Thermal Conductivity of Mixtures of Argon-Helium, Argon-Nitrogen, and Argon-Neon

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A secondary concentric cylinders cell was used to measure the thermal conductivity of binary mixtures of argon-nitrogen, argon-helium, and argon-neon approximately 20, 40, 60, and 80 vol. % at 75°C. and pressures to 2,800 atm. Measurements were made also on the pure gases argon and nitrogen.

The transport properties of dense gas mixtures are important in engineering design and in the theoretical interpretation of molecular interactions. Although limited data have been reported by Junk and Comings (*1*), Keyes (*2*), and Gilmore and Comings (*3*), chemical processes involving mixtures make it important to understand the transport behavior of mixtures at high pressures.

A secondary cell of the type used by Kramer and Comings (*4*) and Gilmore and Comings (*3*) was used to measure the thermal conductivity of binary mixtures of argon-helium, argon-nitrogen, and argon-neon at 75°C. and to 2,800 atm. The conductivity values of carbon dioxide measured by Sengers (*5*) were used for cell calibration. Measurements were also made on the pure gases argon and nitrogen.

EXPERIMENTAL PROCEDURES

The thermal conductivity cell (Figure 1) is similar to the Gilmore-Comings cell (*3*) and consists of two horizontal concentric cylinders totally immersed in the sample fluid. The Gilmore-Comings cell was modified by increasing the number of thermocouple junctions from three to five, which provided a thermopile consisting of five equally spaced thermocouple junctions in each cylinder. The cell was contained in a high pressure bomb with an I.D. of 2.5 in. The O.D. of the receiver was increased to 2.4 in. for a closer fit with the pressure bomb container in order to decrease the time in which the temperature reached equilibrium with the surroundings.

Auxiliary equipment used for generating pressure and making the experimental measurements is described by Gilmore (*3*). A Thermodyne temperature controller (Hallikainen Instruments), installed in the oil bath, maintained a uniform temperature to the degree that variations with time could not be detected within the pressure bomb.

The cell was calibrated by the procedure used by Gilmore (*3*) with carbon dioxide as the calibrating gas. Measurements were made on twelve binary mixtures of approximately 20, 40, 60, and 80 vol. % argon-nitrogen, argon-helium, and argon-neon. Minimum purities of these gases were specified by the manufacturer (the Matheson Company) as nitrogen, 99.996%; argon, 99.998%; helium, 99.99%; neon, 99.7%; and carbon dioxide, 99.96%. Mixture compositions prepared by the Matheson Company were analyzed to 0.1% accuracy.

Experimental data (*6*, *7*), smoothed and interpolated, are presented in Table 1.[*] A regression analysis routine was used to fit polynomials in pressures over the range of measured data.

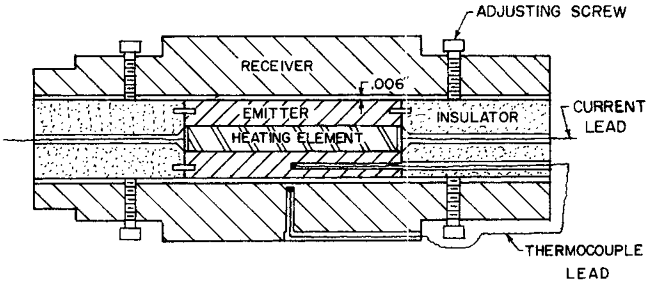

Fig. 1. Thermal conductivity cell.

The variance of the estimate

$$\sigma = \sum_{i=0}^{N} \frac{(k_{ci} - k_i)^2}{N - n - 1}$$

is presented with the data (Table 2).

DISCUSSION OF RESULTS

Results for nitrogen were compared with those measured by Johannin and Vodar (*8*) up to 1,000 atm., their maximum. The values agree to within 2%.

Results for argon, compared to those of Sengers (*9*), show a variation of up to 1.2%. Because Sengers' argon data were measured in the same cell he used to obtain the carbon dioxide data which the authors in turn used to calibrate their cell, one would expect a closer agreement. The variation can be partly attributed both to small errors in Sengers' data and to a small drift in the calibration of the authors' cell. Measurements on pure neon (*11*) were not performed in this investigation.

The argon-nitrogen mixture data are in fairly good agreement with the type of behavior one would expect for a gas mixture. It would be expected that the values for mixtures would be between those for the pure gases and that a first-order estimate of mixture thermal conductivity could be obtained from a linear interpolation between the pure gas thermal conductivities.

In the case of argon-helium mixtures, the mixture thermal conductivities are lower than either of the pure component conductivities in the high pressure range. Pure helium like pure hydrogen (*10*) consists of small molecules with high thermal conductivity and produces systems with high energy exchange rates between colliding molecules. The addition of a gas with a much larger molecular mass, such as argon, reduces the rate of thermal transfer of energy. Complexity in the interaction of these molecules with a corresponding decrease in the transfer rate of thermal energy must be considered whenever molecules of widely different masses are involved. This reduction in the transfer of energy between light and heavy molecules

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[*] Complete tabulations have been deposited as document 01321 with the ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 909 Third Ave., New York 10022 and may be obtained for $2.00 for microfiche or $6.50 for photocopies.

appears to have an increasing effect with higher pressures. Small amounts of impurities in the helium gas should have a pronounced effect on lowering the gas thermal conductivity.

The argon-neon mixture conductivities behave similarly to those of the argon-helium system. Gas mixture conductivities are again lower than the values obtained by linearly interpolating pure gas thermal conductivities. The extent of this deviation is less than for the argon-helium system; however, this would be expected, on the basis of the preceding analysis, for the difference in the molecular masses is smaller for the argon-neon system.

ESTIMATE OF ACCURACY

During the sequence of experimental measurements, the calibration of the cell was repeated several times to ascertain its reproducibility. Gilmore (3) noticed that the calibration tended to change during operation, resulting in a random shift which could not be eliminated. In this work a similar but smaller shift was noted, accounting for a maximum error of 1%.

The maximum random error can be attributed to the determination of the thermopile potential. The minimum thermopile potential measured was 0.78 mv. The reproducibility of the potentiometer in the range of 0.07 to 0.15 mv. is ± 0.2 mv., corresponding to an error of 0.3%. The cell current and potential measurements were reproducible to better than 0.02% and did not contribute significantly to the random error.

Gilmore concludes that the experimental error introduced by convection is negligible provided the temperature drop is below 0.75°C. The temperature drop in these experiments was kept below this value. The effect of thermal radiation between the surfaces as a source of heat

TABLE 1. SMOOTHED VALUES OF THERMAL CONDUCTIVITY (k) FOR PURE GASES AND MIXTURES AT 75°C.
($k \times 10^4$ cal./cm. sec. °C.)

	Nitrogen and Argon (Mole fraction argon)					Nitrogen
	1.00	0.789	0.605	0.413	0.199	
Pressure, atm.						
50	0.511	0.548	0.570	0.629	0.665	0.717
100	0.571	0.607	0.632	0.690	0.730	0.783
200	0.688	0.723	0.752	0.810	0.858	0.914
300	0.802	0.835	0.868	0.928	0.982	1.04
500	1.02	1.05	1.09	1.15	1.22	1.29
800	1.33	1.35	1.40	1.47	1.55	1.64
1,200	1.70	1.71	1.77	1.86	1.95	2.09
1,600	2.03	2.04	2.10	2.22	2.33	2.50
2,000	2.34	2.34	2.41	2.55	2.69	2.89
2,400	2.62	2.62	2.70	2.86	3.03	3.25
2,800	2.89	2.91	2.99	3.16	3.35	3.60
Gas no.	1	2	3	4	5	6

	Helium and Argon (Mole fraction argon)				Helium
	0.805	0.610	0.422	0.216	
Pressure, atm.					
50	0.789	1.20	1.60	2.47	4.00
100	0.826	1.21	1.62	2.50	4.07
200	0.896	1.24	1.65	2.55	4.19
300	0.961	1.29	1.69	2.61	4.29
500	1.09	1.39	1.77	2.71	4.48
800	1.29	1.55	1.90	2.86	4.78
1,200	1.58	1.75	2.09	3.06	—
1,600	1.88	1.94	2.28	3.27	—
2,000	2.14	2.16	2.47	3.49	—
2,400	2.35	2.37	—	3.69	—
2,800	—	—	—	—	—
Gas no.	7	8	9	10	11

	Neon and Argon (Mole fraction argon)			
	0.208	0.406	0.618	0.818
Pressure, atm.				
50	1.002	0.832	0.689	0.593
100	1.040	0.872	0.734	0.642
200	1.116	0.950	0.821	0.739
300	1.191	1.028	0.906	0.833
500	1.339	1.179	1.071	1.016
800	1.555	1.397	1.307	1.277
1,200	1.834	1.675	1.604	1.603
1,600	2.103	1.940	1.884	1.907
2,000	2.365	2.197	2.153	2.194
2,400	2.620	2.448	2.417	2.470
2,800	2.869	2.696	2.679	2.740
Gas no.	12	13	14	15

Table 2. Variance of Estimate

Gas no.	Estimate	Gas no.	Estimate
1	$.8469 \times 10^{-4}$	8	$.2665 \times 10^{-3}$
2	$.4084 \times 10^{-4}$	9	$.4308 \times 10^{-4}$
3	$.1419 \times 10^{-4}$	10	$.5227 \times 10^{-4}$
4	$.2330 \times 10^{-4}$	11	$.2758 \times 10^{-3}$
5	$.1276 \times 10^{-4}$	12	$.1723 \times 10^{-4}$
6	$.4486 \times 10^{-4}$	13	$.1025 \times 10^{-4}$
7	$.2794 \times 10^{-3}$	14	$.9925 \times 10^{-4}$
		15	$.1845 \times 10^{-4}$

transfer is included in the calibration. Absorption of radiation by the gas, thermal diffusion, and the effect of pressure on cell dimensions are small and can be neglected.

Sengers specifies the accuracy of his measurements to be 1%. Since his data are used for cell calibration, this error must be added to that of the present cell. Calibration drift is estimated to be less than 1%. Random error, minimized by the smoothing process, is no more than 0.4%. Thus, the results are estimated to be accurate within 2.5%.

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NOTATION

N = number of data points
n = order of equation
k = thermal conductivity
σ = variance

Subscripts

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

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Van der Waals Forces in a Three-Phase System

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An analysis is made of the Van der Waals forces of two different species when separated by a third continuous component. Results show that under certain circumstances, attractions as well as repulsions can exist between the two different species. The theory is applied to a fibrous bed coalescer to determine what type of material would best serve as a coalescence medium.

In consideration of theoretical aspects of filtration (*8*) and of coalescence in fibrous or porous media (*12*), investigators have had to account for two predominant surface effects. One of these is electrostatic in nature and arises because a zeta potential can become associated with the filtrate and the filter material. By measuring the streaming potential of the filter and the electrophoretic transfer of the filtrate, these two zeta potentials can be established. The second effect is the Van der Waals interaction between the filtrate and filter.

Most investigators consider the Van der Waals effect when the two phases are in the presence of a vacuum. Under this condition there will be an attraction between the two phases. However, if the continuous phase is a gas or liquid, this will not always be true. We shall evaluate the Van der Waals interactions in a three-phase system and consider an application to the coalescence of emulsions in fibrous beds.

THEORY

The importance of the Van der Waals interaction in a three-phase system was first realized in its effect on the contact angle of a liquid resting on a solid in the presence of a gas. The theory, however, is equally applicable to the case when two immiscible liquids are in contact with a solid. If a drop is adhering to a solid surface, as shown in Figure 1, the forces acting at the junction of the two fluid phases and the solid can be properly expressed as

$$\sigma_{31,2} = \sigma_{32,1} - \sigma_{12} \cos \theta \qquad (1)$$

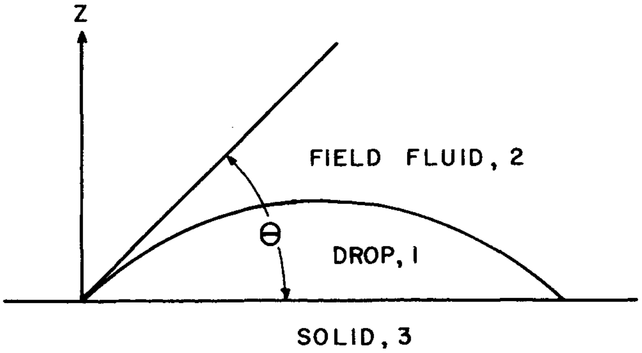

Fig. 1. Contact angle of a drop on a rigid plane surface.