Comment: On the measurement of the thermal conductivity by the column method

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Recently Faubert and Springer[1,2] and Springer and Wingeier[3] reported experimental results on the thermal conductivity coefficients λ of noble gases up to 2500 °K obtained by means of the column method of Blais and Mann.[4] In 1965 we reported[5] a version of this method and results on λ of cesium vapors and argon. In a recent work[6] we analyzed the theory of the method, namely the temperature distribution along the filament, the temperature jump on the filament surface, the excentricity and the thermal expansion of the filament and the convection. Our results of measurement of λ (in W/cm · deg) of inert gases could be approximated as follows[6] (T in °K):

$$\text{Ne: } \lambda\times10^4 = 2.200 + 9.343\times10^{-3}T - 0.896\times10^{-6}T^2 \quad (1100\text{–}2200\,^\circ\text{K}),$$

$$\text{Ar: } \lambda\times10^4 = 0.320 + 4.535\times10^{-3}T - 0.599\times10^{-6}T^2 \quad (1000\text{–}2200\,^\circ\text{K}),$$

$$\text{Kr: } \lambda\times10^4 = 0.832 + 1.975\times10^{-3}T - 0.206\times10^{-6}T^2 \quad (1300\text{–}2300\,^\circ\text{K}),$$

$$\text{Xe: } \lambda\times10^4 = 0.320 + 1.440\times10^{-3}T - 0.170\times10^{-6}T^2 \quad (1100\text{–}2200\,^\circ\text{K}).$$

The deviation from the smoothed data of Refs. 1 and 3 does not exceed 3% in the corresponding temperature ranges.

I would like to point out two errors in Refs. 1–3. The first is connected with the expression for the temperature jump correction λ''. Equation (A9) in Ref. 2 and Eq. (2) in Ref. 3 do not take into account the dependence of the mean free path on the filament temperature. Meanwhile, this dependence leads to an additional factor of $1+(0.5+b)/(1+b)$ (~ 1.7 in these equations, as it is shown in Refs. 5 and 6; here b is defined by $\lambda = aT^b$, and $Q_\lambda = 2\pi(\ln r_0/r_f)^{-1}(1+b)^{-1}T_f\lambda_f$ if $T_f \gg T_0$.

The second error lies in neglecting the thermal expansion of the wire. One has to take into account the dependence of the length L and the radius of the filament on the temperature when differentiating the expression for Q_λ. So a correction $\lambda''' = -[1+(\ln r_0/r_f)^{-1}](1+b)^{-1} \times (d\ln L/d\ln T_f)$ will appear.[6] The value of λ''' is of the order of 1% at $T_f = 2000$ °K.

[1] F. M. Faubert and G. S. Springer, J. Chem. Phys. 57, 2333 (1972).
[2] F. M. Faubert and G. S. Springer, J. Chem. Phys. 58, 4080 (1973).
[3] G. S. Springer and E. W. Wingeier, J. Chem. Phys. 59, 2747 (1973).
[4] N. C. Blais and J. B. Mann, J. Chem. Phys. 32, 1459 (1960).
[5] B. J. Stefanov and L. P. Zarkova, Proceedings of the VII International Conference on Phenomena in Ionized Gases, Vol. II, p. 117, Beograd, 22–27 August 1965.
[6] B. Stefanov, L. Zarkova, and D. Oliver, Teplofiz. Vys. Temp. [High Temp.] (to be published).

Thermal conductivity by the column method: Reply to B. Stefanov

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In his comments Dr. Stefanov[1] points out that three corrections should be applied to data obtained by thermal conductivity columns. The first one includes a factor in the temperature jump correction and compensates for the dependence of the mean free path on temperature. The second correction λ''' contains two terms, one for the dependence of the wire diameter on temperature λ_r''', and one for the dependence of the wire length on temperature λ_L'''.

The first two of these corrections are commonly neglected in conductivity column type measurements. For most gases (as was in the case in our measurements with neon, argon, krypton, xenon, and nitrogen) temperature jump effects are entirely negligible, and corrections for temperature jump (with or without the added factor derived by Dr. Stefanov) are unnecessary. When temperature jump effects are present, as in our helium measurements, this factor may change the results by $\frac{1}{2}$–1%. Unfortunately, in the temperature jump region other factors influence the results more significantly. For example, as was discussed in our paper,[2]

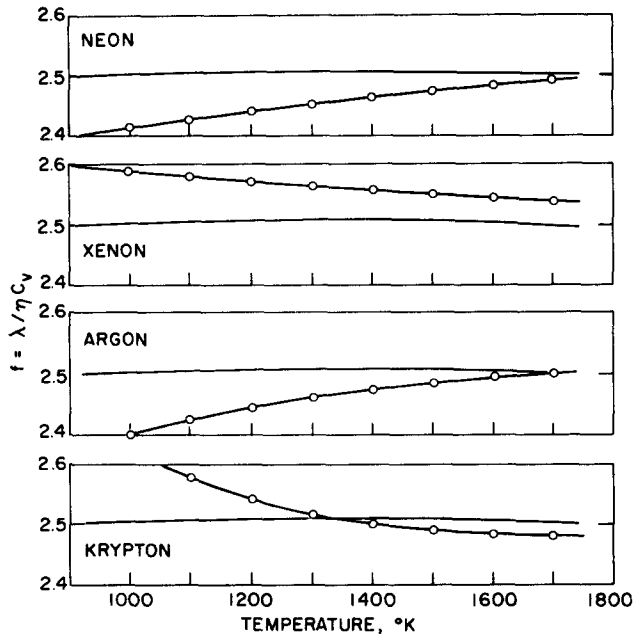

FIG. 1. Eucken factors versus temperature: ——theoretical value; — —computed using Stefanov's thermal conductivity data.

the error introduced by the lack of knowledge of the accommodation coefficient may be as high as 10–30%.

The correction for changes in the wire diameter is generally very small. For the apparatus and conditions employed in our experiments, λ_r''' would have changed the results by less than 0.3%.

Although the above corrections are negligible in practice, Dr. Stefanov is correct in pointing out that they should still be considered in principle.

The correction for wire length λ_L''' is to be considered if a constant value for the length is used to reduce the data. This correction is usually circumvented by measuring the wire length, and by analyzing the data on a unit length basis. We also followed this common practice which negates the need for the analytical correction suggested by Dr. Stefanov.

Finally, we calculated the Eucken factors using the thermal conductivity values given by Dr. Stefanov and the viscosity data quoted in Refs. 2 and 3 (Fig. 1). The Eucken factors based on Dr. Stefanov's data show a systematic variation with temperature and approach the correct analytical value of ~ 2.5 only at high temperatures.

[1]B. Stefanov, J. Chem. Phys. 62, 2258 (1975) (preceding comment).
[2]F. S. Faubert and G. S. Springer, J. Chem. Phys. 58, 2333 (1972).

Comment on the calculation of the isomer shift in ferric hemin

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In a recent paper Moutsos, Adams, and Sharma[1] (MAS) have used a ligand field model to calculate the isomer shift for ferric hemin for comparison with data from Mössbauer effect measurements. To do so they used a calibration procedure derived by Sharma and Sharma[2] (SS) from a study of several iron garnets. It is the purpose of this note to point out that it is not a valid procedure to use the SS calibration for the hemin problem.

Equation (7) of the MAS paper is

$$\delta = K_0[\rho'(0) + C], \tag{1}$$

where δ is the isomer shift in mm/s relative to stainless steel, K_0 is the calibration constant, and $\rho'(0)$ is the shift in charge density at the iron site between the system of interest and a free ferric ion. Thus, we can write

C = (charge density at iron site for a free ferric ion)

– (charge density at iron nuclei in stainless steel).

SS determine both K_0 and C from densities appropriate to the octahedral and tetrahedral sites in rare earth iron garnets:

$$\rho'(0) = 11.5a_0^{-3} \text{ and } \rho'(0) = 12.5a_0^{-3}.$$

The difference between these two values is small compared with the magnitude of either one of them. The value of C corresponds to $\rho'(0) = 0$ and amounts to an extrapolation well outside the small interval used to evaluate it. Thus, small changes in the two data points used to find K_0 and C can give large changes in C. This would be of nó consequence if the application of Eq. (1) was restricted to the immediate neighborhood of the calibrating points. Since, for the hemin chloride calculation, MAS have $\rho'(0) = 6.39a_0^{-3}$ (almost halfway between zero and the calibrating points) we must view their calculated isomer shift with some reservation.

As an example of the errors that this can lead to, we attempt to calculate the charge density difference between the free ferrous and ferric ions, a result which

