Thermal Conductivity of Binary Mixtures of Carbon Dioxide, Nitrogen, and Ethane at High Pressures: Comparison with Correlation and Theory

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A secondary thermal conductivity cell of the horizontal, concentric cylinder type was developed. The thermal conductivity of the pure gases nitrogen and ethane and approximately 20, 40, 60, and 80% binary mixtures of carbon dioxide, nitrogen, and ethane were determined at 75°C. to 3,000 atm. Several predictive techniques were investigated and recommendations are made.

The transport properties of dense gas mixtures have received little attention either from 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.

A secondary cell was 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. 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 (*7*) of the Kramer-Comings cell (*14*), consisting of two horizonal concentric cylinders totally immersed in the sample fluid, and with a nominal gap of 0.006 in. The cell, which has a total length of 6¼ in., is made of copper. The center cylinder or emitter is 2½ in. long with a diameter of 1.015 in. and is drilled axially with a ⅜-in. hole to accept a Supramica core. The Supramica core is slightly shorter than the emitter and is spirally grooved for a 1/32-in. by 0.00275-in., 10-ohm, chromel-2A resistance ribbon. The emitter is drilled to a depth of 1-5/16 in. with three equally spaced No. 42 holes for the three thermocouple junctions. One-inch wide by 1⅞ inch long Supramica end insulators minimize end losses.

The outer cylinder, or receiver, has an I.D. of 1.027 in. and an O.D. of 1-3/4 in. At one end there is a 2-7/16-in. 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 No. 42 holes drilled radially to within 1/16 in. of the inner surface at the longitudinal center of the receiver, three of which are spaced 120 deg. apart, while the fourth is half way 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 to 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 2½ in. Pressures were generated with a Harwood 200,000 lb./sq.in. intensifier system. Separation of the hydraulic fluid and the sample gas was accomplished with a mercury U-tube arrangement consisting of two 1½-liter, 47,500 lb./sq.in. reaction vessels connected with 1/16-in. I.D. tubing at their bottom outlets.

Three Heise gauges with the ranges 0 to 5000 lb./sq.in. with 5 lb./sq.in. subdivisions; 0 to 10,000 lb./sq.in., with 10

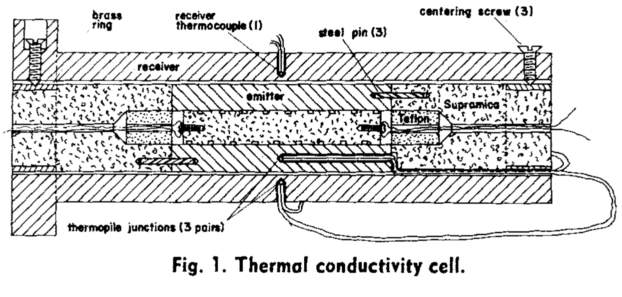

Fig. 1. Thermal conductivity cell.

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lb./sq.in. subdivisions; and 0 to 50,000 lb./sq.in., with 50 lb./sq.in. subdivisions were used. The gauges were calibrated against a Harwood controlled clearance precision dead weight tester and corrections to the gauge 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 a Northrup Type K-3 potentiometer. The bomb was mounted in an agitated hot oil bath, the temperature control of which was sufficiently sensitive so 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 begin to have a serious effect above a ΔT of about 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 carbon dioxide. 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 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 has a relatively small annulus; thus 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, that is, the measured value of the conductivity had no time dependence.

The effect of thermal radiation 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 demonstrated 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 demonstrated that correcting data in this manner can lead to serious overcorrection 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*).

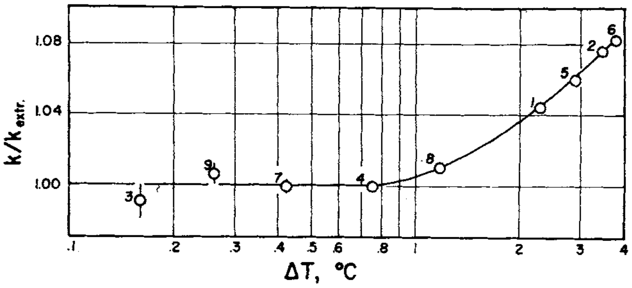

Fig. 2. Convection effect for carbon dioxide at ρ_c.

Pressure has a negligible effect on cell dimensions (*7*). For example, the error introduced in the measured conductivity by increasing the pressure from 1 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

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

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

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

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, Equation (1) converges rapidly. Since k_r is a constant at a particular temperature, Equation (1) may be rewritten as

$$\frac{\Delta T}{q} = \sum_{i=0}^{\infty} C_i k^{-i} \quad (3)$$

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

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

Since the relative precision of the measurements was approximately constant, the data were 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) may be solved by an iterative technique to yield the thermal conductivity of the sample. These calculations were easily performed on a digital computer. Due to a slight drift in the calibration, this sequence was repeated a number of times: calibration, measurement, calibration, measurement, etc.

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 by 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%.

TABLE 1. SMOOTHED VALUES OF THERMAL CONDUCTIVITY (k) FOR PURE GASES AND MIXTURES AT 75°C.

$k \times 10^4$ cal./(cm.)(sec.)(°C.)

	Carbon dioxide and nitrogen Mole fraction carbon dioxide				Carbon dioxide and ethane mole fraction carbon dioxide			
Pressure, atm.	0.194	0.367	0.634	0.762	0.187	0.385	0.581	0.795
1	0.657	0.602	0.550	0.531	0.638	0.611	0.578	0.531
50	0.713	0.669	0.621	0.616	0.785	0.739	0.701	0.636
80	0.750	0.712	0.681	0.687	0.995	0.903	0.834	0.756
100	0.776	0.743	0.730	0.747	1.21	1.07	0.968	0.879
150	0.846	0.834	0.880	0.949	1.56	1.43	1.33	1.28
200	0.921	0.938	1.05	1.17	1.78	1.67	1.58	1.55
300	1.08	1.15	1.36	1.53	2.09	1.99	1.93	1.91
500	1.38	1.49	1.82	2.04	2.53	2.45	2.44	2.39
750	1.73	1.89	2.26	2.51	2.96	2.85	2.91	2.83
1,000	2.05	2.25	2.64	2.90	3.32	3.21	3.29	3.20
2,000	3.12	3.37	3.78	4.06	4.42	4.29	4.31	4.28
3,000	3.99	4.22	4.64	4.93	5.28	5.09	4.97	5.07
Gas No.	1	2	3	4	5	6	7	8

$k \times 10^4$ (cal.)/(cm.)(sec.)(°C.)

	Nitrogen and ethane (argon calibration) Mole fraction nitrogen				Nitrogen	Ethane	Ethane (argon calibration)
Pressure, atm.	0.192	0.368	0.598	0.787			
1	0.675	0.675	0.674	0.695	0.685	0.659	0.663
50	0.803	0.779	0.752	0.763	0.736	0.840	0.845
80	0.944	0.873	0.809	0.802	0.767	1.16	1.19
100	1.06	0.949	0.852	0.832	0.789	1.42	1.45
150	1.35	1.17	0.974	0.912	0.845	1.74	1.73
200	1.55	1.38	1.10	0.996	0.905	1.94	1.92
300	1.84	1.65	1.32	1.16	1.03	2.25	2.22
500	2.29	2.02	1.68	1.48	1.28	2.70	2.66
750	2.69	2.45	2.04	1.85	1.59	3.13	
1,000			2.37	2.18	1.88	3.50	
2,000					2.93	4.64	
3,000					3.83	5.50	
Gas No.	9	10	11	12	13	14	15

Percentage standard error of estimate

Gas No.	
1	$S = 0.218, 1 \leqq P \leqq 3{,}000$
2	$S = 0.392, 1 \leqq P \leqq 3{,}000$
3	$S = 0.339, 1 \leqq P \leqq 637$; $S = 0.214, 497 \leqq P \leqq 3{,}000$
4	$S = 0.243, 1 \leqq P \leqq 627$; $S = 0.230, 498 \leqq P \leqq 3{,}000$
5	$S = 0.262, 1 \leqq P \leqq 497$; $S = 0.189, 497 \leqq P \leqq 3{,}000$
6	$S = 0.206, 1 \leqq P \leqq 613$; $S = 0.216, 497 \leqq P \leqq 3{,}000$
7	$S = 0.250, 1 \leqq P \leqq 601$; $S = 0.091, 384 \leqq P \leqq 3{,}000$
8	$S = 0.191, 1 \leqq \mathrm{P} \leqq 607$; $S = 0.078, 490 \leqq P \leqq 3{,}000$
9	$S = 0.348, 1 \leqq P \leqq 600$; $S = 0.246, 103 \leqq P \leqq 834$
10	$S = 0.338, 1 \leqq P \leqq 493$; $S = 0.260, 381 \leqq P \leqq 3{,}000$
11	$S = 0.202, 1 \leqq P \leqq 493$; $S = 0.338, 379 \leqq P \leqq 3{,}000$
12	$S = 0.181, 1 \leqq P \leqq 491$; $S = 0.174, 378 \leqq P \leqq 3{,}000$
13	$S = 0.154, 1 \leqq P \leqq 3{,}000$
14	$S = 0.212, 1 \leqq P \leqq 610$; $S = 0.195, 390 \leqq P \leqq 3{,}000$
15	$S = 0.329, 1 \leqq P \leqq 503$; $S = 0.283, 391 \leqq P \leqq 1{,}851$

The use of a single calibrating gas at many pressures provides numerous measured 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 percent nitrogen, ethane, and carbon dioxide at 75°C. Sengers' (*22*) data on carbon dioxide were 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 1.* 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

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

for each of the ranges is presented with the data.

DISCUSSION OF RESULTS

The results for nitrogen are compared with those of Johannin and Vodar (*9*) up to a pressure of 1,000 atm., their maximum, in Figure 3. The agreement is good.

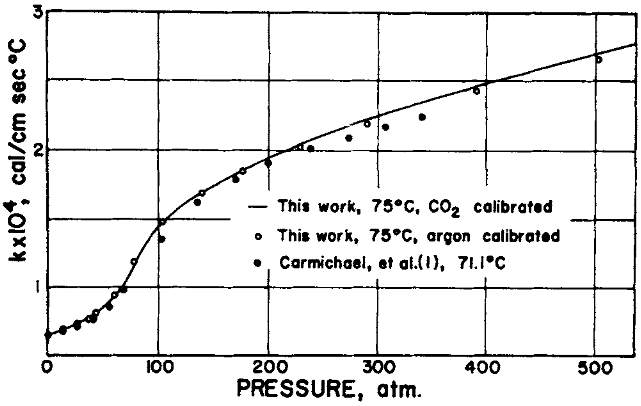

Fig. 4. Comparison with other investigators of ethane.

The results for ethane at 75°C. are compared with those of Carmichael, Berry, and Sage (*1*) at 71.1°C. in Figure 4. 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 an apparent lower 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 5 a comparison is made between the results for argon by using two different carbon dioxide calibrations and Sengers' argon data. Since Sengers' argon data were obtained with the same cell as his carbon dioxide data used to make these calibrations, one would expect the argon data not to vary more than about 0.5% from Sengers' data. However, at the highest pressure, p = 2,463 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 are available for argon is 2,400 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 as that obtained, and the remaining calibrations were made with carbon dioxide. The variation is in the wrong

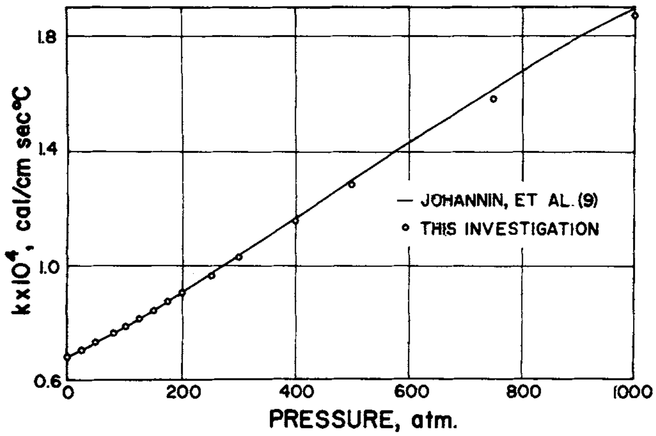

Fig. 3. Comparison with the results of other investigators for nitrogen at 75°C.

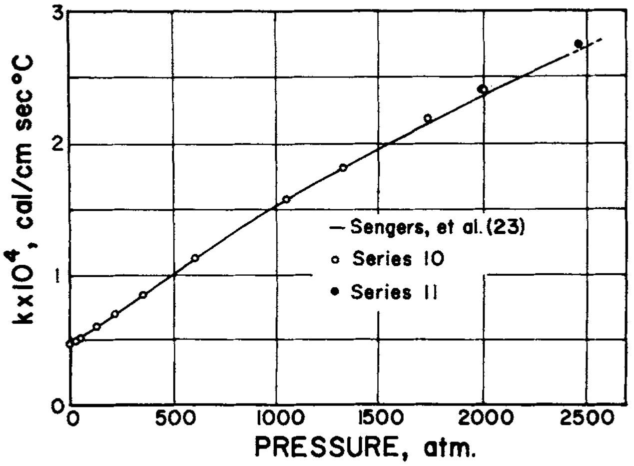

Fig. 5. Comparison with data of other investigators for argon at 75°C.

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* Complete tabulations have been deposited as document 9058 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

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 of the author's cell.

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, causing a systematic error in the data which could not be eliminated. In order to keep this drift from seriously affecting the results, the calibration was checked at frequent intervals, and if the drift exceeded 0.5%, a new calibration was made.

The emitter might have been settling because of inadequate support of the emitter and because of 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%/pressure cycle. The drift also changed direction, now being in a negative direction. However, the same procedure was observed as previously for checking the calibration at frequent intervals and for recalibrating as necessary.

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 μv.); 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 (0.07 to 0.15 mv.) were ± 0.2 μv. This limit of error would correspond to a maximum random error of $(0.0002/0.07) \times 100\% = 0.3\%$. The maximum deviation from smoothed data was 0.66% in two isolated instances, with the 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 No. 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 to be 1%. Since his measurements were used to calibrate the author's cell, this error must be added to those of the present cell. 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 Thorne (2). This relation, which is strictly applicable to hard, monatomic molecules, was used to calculate the conductivities of the binary mixtures of carbon dioxide–nitrogen–ethane by assuming that the contribution of the internal degrees of freedom was additive to the hard sphere conductivity. The results of the calculation were very disappointing, with deviations from the experimental values of as much as +75%. This seems to indicate that the Enskog mixture equations, when applied in this manner, are not good approximations to the physical situation, probably because 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 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:

$$k_r^1 = D\, k_B \left(\frac{\overset{(0)}{r_{PT}}}{k_B\, T} \right)^2 \frac{n_1 n_2 (n_1 + n_2)}{(n_1 + 2n_2)^2} \qquad (6)$$

where n_1 and n_2 are the molecular concentrations of monomer and dimer, respectively, D is the diffusion coefficient, and $\overset{(0)}{r_{PT}}$ 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. That is, 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 situa-

TABLE 2. COMPARISON OF THE LINDSAY-BROMLEY AND THE RECIPROCAL INTERPOLATION TECHNIQUES

75°C. up to 3,000 atm.

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

tion 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*).

$$k = \frac{k_1}{1 + A_{12}\dfrac{x_2}{x_1}} + \frac{k_2}{1 + A_{21}\dfrac{x_1}{x_2}} \tag{7}$$

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

$$A_{12} = \frac{1}{4}\left\{1 + \left[\frac{\mu_1}{\mu_2}\left(\frac{M_1}{M_2}\right)^a \frac{\left(1 + \dfrac{S_1}{T}\right)}{\left(1 + \dfrac{S_2}{T}\right)}\right]^{1/2}\right\}^2 \left(\frac{M_1 + M_2}{2M_2}\right)^b \frac{\left(1 + \dfrac{S_{12}}{T}\right)}{\left(1 + \dfrac{S_1}{T}\right)} \tag{8}$$

where the S_1, S_2, and S_{12} are the Sutherland constants. Kinetic theory indicated that $a = ½$ and $b = ½$. However, Sutherland demonstrated that to make the relation fit experimental data, b must equal $-¼$.

Lindsay and Bromley suggested the use of $a = ¾$ and $b = 0$ and also suggested approximating the Sutherland constants by

$$S_1 = 1.5\,T_b \tag{9}$$

$$S_{12} = \sqrt{S_1 S_2} \tag{10}$$

Reid and Sherwood (*25*) used these relations for dense gas mixtures with Junk's data (*11*) 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 by using the Lenoir, Junk, and Comings correlation with Kay's rule.

The Lindsay-Bromley relation was tested with Equations (7) through (10) with $a = ¾$ and $b = 0$. 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 2. These results 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 (*31*):

$$\frac{1}{k} = \frac{x_1}{k_1} + \frac{x_2}{k_2} \tag{11}$$

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 2. 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 by using the 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.

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 estimated as 3% was limited 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 was 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 vs. 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.

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NOTATION

A_{ij} = coefficients in Lindsay-Bromley equation
D = diffusion coefficient
k = thermal conductivity
k_B = Boltzman constant
k_r = radiation contribution to conductivity; see Equation (2)
k_r^1 = clustering contribution to conductivity
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 constant
S_{12} = Sutherland constant
T = absolute temperature
ΔT = temperature difference
T_b = atmospheric boiling temperature
t = gap thickness
x_i = mole fraction of component i

Greek Letters

ϵ = emissivity
μ_i = viscosity of component i
ρ = density
ρ_c = critical density
σ = radiation constant

Subscripts

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

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