Experimental Data and Procedures for Predicting Thermal Conductivity of Binary Mixtures of Nonpolar Gases

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The thermal conductivities of Ne, Ar, Kr, Xe, H_2, D_2 N_2, and O_2 are measured using a thick hot-wire metal cell at five temperatures in the range 40–175° C. The solution of the heat balance equation as developed by Oldham and Luchsinger is employed, and we estimate an accuracy of 1–2% in our recommended absolute conductivity values. In this temperature range, the thermal conductivities of the binary systems Ne–H_2, Ne–N_2, Ne–O_2, H_2–D_2, N_2–D_2, H_2–N_2, N_2–O_2, Kr–H_2, Xe–H_2, Xe–D_2, and Xe–Ar are also determined as a function of composition. On the basis of these experimental data, the methods of prediction of thermal conductivity of mixtures due to Hirschfelder, Mason and Saxena, Mathur and Saxena, Lindsay and Bromley, Ulybin et al., and Burgoyne and Weinberg are examined with a view to ascertain their relative accuracies. The framework of Chapman-Enskog kinetic theory in conjunction with the experimental data on thermal conductivity is used to generate the diffusion and viscosity coefficients for Xe–Ar, Xe–D_2, Ne–H_2, Ne–N_2, and Ne–O_2, as representative systems.

Recently Saxena and Gupta (*26*) have reported experimental thermal conductivity data on eight pure gases, four of their binary, two ternary and two quaternary systems as a function of composition. The measurements were taken on a metal hot-wire cell with a thick platinum wire as a hot surface, and at temperatures of 40°, 65°, and 93° C. Here we report the thermal conductivities of the binary systems Ne-H_2, Ne-N_2, Ne-O_2, H_2-D_2, N_2-D_2, H_2-N_2, N_2-O_2, Kr-H_2, Xe-H_2, Xe-D_2, and Xe-Ar as a function of composition and of the related eight pure gases at 40°, 65°, 93°, 95°, 135°, and 175° C, using the same hot-wire cell. The details of the experimental arrangement, procedure of calculation, and comparisons of the experimental conductivity values with some of the semitheoretical procedures are given in the following sections.

EXPERIMENTAL

A metal hot-wire cell of nominal length 10.44 cm and an internal diameter of 0.6412 cm was used for measurements; its details of design, construction, and precision are given by Gambhir et al. (*3*). The cell was connected to a high-vacuum pumping system and could be evacuated to less than 10^{-6} cm of mercury pressure. The gas mixtures were made with an accuracy of ±0.01% in a specially designed gas-mixing unit [Gambhir and Saxena (*4*)]. The gas or gas mixture was transferred into the cell at the desired pressure by a mercury lift system. The cell was mounted vertically in a thermostat bath, and the gas was left in it at the desired pressure from 1-4 hr to acquire thermal equilibrium before measurements were taken.

Two different thermostat baths were used. The first one is the same as described by Saxena and Gupta (*26*) and was used for measurements at 40°, 65°, and 93° C. Another bath was carefully designed for work at higher temperatures, and measurements are reported here taken at 95°, 135°, and 175° C. A brief description of this bath is given here. It consisted of a cylindrical double-walled stainless steel bath of diameter 20 cm and depth 28 cm. This bath was enclosed in a fume hood of dimensions 100 × 75 × 150 cm and was ensured to be free from any surrounding mechanical vibrations. The bath was filled with a high-vacuum pump oil of flash point near 300° C. The bath was provided with two 1000-W suspended heaters fed through an individual variac, for initial heating as well as for continuous heating. Three 500-W and two 100-W heaters all connected in parallel and strategically located in the bath were fed through a variac, and this heating was controlled by a "jumbo" contact thermometer in conjunction with an electromagnetic relay.

To further improve upon the temperature control a proportional control system as devised by Shanefield (*27*) was used. An efficient stirring arrangement was devised which achieved a very good temperature constancy and uniformity in the bath up to 200° C. The temperature difference across the entire length of the conductivity cell was negligible as long as the bath temperature remained below 100° C but rose to a few tenths of a degree as the temperature approached 200° C. This was partly remedied by taking measurements of the potential drop across the conductivity cell with current flowing in one direction and then in the reverse direction and using the mean of these two values in the calculation of conductivity. As the temperature drop across the cell remained constant, the thermal emf also remained the same for the two measurements and disappeared in the mean.

The purities of all the eight gases employed in conductivity measurements and of the platinum wire used in the fabrication of cell are reported in Table I, as also the sources of their procurement. The temperature coefficient of resistance for platinum at a temperature t° C was determined by measuring the resistance of a given length of wire at the ice point, steam point, and the boiling point of sulfur. These data were then used to determine the two unknown constants A and B of the quadratic relation, giving the variation of resistance with temperature:

Table I. Purity Levels of Materials

Material	Purity specification	Supplier
Neon	Spectral grade	British Oxygen Co., England
Argon	Spectral grade	
Krypton	99-100%, rest xenon	
Xenon	99-100%, rest krypton	
Nitrogen	99.95%	
Hydrogen	99.95%	
Oxygen	99.95%	
Deuterium	98.6%, rest 0.8% H_2, and 0.6% water vapor	Bhabha Atomic Research Center, Bombay
Platinum wire	99.99%	Ravindra Heraeus & Co., Bombay

Table II. Values of e, K(Cal Cm^{-1} Sec^{-1} Deg^{-1}) and α_t(° C^{-1}) of Platinum Wire as a Function of Temperature

Temp, ° C	e	K	α_t
40	0.0511	0.168	0.003047
70	0.0547	0.170	0.002765
91	0.0573	0.171	0.002595
134	0.0624	0.174	0.002303
174	0.0671	0.176	0.002078

Table III. Values of Thermal Conductivity, k (in 10^{-5} Cal Cm^{-1} Sec^{-1} Deg^{-1}), of Pure Gases as a Function of Pressure, p (Cm of Mercury)

Neon (178.0° C)		Hydrogen (177.0° C)		Oxygen (177.6° C)	
p	k^*	p	k^a	p	k^*
1.5	14.9	1.0	43.2	1.9	9.08
2.9	15.5	1.8	49.7	3.6	9.16
4.9	15.6	2.6	52.0	5.3	9.14
6.8	15.5	3.5	53.1	9.4	9.18
9.8	15.7	5.2	54.6	16.0	9.18
17.4	15.9	7.2	56.2	23.3	9.20
21.4	15.9	9.6	56.7	28.1	9.17
27.0	15.7	12.7	56.4	35.3	9.17
32.0	15.7	15.3	57.0	...	...
...	...	23.1	57.6	...	...

[a] Multiply these values by 41.868 to get thermal conductivity values in μW cm^{-1} deg^{-1}.

Table IV. Comparison of Experimental Thermal Conductivity Values for Pure Gases (in 10^{-5} Cal Cm^{-1} Sec^{-1} Deg^{-1}) with Literature and Theoretical Values

			$[(k - k_{\text{exptl}})/(k_{\text{exptl}})] \times 100$	
Gases	Temp, ° C	Exptl[a]	Literature	Theoretical
Ne	40	12.0	0.0	0.0
	65	12.8	−0.8	−1.6
	93	13.5	0.0	−1.5
	95	13.7	−1.5	−2.2
	135	14.5	−0.7	−1.4
	175	15.4	−0.6	−1.3
Ar	40	4.43	−0.2	−0.9
	65	4.61	+1.5	+1.1
	93	5.03	−0.6	−1.4
Kr	40	2.35	+0.4	−0.4
	65	2.58	−2.1	−2.6
	93	2.74	−0.6	−1.5
Xe	40	1.42	+4.2	−1.4
	65	1.49	+6.7	+4.6
	93	1.70	−1.2	−1.2
H_2	40	43.9	+0.7	+4.5
	65	46.8	+0.9	+3.4
	93	49.2	+1.6	+4.0
	95	51.0	−1.4	+0.8
	135	54.8	−0.2	+0.4
	175	57.2	+2.4	+2.6
D_2	40	32.6	+0.6	0.0
	65	34.4	0.0	0.0
	93	36.1	+0.8	+0.4
	95	37.2	...	−2.2
	135	39.2	...	−0.7
	175	42.1	...	−1.4
N_2	40	6.46	−0.9	+2.8
	65	6.89	−2.0	+2.0
	93	7.38	−2.4	+1.1
	95	7.42	−2.3	+0.8
	135	8.09	−3.6	−0.4
	175	8.66	−1.8	−0.4
O_2	40	6.72	−1.4	−0.1
	65	6.94	+1.8	+2.7
	93	7.49	+1.5	+1.3
	95	7.81	−2.0	−2.3
	135	8.25	0.0	0.0
	175	9.03	−1.4	−2.0

[a] These are partly smoothed by plotting the observed values as a function of temperature. Multiply these values by 41.868 to get thermal conductivity values in μW cm^{-1} deg^{-1}.

$$R_t = R_{\text{ice}}\ (1 + At + Bt^2) \tag{1}$$

This gave $A = 35.21 \times 10^{-4}$ $°C^{-1}$ and $B = -59.0 \times 10^{-8}$ $°C^{-2}$. The temperature coefficient of resistance at a particular temperature t° C is then readily obtained from the following defining relation:

$$\alpha_t = (1/R_t)(dR_t/dt) = (A + 2\ Bt)/(1 + At + Bt^2) \tag{2}$$

The values of α_t computed at the temperatures of our current interest are given in Table II. In these experiments the platinum wire of the conductivity cell acted both as a heater as well as a thermometer. Its resistance in conjunction with Equation 1 enabled us to determine the temperature of the bath as well as monitor its constancy over a period of time. The changes in temperature could be detected with a high degree of accuracy and sensitivity as the resistance of the cell wire changes by about 2 $\mu\Omega$ for a temperature change of 0.01° C around 40° C. We estimate an uncertainty of ±0.05° C in our temperature measurements below 100° C and an uncertainty of ±0.5° C between 100° and 200° C.

A Tinsley vernier potentiometer in conjunction with a Tinsley short period galvanometer was used to measure the electrical signals. The direct range of the potentiometer varied between a maximum of 1.8 V and a minimum of 0.1 μV. The current in the circuit was measured in terms of the potential drop across a Cambridge standard resistance of 0.1 Ω.

The experimentation of Gupta and Saxena (*8*) revealed that for this cell and for temperatures up to about 100° C, the temperature jump effect was insignificant if the gas pressure was above 8 cm of mercury, and convection was negligible for gas pressure below 50 cm of mercury. To re-examine these effects in the higher temperature range of our present investigations was necessary. To resolve this, careful measurements were taken on neon, hydrogen, and oxygen at about 177° C as a function of pressure. These results are reported in Table III.

Conductivity values for neon and oxygen, and to a lesser extent for hydrogen, do not change significantly for pressures lying between 10 and about 30 cm of mercury, and it is appropriate to assume that both convection and temperature jump effects are negligible in this pressure range. We have performed our measurements for gas pressures varying in the range 10 to 16 cm of mercury. The data of Table III conform well to the simple theory of temperature-jump effect [Present (*24*)]. According to this theory, a plot of k^{-1} vs. p^{-1} is linear, and the true thermal

Table V. Comparison of Experimental Thermal Conductivity Values for Binary Gas Systems (in 10^{-5} Cal Cm^{-1} Sec^{-1} Deg^{-1}) with Various Sets of Calculated Values

				$[(k - k_{\mathrm{exptl}})/(k_{\mathrm{exptl}})] \times 100$						
Gas Pair	Temp, °C	x_1	Exptl[a]	Eqs. 8, 9	Eqs. 10, 11	Eqs. 10, 13	Eqs. 10, 14	Eq. 15	Eq. 16	Eq. 17
Ne–H_2	40	0.150	36.9	+3.3	+3.8	+0.3	+1.9	...	−5.2	+0.6
		0.405	27.8	−0.5	+6.5	...	+3.3	...	−7.2	...
		0.665	20.5	−4.4	+4.4	−3.0	+1.5	...	−6.9	−4.4
	65	0.150	39.1	+3.1	+4.2	+0.7	+2.6	−0.3	−4.9	+0.2
		0.405	29.9	−2.4	+5.3	−1.4	+2.3	−1.4	−7.8	−4.1
		0.665	21.6	−4.2	+6.0	−1.4	+2.7	+1.4	−5.2	−5.6
	93	0.150	41.4	+2.9	+3.4	0.0	+1.7	−1.0	−5.5	−1.2
		0.405	31.6	−2.2	+5.1	−1.9	+2.0	−1.9	−8.2	−6.0
		0.665	23.1	−5.3	+4.3	−3.1	+1.3	−0.5	−6.6	−9.6
	95	0.272	36.1	+1.9	+9.5	+3.5	+6.7	...	−3.6	+7.5
		0.293	34.3	+4.4	+12.6	+6.5	+9.7	...	−1.0	+10.8
	135	0.272	41.2	−4.4	+2.5	−3.0	+0.1	−7.1	−9.9	...
		0.293	36.6	+5.0	+13.2	+6.8	+10.3	−0.8	−0.9	+9.0
	175	0.272	44.2	−4.7	+0.2	−5.2	−2.3	−9.1	−11.9	−4.6
		0.293	42.1	−2.8	+2.8	−3.1	+0.1	−9.6	−9.6	−2.5
Ne–N_2	40	0.203	10.4	0.0	−4.2	−1.9	−1.9	...	−0.0	−1.0
		0.511	8.43	+4.3	−4.9	...	−0.2	...	+2.8	...
		0.805	7.24	+1.1	−4.0	−2.2	−1.8	...	+0.3	−2.3
	65	0.203	11.0	0.0	−2.7	0.0	0.0	+1.8	+2.7	−0.9
		0.511	8.93	+3.8	−2.2	+0.8	+1.6	+1.9	+4.8	−1.7
		0.805	7.65	+1.8	−1.8	−0.1	+0.3	+3.5	+2.5	−2.7
	93	0.203	11.6	0.0	−1.7	−0.0	+0.9	+2.6	+2.5	−1.7
		0.511	9.62	+2.0	−3.0	−0.4	+0.3	+0.7	+3.8	−5.5
		0.805	8.17	+0.2	−1.5	−0.2	+0.7	+2.7	+2.9	−4.4
	95	0.256	10.1	+11.4	+20.9	+12.0	+12.7	...	+15.1	+6.9
		0.735	7.89	+8.0	+3.8	+6.2	+6.8	...	+9.6	...
	135	0.256	11.6	+3.4	+11.8	+3.2	+3.9	−7.7	+6.3	−1.6
		0.735	8.77	+4.5	+0.9	+3.3	+3.8	−2.7	+6.5	−5.4
	175	0.256	12.5	+2.2	+11.2	+2.6	+3.2	−8.3	+5.6	−4.2
		0.735	9.36	−3.9	+2.3	+4.6	+5.1	−1.4	+7.9	−6.6
Ne–O_2	40	0.340	9.88	−2.9	−6.7	−0.8	−2.7	...	−1.2	−0.3
		0.496	8.97	−2.6	−6.2	...	−1.9	...	−0.2	...
		0.739	7.67	−0.3	−2.8	+1.8	+0.3	...	+2.0	+2.1
	65	0.340	10.2	−1.0	−3.9	+2.0	−0.0	+2.9	+2.0	+1.0
		0.496	9.43	−1.9	−5.8	+0.5	−1.4	+0.4	+0.1	−1.4
		0.739	8.15	−0.5	−4.4	+0.2	−1.2	−2.7	+0.2	−1.6
	93	0.340	10.8	−0.9	−3.7	+2.8	−0.0	+2.8	+1.9	−1.9
		0.496	10.1	−3.1	−6.3	−0.0	−2.1	+0.0	0.0	−4.9
		0.739	8.66	−0.6	−3.6	+1.0	−0.5	−1.8	+1.2	−3.5
	95	0.229	10.9	+5.8	+5.3	+10.8	+9.0	...	+10.3	+2.4
		0.492	9.10	+8.3	+7.1	+14.3	+12.0	...	+14.0	...
		0.744	8.80	−1.9	−2.0	+2.6	+1.2	...	+2.7	−9.0
	135	0.229	12.25	+0.5	−1.4	+3.7	+2.1	−6.1	+3.3	−5.3
		0.492	10.5	+1.2	−1.6	+5.0	+2.8	−7.6	+4.7	−10.2
		0.744	9.49	−2.0	−4.1	+0.4	−1.0	−2.3	+0.5	−12.4
	175	0.229	13.05	+0.2	−1.4	+3.9	+2.1	−5.8	+3.5	+6.2
		0.492	12.05	−6.5	−8.3	−2.1	−4.1	−6.2	−2.3	−18.7
		0.744	9.86	+0.9	+0.3	+5.0	+3.4	+3.1	+5.0	−10.8
H_2–D_2	40	0.253	38.9	+7.0	+2.3	+4.2	+4.2	...	+3.9	+1.5
		0.497	36.7	+3.6	+0.3	...	+2.5	...	+2.2	...
		0.762	32.6	+5.3	+5.0	+4.0	+6.5	...	+6.5	+3.7
	65	0.253	41.0	+7.1	+2.9	+2.2	+4.9	0.0	+4.2	+0.5
		0.497	38.1	+5.4	+2.4	+1.4	+4.8	+1.4	+3.5	−1.5
		0.762	34.7	+6.1	+4.3	+3.5	+6.1	−1.2	+5.8	+0.8
	93	0.253	45.1	+2.9	−1.5	−2.5	0.0	−4.7	−0.2	−5.6
		0.497	40.6	+0.7	+1.0	−0.2	+3.2	−0.3	+2.5	−5.0
		0.762	37.2	+4.3	+1.9	+1.1	+3.8	−3.2	+3.6	−3.0
	95	0.243	46.4	+0.7	+0.4	−1.4	+1.1	...	+0.7	−2.8
		0.488	41.4	+2.8	+2.6	+1.4	+5.0	...	+4.5	...
		0.762	38.2	+2.1	−2.5	+1.7	+4.3	...	+4.0	−0.4
		0.936	38.1	−2.8	−1.8	−2.0	−1.3	...	−1.3	−2.8
	135	0.243	47.7	+4.9	+3.3	+2.5	+5.1	+2.7	+4.6	−0.8
		0.488	45.2	+1.4	+0.1	−1.0	+2.5	−3.3	+1.8	−6.0
		0.762	39.9	+4.7	−1.1	+3.3	+4.8	+0.5	+4.3	−1.2
		0.936	39.9	−0.8	−1.2	−1.4	−0.6	+0.8	−0.7	−3.0

(continued)

Table V. (*Continued*)

				$[(k - k_{exptl})/(k_{exptl})] \times 100$						
Gas Pair	Temp, °C	x_1	Exptl[a]	Eqs. 8,9	Eqs. 10,11	Eqs. 10, 13	Eqs. 10, 14	Eq. 15	Eq. 16	Eq. 17
H_2-D_2	175	0.243	51.8	+3.1	+0.1	−0.7	+1.8	−0.4	+1.5	−5.7
		0.488	47.9	+1.8	−0.1	−0.7	+2.2	−3.5	+1.8	−8.6
		0.762	43.0	+3.7	−2.1	+2.2	+4.8	−0.2	+4.6	−4.0
		0.936	42.7	−1.0	−0.7	−0.9	−0.2	−0.3	−0.3	−3.1
N_2-D_2	95	0.332	22.4	−5.5	+1.0	+0.6	−0.2	. . .	−4.7	+2.0
		0.496	17.6	−6.0	+1.1	+0.3	−0.3	. . .	−1.8	. . .
	135	0.332	24.2	−6.2	−1.0	−1.4	−2.3	−1.6	−6.2	−1.8
		0.496	18.7	−5.4	+0.8	+0.3	−0.6	−0.8	−1.7	−3.0
	175	0.332	25.8	−5.9	+0.3	−0.1	−1.1	−1.2	−4.8	−2.4
		0.496	20.6	−8.1	−1.1	−1.5	−2.6	−1.5	−3.5	−7.4
H_2-N_2	95	0.260	32.3	−0.0	+3.6	+3.0	−0.7	. . .	−8.5	+4.5
		0.513	21.2	−4.9	+2.5	+1.7	−3.4	. . .	−3.8	. . .
		0.880	10.4	−5.0	−2.2	−2.6	−5.3	. . .	−1.0	−9.6
	135	0.260	34.2	−0.5	+5.2	+4.6	+0.4	+0.9	−6.8	+4.7
		0.513	23.2	−6.4	+1.2	+0.5	−4.6	−1.3	−4.9	−4.3
		0.880	10.9	−2.5	+1.7	+1.2	−1.6	+3.7	+2.9	−8.0
	175	0.260	36.7	−1.1	+2.8	+2.2	−2.0	−0.8	−8.2	+1.2
		0.513	24.2	−4.1	+2.4	+1.6	−3.6	+0.8	−3.4	−5.2
		0.880	11.8	−3.2	+0.8	+0.4	−2.3	+4.2	+2.1	−10.2
N_2-O_2	95	0.227	7.50	+0.1	−3.5	−2.1	−1.2	. . .	−1.2	+2.0
		0.514	7.90	−4.4	−7.3	−5.6	−4.3	. . .	−4.3	. . .
		0.782	7.76	−2.2	−2.8	−1.7	−0.8	. . .	−0.8	+2.2
	135	0.227	8.12	−0.2	−3.4	−2.2	−1.2	0.0	−1.2	−0.7
		0.514	8.49	−4.0	−7.7	−5.9	−4.6	−0.2	−4.6	−3.8
		0.782	8.45	−2.8	−5.2	−4.1	−3.2	−2.5	−3.2	−2.6
	175	0.227	8.57	+1.0	−0.3	+0.9	+1.9	+3.1	+1.9	−0.6
		0.514	8.95	−2.4	−4.3	−2.6	−1.2	+3.3	−1.2	−4.6
		0.782	9.10	−3.4	−3.8	−2.6	−1.8	−0.9	−1.8	−4.0
Kr-H_2	40	0.253	24.2	+8.4	+7.2	+5.0	−2.1	. . .	−15.8	+10.5
		0.469	15.9	−0.6	+1.9	. . .	−9.3	. . .	−8.8	. . .
		0.653	10.1	+1.0	+2.0	−0.4	−10.6	. . .	−0.0	−10.0
	65	0.253	26.5	+5.0	+4.2	+2.3	−4.5	−3.0	−17.0	+6.9
		0.469	16.7	+0.6	+3.6	+1.2	−7.8	+1.8	−7.2	−0.6
		0.653	10.6	+2.8	+3.8	+0.9	−8.8	+3.8	+1.9	−11.4
	93	0.253	28.4	+3.9	+2.5	+0.4	−6.7	−4.6	−18.8	+4.3
		0.469	18.3	−2.1	−0.5	−2.7	−11.5	−1.6	−10.9	−5.4
		0.653	11.4	+1.8	+1.8	−1.8	−10.5	+1.7	0.0	−14.9
Xe-H_2	40	0.160	29.0	+6.6	+0.4	+2.1	−8.7	. . .	−23.6	+8.3
		0.434	15.5	+3.6	−3.5	. . .	−17.8	. . .	−8.1	. . .
		0.608	9.35	+8.0	−0.2	+3.8	−15.9	. . .	+8.0	−10.3
	65	0.160	31.4	+4.1	−1.7	+0.3	−10.3	−2.9	−25.3	+6.4
		0.434	16.6	+2.4	−5.1	−1.1	−18.8	−1.8	−9.7	−1.8
		0.608	10.6	+0.9	−6.6	−2.8	−21.3	−7.5	+0.9	−16.6
	93	0.160	33.9	+3.0	−3.9	−2.1	−12.5	−4.2	−26.2	+3.3
		0.434	18.0	+0.6	−7.2	−3.9	−20.6	−1.6	−11.7	−5.0
		0.608	11.0	+4.5	−4.5	−0.9	−19.3	−0.9	+3.6	−15.6
Xe-D_2	40	0.255	17.6	+1.1	−2.5	+1.7	−7.4	. . .	−16.6	+9.1
		0.496	10.2	−1.0	−4.7	. . .	−12.6	. . .	−3.2	. . .
		0.759	4.95	−4.0	−7.2	−2.6	−14.4	. . .	+8.1	−21.2
	65	0.255	19.1	−1.6	−4.2	−1.0	−10.0	−3.7	−19.4	+6.3
		0.496	10.8	−0.9	−4.6	0.0	−13.0	−0.9	−3.7	−0.9
		0.759	5.27	−3.2	−8.2	−3.8	−15.6	−1.7	+6.6	−23.3
	93	0.255	20.1	−0.5	−4.0	−1.0	−10.0	−2.0	−18.5	+5.5
		0.496	11.8	−3.4	−7.7	−3.4	−15.6	−0.8	−6.8	−5.9
		0.759	5.69	−4.4	−8.6	−4.2	−15.1	+1.8	−6.2	−25.1
Xe-Ar	40	0.241	3.36	−2.4	−0.9	. . .	+1.5	. . .	−1.2	. . .
		0.758	1.92	−4.2	−2.6	−1.5	0.0	. . .	+0.5	−5.7
	65	0.241	3.58	+1.4	−3.1	−2.2	−0.8	−2.2	−3.4	−3.1
		0.758	2.08	0.0	−6.2	−5.3	−3.8	−3.9	−3.4	−11.1
	93	0.241	3.91	−1.8	−2.5	−1.8	−1.0	−1.3	−2.6	−5.1
		0.758	2.34	−5.6	−6.4	−5.6	−4.3	−3.4	−3.4	−14.5

[a] These are partly smoothed by plotting the observed values as a function of temperature. Multiply these values by 41.868 to get thermal conductivity values in $\mu W\ cm^{-1}\ deg^{-1}$.

conductivity value is the value of *k* corresponding to $p^{-1} = 0$.

A least-squares fit to the data of Table III led to thermal conductivity values which agree with the measured values of conductivity beyond 10 cm of mercury within 0.6, 1.1, and 0.1% for Ne, H_2, and O_2, respectively. It seems additional work to understand adequately the jump effect for light gases is desirable. However, the present side investigations described above do indicate the substantial correctness of the adopted approach for measurement of thermal conductivity as well as of the simple theory of the jump effect simultaneously.

We also took measurements at about 175° C for nitrogen and oxygen when everything else was kept unchanged except the excess of the wire temperature over the bath was changed as 4, 6, 10, 15, and 20° C. The conductivity value was then determined by extrapolation for the case when the excess of temperature is zero. Next, the conductivity values corresponding to the case when the wire was 4° C above the bath temperature were reduced at the latter temperature by assuming the gas to be at the mean temperature and the variation *k* with temperature as obtained by Gambhir and Saxena on the basis of the correlation of available experimental data (*5*). These *k* values were about 0.6% smaller than the corresponding values obtained by the extrapolation procedure outlined above.

When a similar procedure was adopted at about 90° C for Ne, N_2, and O_2, the differences in the two sets were less than 0.2%. The correlated values of *k* as a function of temperature for neon as given by Gandhi and Saxena (*6*) were used in the data reduction. These studies again establish our contention of the almost complete absence of convection and the procedure of determining conductivity from readings when the platinum wire was heated about 4° C above the bath temperature. The measurements reported here have indeed adopted this practice. In the light of these comments and the previous detailed error analysis of Saxena and Gupta (*26*), we estimate an uncertainty of 1–2% in the absolute values of thermal conductivity of gases and gaseous mixtures reported here.

THEORY

The theory of the thick-wire variant of the hot-wire method was given by Kannuluik and Martin (*13*) and was used in processing data of our earlier work [Saxena and Gupta (*26*)]. Recently, Oldham and Luchsinger (*21*) have developed more accurate solutions of the heat flow differential equation for such a case, and we have employed their simple and accurate solution. Briefly, we reproduce the working equation used in this work. The steady-state heat balance equation is,

$$\pi r_1^2 K(d^2\theta/dz^2) + 2(\pi r_1 k)(d\theta/dr)_{r=r_1} - (8\pi r_1 r_2 \sigma e T^3\theta)/(r_1 + r_2 - er_1) + I^2 R_0(1 + \alpha_t\theta)/2l = 0 \quad (3)$$

In writing this equation both convection and temperature-jump effects have been neglected. However, these are valid approximations as discussed above. The solution of this equation as given by Oldham and Luchsinger (*21*) is

$$f(\beta l) = [(1/\beta l)^2][1 - (\tanh \beta l/\beta l)] \quad (4)$$

where

$$f(\beta l) = (R_\theta - R_0)/R_0P \quad (5)$$

$$P = I^2 R_0\alpha_t l/2\pi r_1^2\{K + 2kC_2(r_2/r_1)\} \quad (6)$$

and

$$(\beta l)^2 = \frac{2l^2}{r_1\{K + 2kC_2(r_2/r_1)\}}\left[\frac{k}{r_1 \ln(r_2/r_1)} + \frac{4r_2 e\sigma T^3}{r_1 + r_2 - er_1}\right] - P \quad (7)$$

The quantity C_2 is a function of r_1/r_2 only, and for our cell its value is 5.46576. The values of *e* were obtained from the relation given by Geiss (*7*) and are reported in Table II at the temperatures of our current interest. The thermal conductivity of the platinum wire was computed by taking measurements of the wire resistance R_θ corresponding to a particular value of the current *I* when the cell is highly evacuated [Gambhir et al. (*3*)]. The value of *K* thus obtained at 40° C was then used in conjunction with the data of Powell and Tye (*23*) for the temperature variation to generate *K* values of Table II at the required temperatures.

In the earlier solution of the energy balance equation by Kannuluik and Martin (*13*), the measurements in vacuum could then be used to determine the radiation losses. R_0 is the resistance of the cell wire corresponding to zero or more appropriately to an infinitesimally small current. This was obtained from a series of measurements of the resistance of the wire as a function of current when the cell was highly evacuated and for a constant temperature of the bath. A graph between R_θ^{-1} vs. I^2 was plotted and R_0 was obtained from the reciprocal of the intercept at $I^2 = 0$. This procedure was repeated for each temperature of the bath. Thus, the basic measurements of R_θ and R_0 and the knowledge of *e*, α_t, and *K* enable the determination of *k* from the above equations as the dimensions of the conductivity cell are known. As pointed out earlier (*26*), the wall effect correction for this metal cell is quite small, 0.02%.

RESULTS

The conductivity values as obtained by the same cell on the two thermostat assemblies are given for pure gases and for binary systems in Tables IV and V, respectively. As the mean temperatures of the various measurements for different gases and gas mixtures differ by a few tenths of a degree for the same temperature of the bath, interpretation of conductivity data will be very much facilitated if the data were reduced to the corresponding bath temperature in each case. For this reason, the observed and corrected values of thermal conductivities for a gas or a mixture of fixed composition were plotted as a function of temperature and values were read at the bath temperatures and these are reported in Tables IV and V.

The values of thermal conductivities obtained from the solution of the heat balance equation as given by Kannuluik and Martin (*13*) were always smaller than those obtained on the basis of Oldham and Luchsinger (*21*). The differences were always less than 1.1% for the gas systems studied here, and were smaller, the smaller the value of the thermal conductivity. We now discuss our results on pure gases and binary systems.

Pure Gases. Our experimental thermal conductivity values for pure gases are compared in Table IV with the recommended values of Gambhir and Saxena (*5*) and Gandhi and Saxena (*6*) obtained by the critical evaluation of the experimental data available in literature. The present measurements are in satisfactory agreement with the measurements of other workers. The theoretical estimates of the thermal conductivity of these gases are given in the last column of this table. These are according to the calculations based on the theoretical expressions given by Hirschfelder et al. (*12*) and Hirschfelder (*9*) in conjunction with the exponential-six intermolecular potential parameters as given by Mason and Rice (*17, 18*), Mason (*16*), and Vanderslice et al. (*31*). For deuterium the parameters employed were the same as for hydrogen. All these pure gas parameters, α, ϵ/k, and r_m, are reported in Table VI. The agreement between theory and experiment is good in most of the cases and for better theoretical predictions both a sound theory for polyatomic gases and more reliable knowledge of molecular interactions are essential.

Binary Systems. Experimental data for binary systems are reported in Table V as a function of temperature and the mole fraction of the heavier component (x_1). Comparison of the experimental results with the various computing procedures is also indicated in this table. Hirschfelder (*10*) derived the expression for the thermal conductivity of a binary mixture involving polyatomic gases. The principal relations are,

$$k_{\text{mix}} = k^0_{\text{mix}} + \frac{k_1 - k_1^0}{1 + \frac{D_{11}}{D_{12}}\frac{x_2}{x_1}} + \frac{k_2 - k_2^0}{1 + \frac{D_{22}}{D_{12}}\frac{x_1}{x_2}} \tag{8}$$

where

$$k^0_{\text{mix}} = 4\ (x_1^2 L_{22} - 2\ x_1 x_2 L_{12} + x_2^2 L_{11}) / (L_{12}^2 - L_{11} L_{22})$$

$$L_{11} = -\frac{4\ x_1^2}{k_1^0} - \frac{16\ T}{25\ p} \times \frac{x_1 x_2}{D_{12}} \left[\frac{(15/2)\ M_1^2 + (25/4)\ M_2^2 - 3\ M_2^2 B_{12}^* + 4\ M_1 M_2 A_{12}^*}{(M_1 + M_2)^2}\right]$$

$$L_{12} = (16\ T/25\ p) x_1 x_2 M_1 M_2 (55/4 - 3\ B_{12}^* - 4\ A_{12}^*) / D_{12}(M_1 + M_2)^2 \tag{9}$$

L_{22} is obtained from L_{11} by interchanging the subscripts. The theory of Hirschfelder (*10*) and the exponential-six potential led to the values listed in column 5 of Table V. The unlike parameters were obtained from those given in Table VI and the combination rules developed by Mason and Rice (*17*). These unlike interactions are characterized by the potential parameters α_{12}, ϵ_{12}/k and $(r_m)_{12}$ listed in Table VII. This theoretical calculation procedure leads to reasonable estimates inasmuch as the experimental results for the 126 mixtures are reproduced within an average absolute deviation of 3.1%. This is satisfactory because for mixtures involving polyatomic gases, the theory is only approximate.

Mason and Saxena (*19*) developed a semitheoretical procedure according to which the thermal conductivity of a binary mixture is

$$k_{\text{mix}} = k_1 / \left(1 + \phi_{12}\frac{x_2}{x_1}\right) + k_2 / \left(1 + \phi_{21}\frac{x_1}{x_2}\right) \tag{10}$$

where

$$\phi_{12} = \frac{1.065}{2(2)^{1/2}}\left(1 + \frac{M_1}{M_2}\right)^{-1/2}\left[1 + \left(\frac{k_1^0}{k_2^0}\right)^{1/2}\left(\frac{M_1}{M_2}\right)^{1/4}\right]^2 \tag{11}$$

and ϕ_{21} is obtained from ϕ_{12} by interchanging the subscripts and the frozen thermal conductivity of a pure gas from the following relation:

$$k_1^0 = k_1[0.115 + 0.354\ \gamma/(\gamma - 1)]^{-1} \tag{12}$$

Table VI. Exponential-Six Potential Parameters and Sutherland Constants for Pure Gases

Gas	α	ϵ/k, °K	r_m, A	S, °K
Ne	14.5	38.0	3.147	61
Ar	14.0	123.2	3.866	147
Kr	13.5	200.0	4.036	188
Xe	13.0	231.2	4.450	252
H_2	14.0	37.3	3.337	83
D_2	14.0	37.3	3.337	83
N_2	17.0	101.2	4.011	103
O_2	17.0	132.0	3.726	138

Table VII. Exponential-Six Potential Parameters and Sutherland Constants for Binary Gas Pairs

Gas pair	α_{12}	ϵ_{12}/k, °K	$(r_m)_{12}$, A	S_{12}, °K
Ne-H_2	14.2	38.0	3.235	71.2
Ne-N_2	15.8	60.9	3.568	79.1
Ne-O_2	15.8	68.9	3.444	91.7
N_2-H_2	15.6	50.0	3.690	92.5
N_2-O_2	17.0	11.6	3.861	119
Kr-H_2	13.7	92.7	3.627	125
Xe-H_2	13.3	110.1	3.739	145
Xe-Ar	13.4	178.5	4.108	192

Table VIII. Values of ϕ_{ij} at 40° C

	Mason and Saxena (*19*)		Lindsay and Bromley (*14*)		Mathur and Saxena (*20*)	
Gas pair	ϕ_{12}	ϕ_{21}	ϕ_{12}	ϕ_{21}	ϕ_{12}	ϕ_{21}
Ne-H_2	0.481	1.357	0.806	1.278	0.556	1.565
Ne-N_2	0.698	1.715	0.681	1.549	0.656	1.617
Ne-O_2	0.694	1.678	0.685	1.478	0.611	1.478
H_2-D_2	0.870	1.230	0.919	1.092	0.889	1.257
N_2-D_2	0.401	1.970	0.616	1.863	0.404	1.987
H_2-N_2	0.293	2.035	0.578	2.081	0.297	2.064
N_2-O_2	1.074	1.055	1.025	0.974	1.036	1.017
Kr-H_2	1.160	2.327	0.168	2.431	0.472	2.702
Xe-H_2	0.114	2.858	0.108	2.705	0.398	3.523
Xe-D_2	0.159	2.838	0.148	2.638	0.419	3.117
Xe-Ar	0.556	1.797	0.546	1.763	0.658	1.580

The computed values of ϕ_{12} and ϕ_{21} at 40° C are given in Table VIII for all the 11 binary systems, and the same values were used at the higher temperatures because their temperature dependence is sufficiently small (*29*). The calculated thermal conductivity values for all the binary mixtures from Equations 10 to 12 are given in column 6 of Table V. For all the 126 experimental data points, the above procedure of Mason and Saxena (*19*) leads to values which agree with the directly observed values within an average absolute deviation of 3.7%.

To obtain more realistic values for ϕ_{12} and ϕ_{21}, Mathur and Saxena (*20*) suggested employing the following relation:

$$\phi_{12}/\phi_{21} = (M_2/M_1)(\eta_1/\eta_2) \tag{13}$$

and an experimental value of k_{mix} in conjunction with Equation 10.

Following this procedure the values of ϕ_{12} and ϕ_{21} were computed for all the 11 binary systems at 40° C and are listed in Table VIII. These values were also used while calculating k_{mix} at higher temperatures. The computed values for all the 118 mixtures are given in Table V and agree with the corresponding experimental values within an average absolute deviation of 2.4%. Thus, the agreement between theory and experiment, in general, has improved now in comparison to the method of Mason and Saxena (*19*) and even that of Hirschfelder (*10*).

Lindsay and Bromley (*14*), suggested that ϕ_{12} and ϕ_{21} of Equation 10 be determined from the relation

$$\phi_{12} = \frac{1}{4}\left\{1 + \left[\frac{\eta_1}{\eta_2}\left(\frac{M_2}{M_1}\right)^{3/4}\frac{1 + (S_1/T)}{1 + (S_2/T)}\right]^{1/2}\right\}^2\left[\frac{1 + (S_{12}/T)}{1 + (S_1/T)}\right] \tag{14}$$

and ϕ_{21} from Equation 14 when the subscripts 1 and 2 are interchanged. The Sutherland constants are the same as used in our previous work (*26*) and are reproduced in the last column of Table VI for pure gases and for gas pairs in Table VII as obtained on the basis of the geometric mean rule. The ϕ_{12} and ϕ_{21} at 40° C are given in Table VIII for all the gas pairs, and the same values have been used at the higher temperatures. The computed values of k_{mix} for the 126 experimental data points are reported in Table V and these agree with the corresponding experimental values within an average absolute deviation of 4.8%. It is important to note that the overall agreement between computed and experimental results has deteriorated in comparison to the parallel procedure of Mason and Saxena (*19*).

Ulybin et al. (*30*) suggested an empirical procedure in which k_{mix} at a higher temperature is obtained from its value at some lower temperature on the basis of the following relation:

$$k_{mix}(T_2) = k_{mix}(T_1)\left[x_1 \frac{k_1(T_2)}{k_1(T_1)} + x_2 \frac{k_2(T_2)}{k_2(T_1)}\right] \tag{15}$$

The k_{mix} values currently measured at 40° C were employed to compute k_{mix} for 84 mixtures at higher temperatures of Table V. The computed values are in good agreement with the directly measured values, the average absolute deviation being 2.5%.

In Table V are also reported the computed k_{mix} values according to two simple expressions (*1, 26*):

$$k_{mix} = 0.5\left[(x_1k_1 + x_2k_2) + \frac{1}{\left(\frac{x_1}{k_1} + \frac{x_2}{k_2}\right)}\right] \tag{16}$$

and

$$k_{mix} = x_1^2 k_1 + x_1x_2k_{12} + x_2^2 k_2 \tag{17}$$

k_{12} is an empirical constant and was determined from one known value of k_{mix}. Both the methods are relatively less satisfactory and lead to results which in many cases are appreciably different from the corresponding experimental values. These calculations also indicate the insufficiency of these simple functions to correlate the composition dependence of thermal conductivity data. The surprising success of the Ulybin et al. method is easily reconciled in view of the theoretical evaluation of the computing relation by Saxena (*25*). This large body of experimental data does substantiate the previous conclusions (*26*) drawn regarding the relative appropriateness of these computing procedures.

DIFFUSION AND VISCOSITY COEFFICIENTS

The methods of generating viscosity and diffusion coefficients from thermal conductivity data on the basis of kinetic theory are well known and were recently elaborated by Saxena and Gupta (*26*). In such a procedure all the quantities involving the knowledge of intermolecular forces are replaced by either suitable experimental quantities or by an appropriate average value. For example, A_{12}^* and B_{12}^* in Equation 9 were given the value of 1.10 in view of the detailed tabulations available for these quantities over a wide temperature range and for a variety of intermolecular potential functions (appendix of reference *12*). The major implication involved here is that the intermolecular forces are central. For nonatomic gas pairs pD_{12} is obtained from Equation 9 if k_{mix}^0, k_1^0, and k_2^0 are known. This procedure led to the values for D_{12} reported in column 3 of Table IX for each of the mixtures of the Xe–Ar system. As the diffusion coefficients are independent of composition to a first approximation, in the next column are given the means, D_{12}, obtained by averaging the D_{12} values at different compositions. These values are in good agreement with the directly measured values of Malinauskas (*15*) and the theoretically calculated values on the exponential-six potential.

Table IX. Indirectly Generated Coefficients of Diffusion, D_{12}, (Cm^2 Sec^{-1}) at 1 Atm and Viscosity, η_{mix}, 10^{-7} (Gm Cm^{-1} Sec^{-1}) for Binary Systems

		D_{12}				Generated
Gas pair	X_1[a]	Generated	Mean	Measured	Theoretical	η_{mix}
Xe–Ar						
40° C	0.241	0.132	0.135	0.125	0.126	2530
	0.758	0.138				2483
65° C	0.241	0.145	0.150	0.146	0.146	2664
	0.758	0.155				2628
93° C	0.241	0.175	0.179	0.170	0.170	2853
	0.758	0.183				2851
Xe–D_2						
40° C	0.255	0.473	0.518		0.505	2376
	0.496	0.528				2477
	0.759	0.554				2440
65° C	0.255	0.622	0.624		0.579	2570
	0.496	0.605				2672
	0.759	0.644				2620
93° C	0.255	0.706	0.733		0.669	2766
	0.496	0.742				2885
	0.759	0.751				2832
Ne–H_2						
40° C	0.150	1.303	1.38	1.242	1.239	1588
	0.405	1.377				2377
	0.663	1.456				2882
65° C	0.150	1.456	1.56	1.394	1.409	1667
	0.405	1.609				2495
	0.663	1.615				3025
93° C	0.150	1.709	1.81		1.618	1769
	0.405	1.824				2645
	0.663	1.893				3196
135° C	0.272	2.279	2.00		1.942	2311
	0.293	1.714				2383
175° C	0.272	2.483	2.38		2.283	2423
	0.293	2.271				2503
Ne–N_2						
40° C	0.203	0.365	0.358		0.350	2881
	0.511	0.335				2406
	0.805	0.374				2084
65° C	0.203	0.400	0.390		0.399	2984
	0.511	0.372				2484
	0.805	0.399				2135
93° C	0.203	0.454	0.446		0.457	3143
	0.511	0.434				2622
	0.805	0.449				2358
135° C	0.256	0.504	0.498		0.548	3158
	0.735	0.492				2452
175° C	0.256	0.600	0.581		0.638	3359
	0.735	0.561				2617
Ne–O_2						
40° C	0.340	0.386	0.375		0.357	2846
	0.496	0.379				2663
	0.739	0.359				2397
65° C	0.340	0.418	0.430		0.407	3009
	0.496	0.434				2821
	0.739	0.437				2543
93° C	0.340	0.476	0.490		0.466	3170
	0.496	0.504				2976
	0.739	0.489				2690
135° C	0.229	0.589	0.592		0.560	3552
	0.744	0.594				2887
175° C	0.229	0.631	0.616		0.656	3614
	0.744	0.600				2971

[a] Mole fraction of the heavier component in the mixture.

For mixtures involving polyatomic gases the procedure is more involved and the starting relation is Equation 8. The values of k_1^0 and likewise of k_2^0 were obtained from k_1 and k_2, respectively, on the basis of a relation of the type given by Equation 12. Pure diffusion coefficients were generated from the thermal conductivity data and the relation

$$D_{11} = (8.8\ Tk_1/25\ p)[0.115 + 0.354\ \gamma/(\gamma - 1)]^{-1} \tag{18}$$

The values of diffusion coefficients for the systems Xe–D_2, Ne–H_2, Ne–N_2, and Ne–O_2 thus generated are reported in Table IX as for Xe–Ar. The directly measured D_{12}

values for Ne-H_2 system of Paul and Srivastava (*22*) are also included here for comparison. The agreement is not very satisfactory and can be ascribed to many different sources. Equation 8 may not be an accurate representation for thermal conductivity, and the experimental uncertainties in conductivity and diffusion data may be responsible for a part of the disagreement.

As earlier pointed out by Saxena and Gupta (*26*), the coefficient of viscosity for a binary system is given by

$$\eta_{mix} = (x_1^2 H_{22} - 2\, x_1x_2H_{12} + x_2^2 H_{11})/(H_{11}H_{22} - H_{12}^2) \qquad (19)$$

$$H_{11} = x_1^2/\eta_1 + [2\, x_1x_2/(M_1 + M_2)]RT/pD_{12}\,[1 + (3.30\, M_2/5\, M_1)] \qquad (20)$$

$$H_{12} = -[0.68\, x_1x_2RT/(M_1 + M_2)pD_{12}] \qquad (21)$$

and

$$\eta_1 = (4\, M/15\, R)k_1^0 \qquad (22)$$

H_{22} and η_2 are obtained from H_{11} and η_1, respectively, by interchanging the subscripts 1 and 2. Once pD_{12} is computed H_{11}, H_{22}, and H_{12} are readily obtained from the Equations 20 and 21, respectively, as Equation 22 gives η_1 from k_1^0. Values of η_{mix} thus generated are given in the last column of Table IX. Thornton (*28*) has measured the viscosity of Xe-Ar system as a function of composition at 18.2° C within an estimated accuracy of $\pm1\%$. This measurement indicates that η_{mix} varies very slowly with composition and there is a broad maximum in the composition range 30–70% of xenon in the mixture. The data of Table IX do confirm this trend and are in qualitative agreement also, as far as temperature is concerned. There are no other direct measurements for comparison. The directly measured viscosities for the Ne-H_2 system are available at 293°, 373°, 473°, and 523° C (*11*).

Our generated data exhibit the same composition dependence but our values at 93° C are about 4% larger than the directly measured values at 100° C. This disagreement may be real because our D_{12} values are also not in good agreement with the directly measured values as pointed out above. We guess the major source of discrepancy to be in the theory, Equation 8, and only a small part in the experimental uncertainties. We can employ the accurate viscosity data of Di Pippo et al. (*2*) on the Ne-N_2 system at 30° C and 1.05 atm to compare with the values at 40° C of Table IX. The two sets of data have similar dependences on composition, and the data at 40° C are systematically greater than those at 30° C by about 3%. The data of Di Pippo et al. (*2*) at 30° C are systematically greater than their data at 20° C also by about 3%. Thus, we see that fair estimates of transport coefficients are possible, and this is encouraging because experimental measurements are not simple, and in many engineering problems transport coefficients are needed.

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NOMENCLATURE

A = a constant in the equation giving the variation of resistance with temperature, ° C^{-1}
A_{12}^* = ratio of certain collision integrals characterizing molecules of gases 1 and 2
B = a constant in the equation giving the variation of resistance with temperature, ° C^{-2}
B_{12}^* = ratio of certain collision integrals characterizing molecules of gases 1 and 2
D_{11} = self-diffusion coefficient for gas 1, cm^2 sec^{-1}
D_{22} = self-diffusion coefficient for gas 2, cm^2 sec^{-1}
D_{12} = binary diffusion coefficient of components 1 and 2, cm^2 sec^{-1}
e = common emissivity of the wire and tube
I = electrical current through the wire, amp
k = thermal conductivity of the gas, cal cm^{-1} sec^{-1} deg^{-1}
k_1 = thermal conductivity of the heavier component in the mixture, cal cm^{-1} sec^{-1} deg^{-1}
k_2 = thermal conductivity of the lighter component in the mixture, cal cm^{-1} sec^{-1} deg^{-1}
k_{mix} = thermal conductivity of the mixture, cal cm^{-1} sec^{-1} deg^{-1}
k_1^0 = k_1 with internal degrees of freedom of the gas frozen, cal cm^{-1} sec^{-1} deg^{-1}
k_2^0 = k_2 with internal degrees of freedom of the gas frozen, cal cm^{-1} sec^{-1} deg^{-1}
k_{mix}^0 = k_{mix} with internal degrees of freedom of the gases frozen, cal cm^{-1} sec^{-1} deg^{-1}
$k_{mix}(T_1)$ = k_{mix} at T_1, cal cm^{-1} sec^{-1} deg^{-1}
$k_{mix}(T_2)$ = k_{mix} at T_2, cal cm^{-1} sec^{-1} deg^{-1}
$k_1(T_1)$ = k_1 at T_1, cal cm^{-1} sec^{-1} deg^{-1}
$k_1(T_2)$ = k_1 at T_2, cal cm^{-1} sec^{-1} deg^{-1}
$k_2(T_1)$ = k_2 at T_1, cal cm^{-1} sec^{-1} deg^{-1}
$k_2(T_2)$ = k_2 at T_2, cal cm^{-1} sec^{-1} deg^{-1}
k_{12} = an empirical constant in Equation 17, cal cm^{-1} sec^{-1} deg^{-1}
K = thermal conductivity of the platinum wire, cal cm^{-1} sec^{-1} deg^{-1}
$2\,l$ = length of the hot-wire, cm
M_1 = molecular weight of the heavier component in the mixture
M_2 = molecular weight of the lighter component in the mixture
p = pressure, atm
r = radial direction
r_1 = radius of the platinum wire, cm
r_2 = internal radius of the metal tube, cm
r_m = molecular separation between identical molecules when their interaction energy is minimum, A
$(r_m)_{12}$ = molecular separation between molecules 1 and 2 when their interaction energy is minimum, A
R_{ice} = resistance of a given sample of platinum wire at the ice point, Ω
R_0 = resistance of the wire for $I = 0$ at the bath temperature, Ω
R_t = resistance of the given sample of platinum wire at t° C, Ω
R_θ = resistance of the wire for a current which heats it θ° above the bath temperature, Ω
S_1 = Sutherland constant for the heavier gas in the mixture, ° K
S_2 = Sutherland constant for the lighter gas in the mixture, ° K
S_{12} = Sutherland constant for the gas pair 1 and 2, ° K
t = temperature, ° C
T = temperature, ° K
x_1 = mole fraction of the heavier component in the mixture
x_2 = mole fraction of the lighter component in the mixture
z = axial direction

GREEK LETTERS

α = parameter representing the steepness of repulsive potential between two similar molecules
α_{12} = value of α referring to molecules 1 and 2
α_t = temperature coefficient of resistance of the platinum wire at temperature t° C, ° C^{-1}
ϵ/k = depth of the interaction potential well for two similar molecules reduced by the Boltzmann constant
ϵ_{12}/k = value of ϵ/k referring to molecules 1 and 2
η_1 = viscosity of the heavier component in the mixture, g cm^{-1} sec^{-1}
η_2 = viscosity of the lighter component in the mixture, g cm^{-1} sec^{-1}
η_{mix} = viscosity of a binary mixture, g cm^{-1} sec^{-1}
θ = excess of the wire temperature over the bath temperature, ° C
σ = Stefan-Boltzmann constant
ϕ_{ij} = Sutherland constants for molecules 1 and 2

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Dielectric Constants, Viscosities, Fusion Point Curves, and Other Properties of Three Nonaqueous Binary Systems

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Dielectric constants, viscosities, densities, refractive indices, molar excess volumes, and dielectric constant deviations are reported for *N*-methylacetamide–ethylene carbonate, *N*-methylacetamide–dimethylsulfoxide, and ethylene carbonate–dimethylsulfoxide mixtures at 40° C. Fusion point curves also have been determined for these systems.

N-methylacetamide (NMA), ethylene carbonate (EC), and dimethylsulfoxide (DMSO) are excellent electrolytic solvents which have convenient freezing points and medium cryoscopic constants. Each of these solvents can be highly purified through a series of fractional freezings or by zone refining. The useful data reported herein were accumulated in the course of physicochemical investigations dealing with pure and mixed nonaqueous media.

EXPERIMENTAL

Each solvent was purified through a sequence of fractional freezings under nitrogen (*4*) until a constant maximum freezing point (indicated in Table II) was obtained. All solutions were prepared in glass-stoppered flasks on a weight basis in sufficient quantity to permit separate portions to be used for each measurement.

A Twin-T impedance bridge assembly was used to make capacitance measurements at 1 MHz. The jacketed stainless steel cells plugged directly into the bridge. The standard media used for the determination of cell constants were air and water which have dielectric constants of unity and 73.15 (*11*), respectively, at 40° C. Size 50 or 100 Cannon-Fenske viscometers were used to obtain efflux times of 200 sec or more thereby making kinetic energy corrections negligible. Calibration data for the viscometers were provided by the Cannon Instrument Co. To minimize atmospheric contamination, the viscometers were equipped with top adapters vented through tubes filled with calcium chloride and Ascarite. Timers were calibrated against NBS Station WWV time signals. Densities were determined using 25-ml Reischauer pycnometers which had been calibrated with freshly distilled water. Appropriate buoyancy corrections were applied prior to the calculation of densities or compositions. Refractive indices were measured with a Spencer-Abbe Model 2214 refractometer. The temperature was controlled within 0.02° C with a Sargent S-84815 thermostatic water bath assembly. The bath thermometer was compared against a NBS-calibrated thermometer.

All measurements were made in duplicate, and corre-

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