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ARGONNE NATIONAL LABORATORY  
9700 South Cass Avenue  
Argonne, Illinois 60439

THERMAL CONDUCTIVITY OF THE  
HELIUM-ARGON SYSTEM

by

A. Purohit and J. R. Moszynski\*

Materials Science Division

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT . . . . .	1
I. INTRODUCTION . . . . .	1
II. SOURCES OF DATA . . . . .	4
III. PREDICTION METHODS . . . . .	5
REFERENCES . . . . .	14

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## ABSTRACT

A semiempirical relation for the thermal conductivity of helium-argon gas mixtures is suggested. The analyses used in support of the proposed conductivity relations are based on low-temperature ( $T < 800^{\circ}\text{C}$ ) thermal conductivity data for helium, argon and helium-argon mixtures. The report is a compilation of available data and theories, and does not contain any new experimental results. With the approach presented here, one should be able to predict thermal conductivities of helium-argon mixtures to within 5% of their true values for temperatures up to 1200 K. The recommended equations are "best estimates" and should be treated as such. A definite need exists for experimental data to verify or modify the recommendation.

## I. INTRODUCTION

The need for thermal-conductivity data on mixed gases has increased substantially in recent years. This is particularly true for several irradiation experiments in EBR-II and FTR, where material-performance data at temperatures significantly higher than the liquid-sodium coolant temperature can be obtained by what is commonly known as 'gas gapping' the specimens. This involves the placement of a known thermal-conductivity barrier between the specimen and the liquid-sodium coolant. The gap size can be chosen to obtain a prescribed temperature gradient along the axial length of a subassembly in the reactor. Helium-argon gas mixtures are frequently used because any desired

value of thermal conductivity between the high value of helium and the low value of argon can be achieved by adjusting the ratio of the two gases. The ability to vary the thermal conductivity gives the experimenter a wide latitude in sizing the physical extent of the gap. However, existing thermal-conductivity data on helium-argon gas mixtures are not only limited to temperatures of 800K, but are also contradictory for certain values of concentration ratio and temperature. In the course of designing an in-reactor experiment for the Gas-Cooled Fast Reactor cladding-development program, the need arose for (a) a "best estimate" of existing low-temperature data and (b) some extrapolation method for higher temperatures (at least until high-temperature data are available). Both of these objectives were achieved by the present authors and the details, including thermal-conductivity estimates, were made available to the EBR-II staff at ANL. They felt that such information would be of wider interest and should be made available in the form of a separate report. The primary intent of the present report is to give reactor experiments the current "best estimate" of thermal-conductivity values for the helium-argon system. Some theoretical background is also included for those who wish to consider the complexity of the theoretical modeling.

The transport properties of dilute monatomic gases can, in principle, be calculated on the basis of now standard theory.<sup>1-3</sup> (By "dilute" we mean gases in which binary molecular collisions play a dominant role and multiple collisions contribute only negligible or very minor corrections.) The reservation "in principle" is necessary because the knowledge of intermolecular interaction potentials is inadequate to permit a direct calculation of all properties of interest for even the most simple gases. Even semiempirical schemes in which the intermolecular potential is deduced from one or more sets of data and then used to predict other data are not wholly successful.

A recently proposed<sup>4-6</sup> variant of the semiempirical approach, based on the theory of corresponding states, uses experimental data to determine a minimal set of scaling parameters describing the potential for a particular binary interaction and then makes use of universal functionals for the intermolecular potentials. This method, described in Section IIIB below, has been remarkably successful in correlating a wide variety of experimental data on viscosity, diffusion and second virial coefficients for monatomic and polyatomic gases and their mixtures. However, the method is much less successful with thermal-conductivity data, even for pure monatomic gases. This has led the architect of the method, J. Kestin, to observe<sup>5,6</sup> that the available experimental thermal-conductivity data appear thermodynamically inconsistent with other experimental data of high precision, and to suggest that theoretically predicted thermal conductivities may be more reliable than the experimentally measured values, at least within clearly defined limits of the theory. The opposite view would hold that carefully and critically analyzed experimental data provide the only reliable test of any theory and that even with the aid of empirical equations, limited extrapolations of well-correlated, precise data offer the best chance of accurate predictions.

The determination of the thermal conductivity of helium-argon systems at 1000-1200K seems to require only a minor extrapolation of reported data. A careful examination of the data reveals certain possible shortcomings. Hence, complete reliance on empirical extrapolation is unsatisfactory. Happily, however, the proposed empirical extrapolation agrees quite well with the predictive method of Kestin and his coworkers and an averaging scheme is proposed which should yield results that are sufficiently accurate (i.e., within +5%) for most engineering purposes.

## II. SOURCES OF DATA

Two major compendia of recommended thermal-conductivity data for gases are available,<sup>7,8</sup> but only one of these<sup>7</sup> offers data for mixtures. As far as pure gases are concerned, both provide data well beyond 1200K.

In the case of pure helium, the TPRC data<sup>7</sup> appear somewhat more reliable than those of Vargaftik.<sup>8</sup> While below 1200K the differences are small (between -3% and +3% with a crossover at 700K), at 2000K Vargaftik's values are almost 15% lower than the TPRC values. The latter are preferred because Vargaftik relies largely on his own measurements, which are then correlated and smoothed in some fashion; in the higher-temperature range, the TPRC values are based on experimental data from several investigators,<sup>9-11</sup> which show a remarkable degree of agreement where they overlap. Finally, purely analytical extrapolation of lower-temperature data, using the Kestin method, shows excellent agreement with the TPRC recommended values.

In the case of pure argon, the situation is similar; Vargaftik's values are about 2% higher than the TPRC values up to 1200K. The TPRC recommended values are based on both Russian<sup>12</sup> and German<sup>13,14</sup> experimental data at temperatures above 1000K and on a large number of data at lower temperatures. Calculations using the Kestin procedure yield data in good agreement with TPRC recommendations. Vargaftik's recommended data appear to have been based on his own measurements up to about 1000K, and on a set of calculated data not considered by TPRC workers. The high-temperature (to 1500K) values in Vargaftik's 1970 standards publication appear to have been obtained by extrapolation.

As regards mixtures, TPRC<sup>7</sup> presents both original experimental and smoothed data. Most are at room temperature, with the highest at 793K. In many cases the accuracy of these data is unlikely to match the authors' claims of +2%, since even the pure-component data randomly differ from TPRC recommendations by as much as +2%.

One is thus drawn again to Kestin's conclusions that a well-founded calculation procedure may produce data at least equal in accuracy to extrapolations of available experimental data.

Both procedures will be offered in the following.

### III. PREDICTION METHODS

#### A. Simple Empirical Formulas

##### 1. Helium

Blais and Mann<sup>9</sup> suggest a simple linear equation for the thermal conductivity  $k$ :

$$k = 4.149 + 0.002839 (T-1200) . \quad (1)$$

where  $k$  is in mW/cm K and  $T$  is in K.

Petersen and Bonilla<sup>10</sup> prefer

$$k = 0.02273T^{0.7352} . \quad (2)$$

A refinement of the Blais and Mann linear equation (1) gives

$$k = 0.45 + 0.003641T - 0.00458 \times 10^{-4} T^2 . \quad (3)$$

Finally, Keyes<sup>16</sup> has proposed:

$$k = \frac{0.1698 \sqrt{T}}{1 + \frac{602}{T} \times 10^{-99.7/T}} \quad (4)$$

As shown in Table I, all of the above equations reproduce recommended TPRC values adequately in the range  $500K < T < 1300K$ . Equation (3) is recommended for simplicity and accuracy.



Table I. Thermal Conductivity of Helium

T, K	k, mW/cm K					
	TPRC recommended value <sup>a</sup>	Calculated from Eq.				Calculated from Kestin's theory of corresponding states <sup>b</sup>
		(1)	(2)	(3)	(4)	
500	2.11	2.16	2.20	2.16	2.16	2.22
600	2.47	2.45	2.51	2.46	2.47	2.52
700	2.78	2.73	2.82	2.77	2.77	2.81
800	3.07	3.01	3.11	3.07	3.07	3.09
900	3.35	3.30	3.39	3.36	3.36	3.36
1000	3.63	3.58	3.66	3.63	3.63	3.64
1100	3.89	3.87	3.93	3.90	3.90	3.88
1200	4.16	4.15	4.19	4.16	4.16	4.15
1300	4.43	4.43	4.44	4.41	4.41	4.38

<sup>a</sup>From Ref. 7.

<sup>b</sup>Discussed in Section III.B.

## 2. Argon

In the case of argon the choice of equations that adequately represent TPRC recommended data is more limited;

$$k = .049 + .00048T - 1 \times 10^{-7} T^2 \quad (5)$$

or

$$k = \frac{0.016 \sqrt{T}}{1 + \frac{182.5}{T} \times 10^{-1.57/T}} \quad (6)$$

Equations (5) and (6) are compared with TPRC data in Table II. Equation (6) is recommended.

Table II. Thermal Conductivity of Argon

T, K	k, mW/cm K			
	TPRC recommended value <sup>a</sup>	Calculated from Eq.		Calculated from Kestin's theory of corresponding states
		(5)	(6)	
500	0.264	0.264	0.263	0.267
600	0.301	0.301	0.301	0.305
700	0.336	0.336	0.336	0.341
800	0.369	0.369	0.369	0.374
900	0.398	0.400	0.399	0.406
1000	0.427	0.429	0.428	0.436
1100	0.454	0.456	0.455	0.465
1200	0.481	0.481	0.481	0.486
1300	0.508	0.504	0.506	0.519

<sup>a</sup>From Ref. 7.

### 3. Mixtures

The following empirical mixing rule is recommended:

$$k_{\text{mix}}(T) = \frac{k_{\text{He}}(T)}{1 + 2.757 \frac{x_{\text{Ar}}}{x_{\text{He}}}} + \frac{k_{\text{Ar}}(T)}{1 + 0.3322 \frac{x_{\text{He}}}{x_{\text{Ar}}}}, \quad (7)$$

where  $x$  denotes the molar fraction. The quasi-Wassiliewa coefficients (2.757 and 0.3322) have been determined by a least-squares fit to the available

higher-temperature data.

Predicted values at 1000K and 1200K, based on both Eq. 7 and the Kestin procedure,<sup>4-6</sup> are given in Table III.

Table III. Thermal Conductivity<sup>a</sup> of Helium-Argon Mixtures

	Molar % He						
	0	20	40	50	60	80	100
<u>1000K</u>							
Eq. (7)	0.428	0.696	1.06	1.29	1.56	2.33	3.63
Kestin method	0.436	0.671	1.09	1.33	1.60	2.24	3.64
<u>1200K</u>							
Eq. (7)	0.481	0.789	1.20	1.47	1.74	2.67	4.16
Kestin method	0.486	0.750	1.12	1.36	1.66	2.54	4.15

<sup>a</sup>In mW/cm K.

#### B. Kestin's Method, Based on the Theory of Corresponding States

For a full account of the theory the reader should see Refs. 2 and 4-6. Kestin's method for the calculation of the thermal conductivity of a dilute gas mixture requires the determination of the thermal conductivities associated with the separate pure gases, and of a mixture conductivity. The conductivities of the pure gases arise from collisions between like molecules and, according to the kinetic theory of gases, may be expressed as

$$k = \frac{75}{64} \left( \frac{k_B^3 NT}{\pi M} \right)^{1/2} \frac{F(T^*) f(T^*)}{\sigma^2 \Omega^2, 2(T^*)} \quad (8)$$

where  $k_B = 1.38044 \times 10^{-23}$  J/molecule K (Boltzmann's constant)  
 $N = 6.0268 \times 10^{26}$  molecules/kmole (Avogadro's number)  
 $M$  = molecular weight  
 $\sigma$  = scaling-length parameter (collision diameter)  
 $T^*$  = reduced temperature =  $T/(\epsilon/k_B)$   
 $\epsilon$  = scaling-energy parameter (depth of intermolecular potential well)

$F(T^*)$  = universal thermal-conductivity correction

$\Omega^{2,2}(T^*)/f(T^*)$  = universal viscosity collision integral

$$\Omega^{2,2}(T^*)/f(T^*) = \exp\{0.45667 - 0.53955 \ln T^* + 0.18265(\ln T^*)^2 - 0.03629(\ln T^*)^3 + 0.00241(\ln T^*)^4\} \quad (9)$$

$$F(T^*) = 1 + 0.0042\{1 - \exp[0.33(1 - T^*)]\} \quad (10)$$

For any pure monatomic gas, Eqs. (8)-(10), together with the two scaling parameters  $\sigma$  and  $\epsilon$ , are all that are necessary to determine the thermal conductivity at any temperature. The optimal scaling parameters have been determined by Kestin and his coworkers as follows: For helium,  $\sigma = 2.556 \text{ \AA}$  and  $\epsilon/k_B = 11.29$ ; for argon,  $\sigma = 3.291 \text{ \AA}$  and  $\epsilon/k_B = 153.61$ . These data, together with the molecular weights of 4.003 and 39.948, respectively, were used in calculating the last columns of Tables I and II.

Binary collisions between unlike molecules are accounted for by introducing a mixture conductivity and mixture scaling parameters. In contrast to the more usual "combination rules" for this conductivity, in Kestin's theory the mixture conductivity is given by an equation of the same form as (8) with universal collision functionals given by Eqs. (9) and (10). For the helium-argon system the appropriate scaling parameters are  $\sigma_{12} = 2.904 \text{ \AA}$  and  $\epsilon_{12}/k_B = 55.24$ . For

collisions involving species 1 and 2,

$$k_{12} = \frac{75}{64} \left[ \frac{k_B^3 (M_1 + M_2) NT}{2\pi M_1 M_2} \right]^{1/2} \frac{F(T_{12}^*)}{\Omega^{(2)}(T_{12}^*) \cdot \sigma_{12}^2} \quad (11)$$

where  $T_{12}^* = T/(\epsilon_{12}/k_B)$ . It should be noted that this conductivity is independent of the molar composition of the mixture.

Finally, the thermal conductivity of a binary mixture of specified composition is (Refs. 1 and 2)

$$k_{\text{mix}} = \frac{1 + Z}{X + Y} \quad (12)$$

where

$$X = \frac{x_1^2}{k_1} + \frac{2x_1 x_2}{k_{12}} + \frac{x_2^2}{k_2} \quad (13)$$

$$Y = \frac{x_1^2}{k_1} U_1 + \frac{2x_1 x_2}{k_{12}} U_y + \frac{x_2^2}{k_2} U_2 \quad (14)$$

$$Z = x_1^2 U_1 + 2x_1 x_2 U_z + x_2^2 U_2 \quad (15)$$

$$U_1 = \frac{4}{15} A_{12}^* - \frac{1}{12} \left( \frac{12}{5} B_{12}^* + 1 \right) \frac{M_1}{M_2} + \frac{1}{2} \frac{(M_1 - M_2)^2}{M_1 M_2} \quad (16)$$

$$U_2 = \frac{4}{15} A_{12}^* - \frac{1}{12} \left( \frac{12}{5} B_{12}^* + 1 \right) \frac{M_2}{M_1} + \frac{1}{2} \frac{(M_1 - M_2)^2}{M_1 M_2} \quad (17)$$

$$U_y = \frac{4}{15} A_{12}^* \frac{(M_1 + M_2)^2}{4M_1 M_2} \frac{k_{12}^2}{k_1 k_2} - \frac{1}{12} \left( \frac{12}{5} B_{12}^* + 1 \right) - \frac{5}{32A_{12}^*} \left( \frac{12}{5} B_{12}^* - 5 \right) \frac{(M_1 - M_2)^2}{M_1 M_2} \quad (18)$$

$$U_z = \frac{4}{15} A_{12}^* \left\{ \left[ \frac{(M_1 + M_2)^2}{4M_1 M_2} \right] \left( \frac{k_{12}}{k_1} + \frac{k_{12}}{k_2} \right) - 1 \right\} - \frac{1}{12} \left( \frac{12}{5} B_{12}^* + 1 \right); \quad (19)$$

$x_1$  and  $x_2$  are the mole fractions of each component and  $A_{12}^*$  and  $B_{12}^*$  are additional universal functionals of the reduced temperature, given by

$$A^* = \exp[0.10967 - 0.09555 \ln T^* + 0.08965 (\ln T^*)^2 - 0.02629 (\ln T^*)^3 + 0.00241 (\ln T^*)^4] \quad (20)$$

and

$$B^* = \exp[0.15529 - 0.042985 \ln T^* - 0.000213 (\ln T^*)^2 + 0.003068 (\ln T^*)^3 - 0.000229 (\ln T^*)^4] \quad (21)$$

The calculation procedure has been checked against the TPRC smoothed data for helium-argon mixtures at 343.2 and 793.2K. The agreement is within 2% and 4%, respectively. The corresponding-states procedure is not difficult to perform, even with a hand calculator. Thus, for temperatures less than about 800K, Kestin's method is recommended. For higher temperatures, however, the error due to Kestin's method may increase beyond 4% and therefore an empirical correlation is suggested as described below.

Since the mixture data extrapolated to pure components show progressively worse agreement with other pure-component measurements at higher temperatures, the increasing discrepancy between the mixture data and the Kestin prediction may well be due to experimental errors rather than faulty theory. Until this matter is resolved

by more precise measurements, it is recommended that for mixtures with small concentrations of either component the Kestin prediction method be used, while for other mixtures the modified procedure outlined in section C be employed.

### C. Numerical Data Fitting

For helium-argon gas mixtures in which the argon mole fraction ( $X$ ) varies from 0.2 to 0.8, the following expression is recommended:

$$k_m = (k_K + k_E)/2 \quad (22)$$

where  $k_m$  = conductivity of the mixture,

$k_K$  = conductivity calculated by Kestin's method as recommended above,

and

$$k_E = A_0 + A_1 T + A_2 X + A_3 X^2 + A_4 Q_1 + A_6 Q_1 \ln T + A_7 Q_1 T^{-2} + A_8 Q_2 T^{-2} \quad (23)$$

where

$$A_0 = 0.75$$

$$A_1 = 2.64 \times 10^{-3}$$

$$A_2 = -3.92$$

$$A_3 = 1.50$$

$$A_4 = 12.16$$

$$A_5 = 0.866$$

$$A_6 = -4.45$$

$$A_7 = 6.67 \times 10^3$$

$$A_8 = -1.369 \times 10^5$$

$X$  = mole fraction argon

$$Q_n = [1 - \exp(-2X^{n+1})] \quad n = 1, 2$$

$T$  = temp. in degrees Kelvin.

The expression shown in Eq. (23) was arrived at by a trial-and-error procedure which attempted to minimize the mean square error between Eq. (23) and the raw data given in Ref. 7.

The overall accuracy of the expression given in Eq. (22) is estimated to be better than  $\pm 4\%$  in the temperature range of 800-1200K. The accuracy of  $k_E$  (Eq. 23) alone is estimated to be  $\pm 5\%$ . The raw TPRC data<sup>7</sup> available up to about 793K for helium-argon mixtures, as well as the calculated values of  $k_E$  based on Eq. (23), are shown in Fig. 1.

An accuracy of  $\pm 5\%$  can be achieved by using either the method recommended by Kestin [Eq. (12)] or Eq. (23) (or Fig. 1). However, it appears that for the high-temperature regime ( $T > 800K$ ). Eq. (23) overpredicts the thermal conductivity value, while Eq. (12) underpredicts it. Therefore, Eq. (22), which gives an average of the two values, is recommended when greater accuracy is desired.

It should again be noted that the above recommendation is based on empirical analysis and on the theoretical model of Kestin, and is therefore only a "best estimate." Actual experimental data are required to verify the accuracy of the recommended procedure.



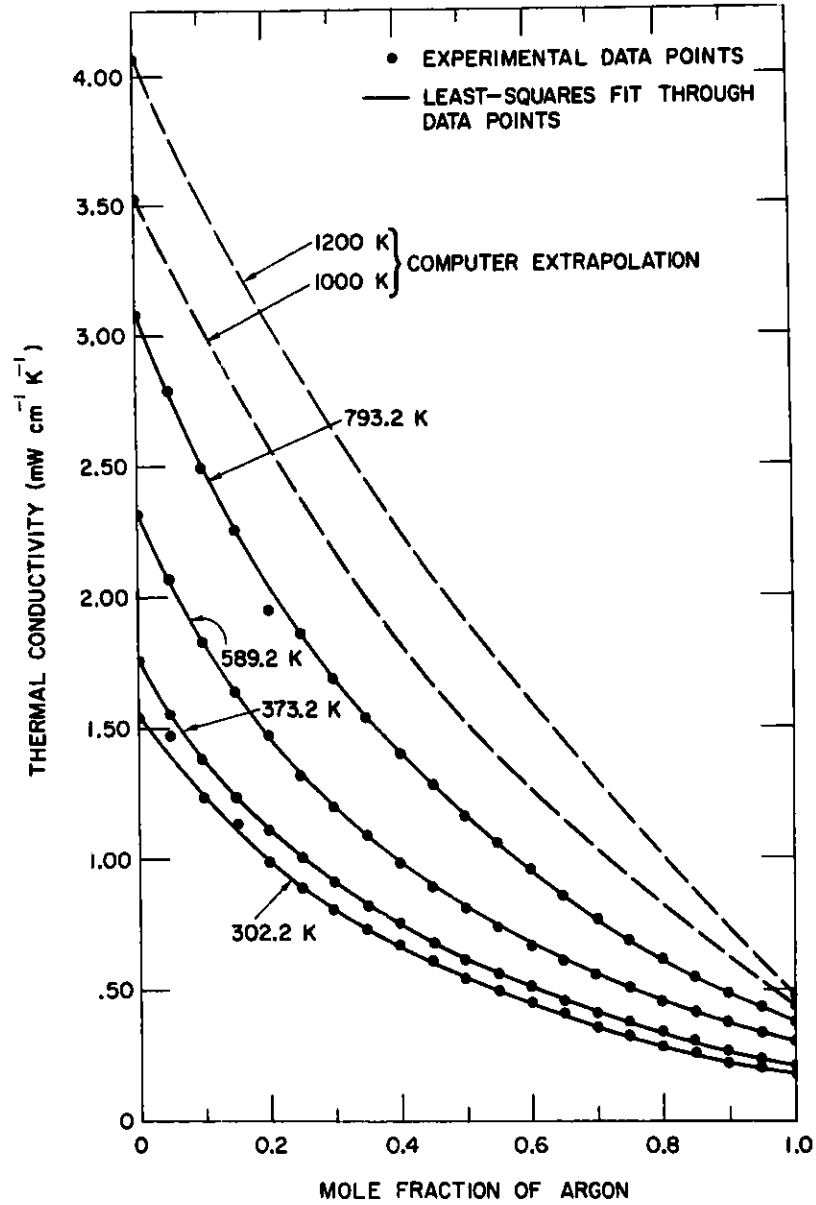


Fig. 1. Thermal Conductivity of Helium-Argon Systems at Selected Temperatures. Neg. No. MSD-64184.

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