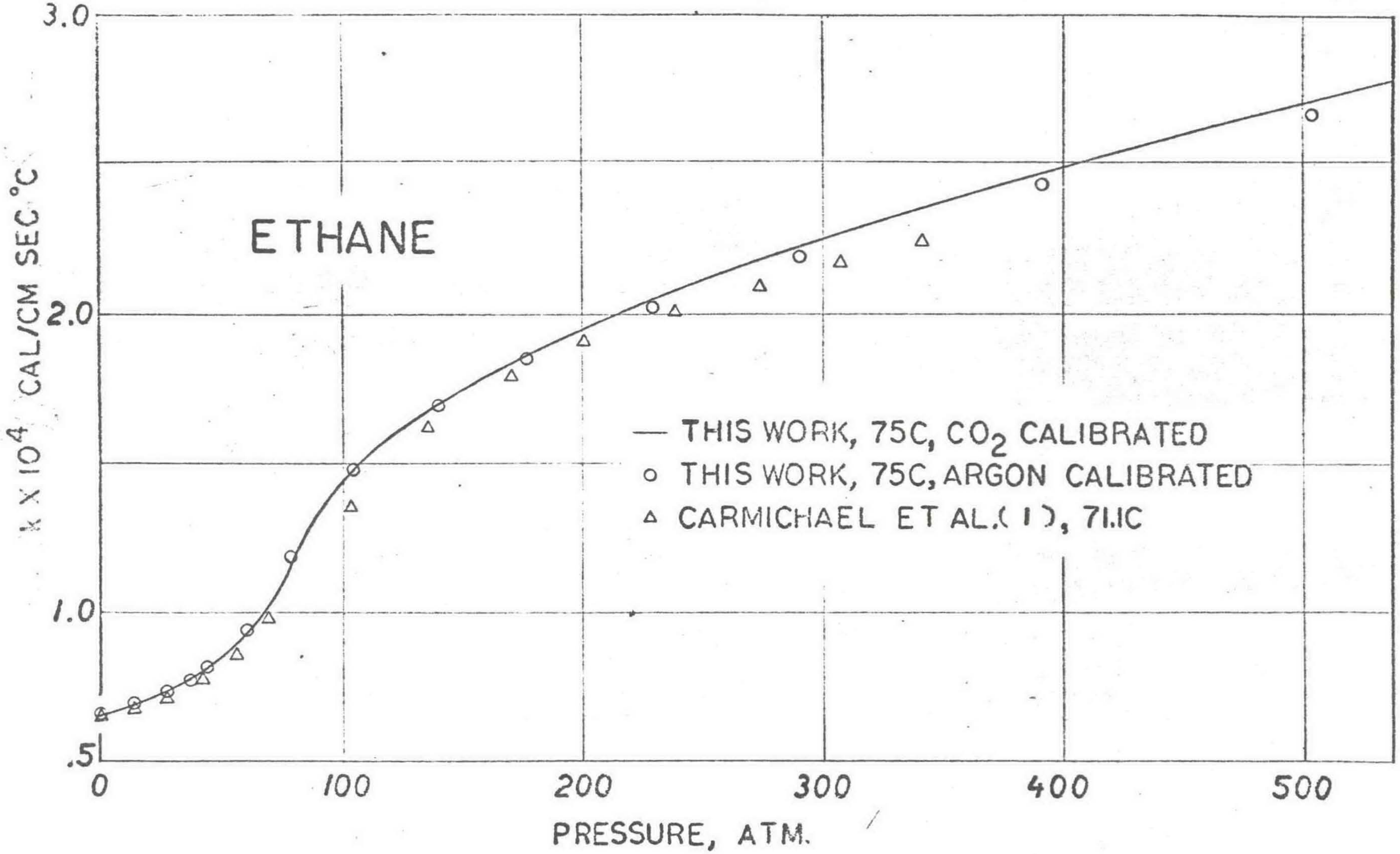

FIGURE 10. COMPARISON WITH OTHER INVESTIGATORS

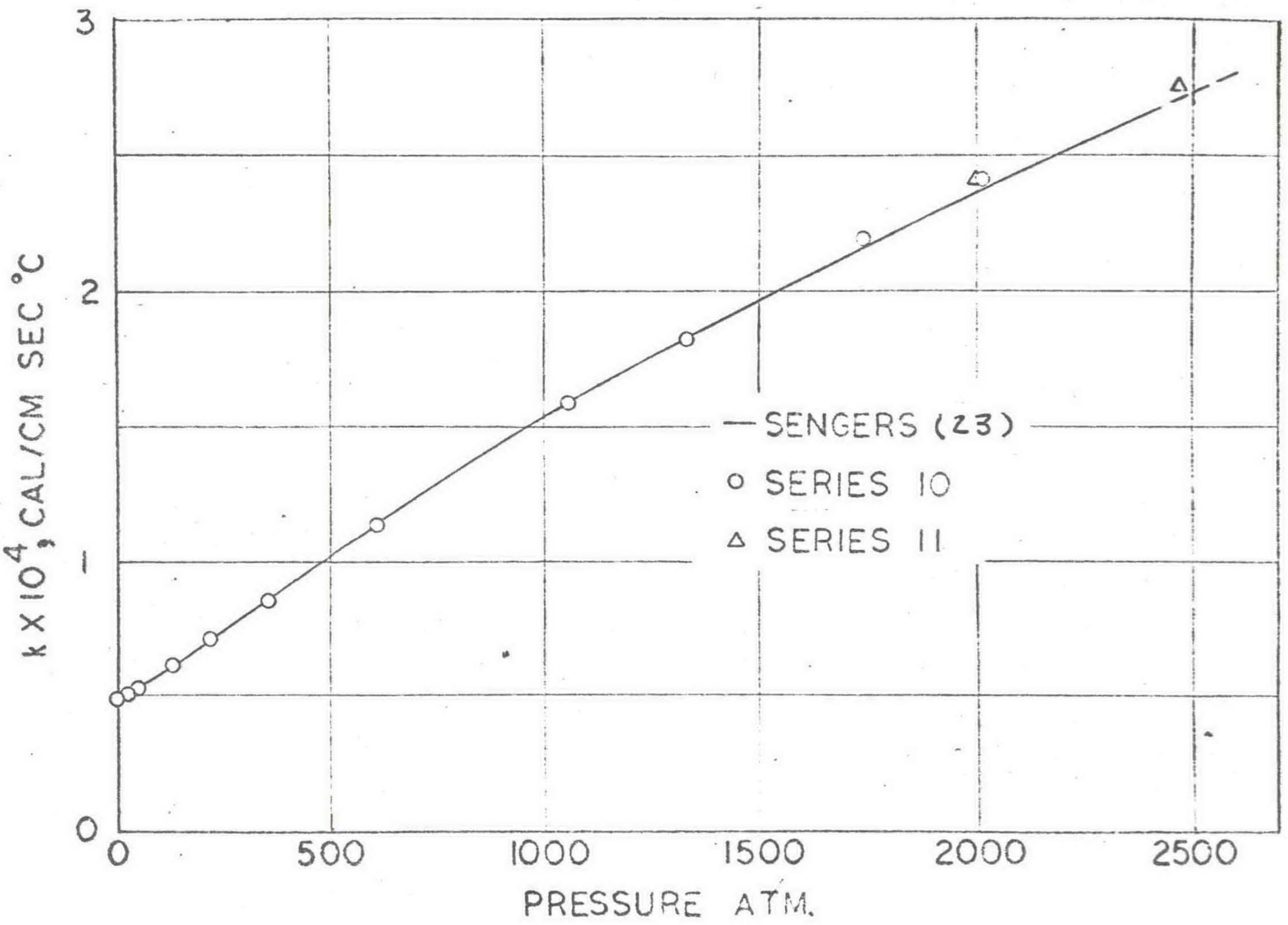

FIGURE 11. COMPARISON WITH DATA OF OTHER INVESTIGATORS: ARGON AT 75°C

than about 0.5% from Sengers' data. However, at the highest pressure, p = 2463 atm., the value of argon thermal conductivity is 1.7% greater than the value obtained by Sengers. When this was first noticed it was attributed to absorption of radiation by the carbon dioxide during calibration. The next calibrations were made with argon, thus putting a lower limit on the highest conductivity that could be measured since the maximum pressure for which data is available for argon is 2400 atm. This corresponds to a conductivity of 2.6×10^{-4} cal/cm sec°C (23). Subsequent studies as already discussed indicated that absorption of radiation could not have an effect as large at that obtained and the remaining calibrations were made with carbon dioxide. The variation is in the wrong direction to have been caused by convection of the carbon dioxide and argon is well away from the critical Rayleigh number of about 600. Its maximum Rayleigh number is only 15 for the present cell at a ΔT of 1°C. Sengers did not state the purity of the argon used other than that it was spectroscopically pure. The argon used in this work was 99.998% pure, and the deviations are again in the wrong direction to have been caused by impurities. The variation can, however, be attributed to a drift in the calibration.

Estimate of Accuracy

The cell as originally modified from Kramer's design had only two steel pins in each end supporting the emitter between the two end insulators (Figure 1). The pairs of pins were set at right angles to each other. The calibration with this design tended to drift during operation, necessitating frequent recalibration, and also causing a systematic error in the data which could not be eliminated. The emitter might have been settling because of inadequate support of the emitter and due to increased vibration in the laboratory when the system was being pressurized. Therefore the pairs of pins were replaced by three pins at each end set in a delta configuration. When this was done, centering the emitter in the receiver was more easily accomplished and with greater accuracy. The drift in calibration was decreased by more than 50%, usually being on the order of only 0.2% per pressure cycle. The drift also changed direction, now being in a negative direction.

The major random error may be attributed to the determination of the thermopile potential. The minimum thermopile potential used was about 0.07 mv. The limit of error of the potentiometer in this range is ± (0.015% + 0.5 μ v); however, because the cell is calibrated with the same potentiometer, the absolute accuracy is unimportant, but the linearity and reproducibility of the potentiometer in the range used are the important specifications. Tests indicated that the linearity and reproducibility of the potentiometer in the range used (0.07 to 0.15 mv) was ± 0.2 μ v. This limit of error would correspond to a maximum random error of (0.0002/0.07) x 100% = 0.3%. The maximum deviation from smoothed data was 0.66% in two isolated instances, with the large majority of the data having deviations of less than 0.3%, as is evident from the standard errors of estimate obtained in the smoothing process. Two points for gas number 10 were discarded because they were more than three standard errors of estimate from the smoothed data. The cell current and potential measurements could be made with a reproducibility of better than 0.02%, and therefore did not contribute significantly to the random error.

Sengers (22) specified the accuracy of his measurements as being 1%. The effect of calibration drift on the accuracy is conservatively estimated to be no more than 1.5%. Random error should be minimized by the smoothing procedure, both in calibration and in the determinations, and can be assumed to contribute no more than 0.4%. Therefore, the accuracy of the results should be better than 3%.

Comparison With Prediction Techniques

The Enskog Equations

The Enskog equations have been discussed by numerous authors (2), and were extended to mixtures by H. H. Thorne. His results, which were obtained only to a first approximation, were reported by Chapman and Cowling (2). This relation, which is strictly applicable to hard, monatomic molecules, was used to calculate the conductivities of the binary mixtures of CO_2-N_2-C_2H_6 by assuming that the contribution of the internal degrees of freedom were additive to the hard sphere conductivity:

$$k = k_{hs} + k_{ie} \tag{6}$$

where, for pure compounds,

$$k_{ie} = F\rho D\left(C_v - \frac{3}{2}\frac{k_B}{m}\right) \tag{7}$$

The factor F is an arbitrary weighting factor to be determined by regression analysis on the data for the pure compounds along with the effective molecular diameter, σ. In the curve fit for pure gases, the product ρD was assumed constant, and the one atmosphere values were used. The values obtained for molecular diameter, F, and the standard errors of estimate are:

Gas	σ, Å	F	S, %	Max. Dev., %
Carbon Dioxide	4.56	1.045	4.6	-8.3
Nitrogen	3.97	1.113	4.4	+7.0
Ethane	5.04	.68	3.9	-7.5

The calculated monatomic thermal conductivities were first approximations since the mixture equation is a first approximation.

These values of σ were used to calculate mixture hard sphere conductivities using Thorne's equations. The contribution due to internal energy was calculated by the relation

$$k_{ie}(X,P) = x_1 F_1 \rho_1(1\,atm) D_{11}(1\,atm)\left[C_{v_1}(P) - \frac{3}{2}\frac{k_B}{m_1}\right] + x_2 F_2 \rho_2(1\,atm) D_{22}(1\,atm)\left[C_{v_2}(P) - \frac{3}{2}\frac{k_B}{m_2}\right] \tag{8}$$

The results of the calculation were very disappointing, with deviations from the experimental values of as much as +75%. Selected individual results are given in Table II, along with values of k_{ie}. The deviations were much larger than those obtained for the pure gases, and were, in almost every case, positive deviations which were larger than the calculated contribution of the internal energy. This seems to indicate that the Enskog mixture equations, when applied in this manner, are not good approximations to the physical situation. This is probably due to the fact that they do not include the effects of attractive forces between molecules.

The Cluster Theory

It is well known that gases at low temperatures form clusters (8, 19) of two or more molecules. These clusters can be considered as short-lived compounds which have finite heats of reaction. The equilibrium concentrations are functions of temperature, and if the relaxation time is short, equilibrium will be approached at every point in a gas through which heat is being transferred. If the reaction between two monomers to form a dimer is exothermic, the equilibrium concentration of

TABLE II

SELECTED RESULTS OF CALCULATION OF DENSE GAS MIXTURE CONDUCTIVITIES BY ENSKOG EQUATION

P, atm.	Calculated k x 10^4, Cal./cm sec °C	% Dev.	k_{ie} x 10^4, Cal./cm sec °C
76.2% CO_2,	23.8% N_2		
1	0.539	1.65	.240
102	0.830	10.0	.316
627	4.00	74.4	.338
3069	7.33	47.0	.403
38.5% CO_2,	61.5% C_2H_6		
1	0.611	.23	.348
78	0.899	1.56	.430
171	2.18	41.8	.489
59.8% N_2,	40.2% C_2H_6		
1	.660	-1.99	.302
61	.766	-.43	.331
168	1.114	9.0	.369

dimers will be greater in the cool regions and smaller in the hot regions, with the dimerization reaction releasing heat and the decomposition reaction absorbing heat as the monomers and dimers circulate, thus increasing the effective rate of heat transfer.

For a gas at its normal boiling temperature and lower, Waelbroeck, Lafleur, and Prigogine (28, 29) applied the thermodynamics of irreversible processes to obtain the heat transferred by the reactive circulation of monomers and dimers, k_r^1, as follows:

$$k_r^1 = D k_B \left(\frac{r_{PT}^{(0)}}{k_B T}\right)^2 \frac{n_1 n_2 (n_1 + n_2)}{(n_1 + 2 n_2)^2} \tag{9}$$

where n_1 and n_2 are the molecular concentrations of monomer and dimer, respectively, D is the diffusion coefficient, and $r_{pT}^{(0)}$ is the heat of the dissociation reaction. The authors estimated that for argon at its boiling temperature, k_r^1 contributes about 6% to the thermal conductivity.

At higher temperatures and at low pressures, the concentration of dimer is small. However, near the critical point the concentrations of dimer and much larger clusters become significant, thus accounting for the large increase in the conductivity at temperatures close to the critical temperature and at densities near the critical density.

This effect apparently carries over at temperatures on the order of 40°C greater than the critical temperature since the conductivities of carbon dioxide and ethane both increase rapidly at the critical density at 75°C. The presence of a number of foreign molecules, with different force fields, would tend to decrease the clustering effect because of dilution and interference with colliding molecules. Thus, a mixture of molecules at a temperature not far from the critical temperature and at a pressure not far from that corresponding to that of the critical density of one of the components would have a conductivity somewhat less than that of the component which is near its critical temperature, i.e., the contribution of the clustering effect to the conductivity would be damped to a certain extent. This is the case for the carbon dioxide-nitrogen mixtures and the ethane-nitrogen mixtures. In both of these cases, the conductivity-mole fraction curves are nearly linear at the lowest and the highest pressures, but in the pressure region corresponding to the pressure of the critical density of one of the components, the "extra conductivity" of that component is not felt by the mixture, thus giving a negative deviation from linearity. The situation of ethane-carbon dioxide mixtures, where both components are equally far from their critical temperatures, is clouded, but is an interesting one since both gases have nearly equal thermal conductivities.

It appears in this case that the conductivities of the pure gases are not strongly affected by the presence of the foreign molecules, which indicates that clusters may be formed which contain both carbon dioxide and ethane molecules.

Lindsay-Bromley Correlation

Lindsay and Bromley (16, 17) developed a semiempirical correlation for mixtures at normal pressures based on the Wassiljewa equation (30).

$$k = \frac{k_1}{1 + A_{12} \frac{x_2}{x_1}} + \frac{k_2}{1 + A_{21} \frac{x_1}{x_2}} \qquad (10)$$

Sutherland (27) has shown, using simple kinetic theory, that the coefficients A_{12} and A_{21} could be calculated from the equation

$$A_{12} = \frac{1}{4}\left[1 + \left[\frac{\mu_1}{\mu_2}\left(\frac{M_1}{M_2}\right)^2 \frac{\left(1 + \frac{S_1}{T}\right)}{\left(1 + \frac{S_2}{T}\right)}\right]^{1/2}\right]^a \left(\frac{M_1 + M_2}{2M_2}\right)^b \frac{\left(1 + \frac{S_{12}}{T}\right)}{\left(1 + \frac{S_1}{T}\right)}, \qquad (11)$$

where the S_1, S_2 and S_{12} are the Sutherland constants. Kinetic theory indicated that a = 1/2 and b = 1/2. However, he demonstrated that to make the relation fit experimental data, b must equal -1/4.

Lindsay and Bromley suggested approximating the Sutherland constants by

$$S_1 = 1.5 T_b , \qquad (12)$$

$$S_{12} = \sqrt{S_1 S_2} . \qquad (13)$$

Reid and Sherwood (25) use these relations for dense gas mixtures using Junk's data for ethylene-carbon dioxide and ethylene-nitrogen mixtures with only fair success and with errors of approximately the same magnitude but in the opposite direction as those obtained using the Lenoir, Junk, and Comings correlation with Kay's rule.

The Lindsay-Bromley relation was tested using equations (10) through (13). The pure dense gas viscosities were obtained from references (5, 20, 21) and fit by least squares to polynomials in density for interpolation. The results are summarized in Table III, and were significantly better than those calculated by the Enskog equation, with the maximum deviations occurring at the pressures corresponding to the critical density. Good approximations were obtained at the highest and the lowest pressures.

Other Interpolation Techniques

The results were also interpolated by a simple reciprocal relation,

$$\frac{1}{k} = \frac{x_1}{k_1} + \frac{x_2}{k_2} . \qquad (14)$$

This equation was tried only because it gives negative deviations from linearity. A summary of the results of this interpolation is also presented in Table III. The simple reciprocal relation gives the best overall fit of any of the interpolation techniques tried; however, the Lindsay-Bromley relation gives smaller deviations in some cases at the lowest and highest pressures investigated. Similar results were obtained when the relation was applied to Junk's (11) data on ethylene-carbon dioxide mixtures. However, large (~ 30%) deviations were found when it was applied to Junk's ethylene-nitrogen data.

Spot checks were made using Lenoir, Junk, and Comings' correlation with Kay's rule. The deviations obtained were large in some cases, and the method cannot be recommended over the simple reciprocal interpolation.

TABLE III

COMPARISON OF THE LINDSAY-BROMLEY AND THE RECIPROCAL INTERPOLATION TECHNIQUES
75°C up to 3000 atm.

	LINDSAY-BROMLEY		EQUATION (14)	
Mixture	Variance	Max. Dev.,%@P,atm.	Variance	Max. Dev.,%@P,atm.
0.194 M/F CO_2 0.806 M/F N_2	5.9	11.3 @ 175	4.1	7.8 @ 175
0.367 M/F CO_2 0.633 M/F N_2	11.2	22.6 @ 175	8.3	16.9 @ 175
0.634 M/F CO_2 0.366 M/F N_2	14.2	29.9 @ 175	11.1	24.5 @ 150
0.762 M/F CO_2 0.238 M/F N_2	12.0	26.7 @ 150	9.7	22.7 @ 150
0.187 M/F CO_2 0.813 M/F C_2H_6	6.1	10.5 @ 90	4.4	6.4 @ 90
0.385 M/F CO_2 0.615 M/F C_2H_6	8.4	11.1 @ 90	6.6	8.3 @ 250
0.581 M/F CO_2 0.419 M/F C_2H_6	8.8	11.2 @ 175	7.2	11.2 @ 175
0.795 M/F CO_2 0.205 M/F C_2H_6	8.3	9.2 @ 300	6.6	9.4 @ 300
0.192 M/F N_2 0.808 M/F C_2H_6	11.1	21.7 @ 100	7.6	15.8 @ 100
0.368 M/F N_2 0.632 M/F C_2H_6	12.2	24.3 @ 100	7.8	15.6 @ 100
0.598 M/F N_2 0.402 M/F C_2H_6	12.4	21.4 @ 100	7.0	12.8 @ 100
0.787 M/F N_2 0.213 M/F C_2H_6	6.3	10.3 @ 125	2.8	4.8 @ 100

CONCLUSIONS

The thermal conductivity cell of Kramer (13, 14) was modified to improve the sensitivity and accuracy of the measurements. The sensitivity of the cell was significantly improved, and the rate and ease with which data could be obtained were improved. The accuracy of the measurements was limited, however, by a drift in the calibration which was only partially eliminated by modification of the emitter supports.

The Enskog dense gas mixture equation was compared with the data, and found to give very poor predictions. It was felt that the deviations were due to the attractive forces between real molecules which the Enskog equation does not consider. When the conductivity was plotted versus mole fraction, there were large negative deviations from linearity in some pressure ranges. This was attributed to the interference with cluster formation of the molecules of one of the components by the molecules of the other component.

The equations of Lindsay and Bromley and a simple reciprocal interpolation relation were tested and it was found that the reciprocal relation gave better overall results, while the Lindsay-Bromley relation was superior at the highest and lowest pressures in some cases. The Lindsay-Bromley relation requires knowledge of pure dense gas viscosities and conductivities, while the simple reciprocal relation requires only dense gas conductivities. Therefore, it is recommended that the reciprocal relation be used for the prediction of dense gas mixture conductivities until a better method is developed.

NOMENCLATURE

A_{ij}	coefficients in Lindsay-Bromley equation
c_v	heat capacity at constant volume
D	self diffusivity
D_{ij}	mass diffusivity
k	thermal conductivity
k_B	Boltzman constant
k_{hs}	hard sphere contribution to conductivity
k_{ie}	contribution of internal energy to conductivity
k_r	eqn. (2)
k_r^1	clustering contribution to conductivity
m	mass of molecule
M_i	molecular weight of component i
N	number of data points
n	order of equation
n_1	concentration of monomer
n_2	concentration of dimer
q	heat dissipated by cell heater
$r_{pT}^{(0)}$	heat of dissociation reaction
r_i	radius of emitter surface
r_o	radius of receiver surface
S	standard error of estimate
S_i	Sutherland constants
S_{12}	Sutherland constant
T	temperature

ΔT	temperature difference
T_b	atmospheric boiling temperature
t	gap thickness
x_i	mole fraction of component i
ϵ	emissivity
μ_i	viscosity of component i
ρ	density
ρ_c	critical density
σ	hard sphere molecular diameter

SUBSCRIPTS

ci	calculated i^{th} value
i	experimental i^{th} value

REFERENCES

1. Carmichael, L. T., V. Berry, and B. H. Sage, J. Chem. Eng. Data 8, 281 (1963).

2. Chapman, S., and T. G. Cowling, "The Mathematical Theory of Non-Uniform Gases," Cambridge, University Press, Chapter 16 (1961).

3. Comings, E. W., W. Lee, and F. R. Kramer, Proc. Conf. on Therm. and Trans. Prop., London, Inst. Mech. Engrs., p. 188 (1957).

4. Deissler, R. G., ASME Paper No. 63-HT-13.

5. Eakin, B. E., K. E. Starling, J. P. Dolan, and R. T. Ellington, J. Chem. Eng. Data 7, 33 (1962).

6. Gilmore, T. F., M. S. Thesis, U. of Del. (1962).

7. Gilmore, T. F., Ph.D. Diss., U. of Del. (1965).

8. Hirschfelder, J. O., C. F. Curtiss, and R. Byron Bird, "Molecular Theory of Gases and Liquids," New York, Wiley, Chapters 3 and 9 (1954).

9. Johannin, P., and B. Vodar, Ind. Eng. Chem. 49, 2040 (1957).

10. Jones, R. C., and W. H. Fury, Rev. Modern Phys. 18, 151 (1946).

11. Junk, W. A., and E. W. Comings, Chem. Eng. Prog. 49, 263 (1953).

12. Keyes, F. G., Trans. Am. Soc. Mech. Engrs. 73, 597 (1951).

13. Kramer, F. R., Ph.D. Diss., Purdue Univ. (1959).

14. Kramer, F. R., and E. W. Comings, J. Chem. Eng. Data 5, 462 (1960).

15. Leidenfrost, W., Int. J. Heat Mass Transfer 7, 447 (1964).

16. Lindsay, A. L. and L. A. Bromley, Ind. Eng. Chem. 42, 1508 (1950).

17. Lindsay, A. L. and L. A. Bromley, AEC 350-A20753.

18. McFarlin, D. J., M. M. E. Thesis, U. of Del. (1963).

19. Mayer, J. E., and M. G. Mayer, "Statistical Mechanics," New York, Wiley, Chapters 12 and 14 (1940).

20. Michels, A., A. Botzen and W. Schuurman, Physica 23, 95 (1957).

21. Michels, A., and R. O. Gibson, Proc. Roy. Soc. (London) 134A, 288 (1931).

22. Michels, A., J. V. Sengers, and P. S. van der Gulik, Physica 28, 1201 (1962).

23. Michels, A., J. V. Sengers, and L. J. M. van de Klundert, Physica 29, 149 (1963).

24. Probstein, R. F., AIAA J. 1, 1202 (1963).

25. Reid, R. C., and Sherwood, T. K., "The Properties of Gases and Liquids. Their Estimation and Correlation," New York, McGraw-Hill, p. 242 (1958).

26. Shorin, S. N., Izv. Akad. Nauk S.S.S.R., Otd. Tekh. Nauk, No. 3, 389 (1951) (Abridged English Translation in Engineer's Digest 12, 324 (1951).

27. Sutherland, W., Phil. Mag. 40, 471 (1895).

28. Waelbroeck, F. G., Proc. Int. Symp. Trans. Proc. Stat. Mech., I. Prigogine, ed., New York, Interscience, p. 382 (1958).

29. Waelbroeck, F., S. LaFleur, and I. Prigogine, Physica 21, 667 (1955).

30. Wassiljewa, A., Physik Z. 5, 737 (1904).