reference 1, and in the case of nitrogen it is somewhat better.

The alternative procedure proposed by Eckert is to define the heat-transfer coefficient in terms of enthalpy difference:

$$q_w = h_i(i_r - i_w) \qquad (6)$$

where now the enthalpy recovery factor r_i is given by

$$r_i = \frac{i_r - i_s}{(u_s^2)/2} \qquad (7)$$

The value of the enthalpy recovery factor r_i as taken from the boundary-layer solutions is reported in column 9 of Table 2 and compared with the approximate value given as $\sqrt{(Pr^*)}$ in column 10. The resulting error in the use of the reference method is comparable to that in reference [1], being of the order of 1 to 2 per cent.

The heat-transfer coefficient h_i is reported in dimensionless form as $(C_f/2\ St_i)$ and the boundary-layer calculations are shown in column 10 of Table 2. The reference method proposed a value of (Pr^*) for this ratio. The agreement of the approximate and exact values is even better than that reported in reference [1].

Conclusions and recommendation

The use of the reference temperature method yields approximations for N_2 and CO_2 laminar boundary layers which are as good as those of reference [1] for the air. If the specific heat varies over a wide range or if dissociation occurs it is recommended as in reference [1], though this remains to be verified, that properties be evaluated at a reference enthalpy rather than the reference temperature, where the reference enthalpy is given by:

$$i^* = i_s + 0{\cdot}5(i_w - i_s) + 0{\cdot}22(i_r - i_s).$$

ACKNOWLEDGEMENT

The authors wish to express their gratitude for the support of the National Aeronautics and Space Administration grant NsG-356 which has made this study possible.

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ON THE REPRESENTATION OF THE DENSITY DEPENDENCE OF THE THERMAL CONDUCTIVITY OF SUPERHEATED STEAM

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(*Received* 5 *July* 1966)

INTRODUCTION

THERMAL conductivity data on superheated steam have a large number of practical applications. Consequently, the study of this property has recently drawn considerable attention. Kestin *et al.* [1] have attempted to represent the density dependence of the thermal conductivity of superheated steam by a second order polynomial in the densities. Such representation of viscosity and thermal conductivity has been tried by Curtis *et al.* [2] for moderately dense gases. However, their method cannot at present be applied to the data on steam as they did not consider association which plays a very significant role in steam [3].

Kestin *et al.* [1] considered the two most reliable sets of data reported by Keyes and Vines [4] (henceforth to be referred to as MIT data) and by Vargaftik *et al.* [5–9] (henceforth to be referred to as VTI data). However, it was observed [1] that the two sets of data cannot be represented by the same set of coefficients in the polynomial series. Moreover, the first coefficient $a(T)$ for the two sets of data showed a very different dependence on temperature.

In this paper we have attempted to look into the coefficients of the polynomial series from the point of view of their physical significance. Our analysis is expected to throw light on the temperature dependence of $a(T)$ and may show which set of data is more reasonable from the theoretical standpoint.

CALCULATION OF THERMAL CONDUCTIVITY

Because of hydrogen bonding steam shows association which increases with the increase of pressure and decrease of temperature. At not too high pressures larger clusters are supposed to be present in negligible proportions and consequently under such circumstances it is reasonable to consider steam to be a mixture of monomers and dimers [10] according to the equilibrium

$$2\,H_2O \rightleftharpoons (H_2O)_2\ . \qquad (1)$$

The presence of dissociation reaction results in an extra transport of heat energy. The dimers dissociating in the neighbourhood of hot plate associate again near the cold plate with a consequent release of energy. This problem of heat transfer in a chemically reacting gas mixture, placed in a conductivity cell has been treated in detail by Hirschfelder [11] and Butler and Brokaw [12]. Following Stogryn and Hirschfelder [13] we can represent the conductivity K_p of steam at a pressure P as

$$K_p = K_{mix} + K_r + K_c \qquad (2)$$

where K_{mix} is the thermal conductivity of a binary mixture of monomers and dimers of H_2O. K_r and K_c are the contributions of chemical reaction and collisional transfer to the total conductivity.

(*i*) *Calculation of* K_{mix}

The mole fractions of monomers and dimers of steam were calculated by the method described in reference [10]. It has been observed [3] that long range dipole forces do not play any significant role in transport properties. Consequently, we have used the Lennard–Jones (12:6) model for all the calculations. The force constants for H_2O for this model were determined from the experimental values of K_o and applying Eucken correction [14]. K_o is the value of thermal conductivity corresponding to zero pressure. The force parameters thus obtained are $\sigma = 2{\cdot}854$ Å, $\epsilon/k = 1042$°K. These should be compared with the values $\sigma = 2{\cdot}71$ Å, $\epsilon/k = 506$°K as determined from viscosity data [10]. This difference in the two sets of parameters may be due to the neglect of resonance exchange in the calculation of K_o. However, these force constants will reproduce the thermal conductivity of steam at zero pressure quite accurately and we are mainly interested in the pressure dependence of thermal conductivity. The specific heats of monomer were taken from the standard tables and those of dimers were calculated by the method of Stogryn and Hirschfelder [13].

(*ii*) *Calculation of* K_r

On the local chemical equilibrium assumption the heat transfer due to reaction $2\,H_2O \rightleftharpoons (H_2O)_2$ may be written as [13]

$$K_r = (nRD_{12}/V)(\Delta H/RT)^2_{x_2} + \ldots \qquad (3)$$

where n is the number of moles, V the volume, D_{12} the diffusion coefficient between monomers and dimers, ΔH is the heat of reaction and x_2 the mole fraction of dimers. ΔH was determined from the table given in reference [13].

(*iii*) *Calculation of* K_c

According to the modified formulation of Stogryn and Hirschfelder [13] at not too high pressures,

$$K_c = (23/40)\left[B(T) + T\frac{\mathrm{d}B(T)}{\mathrm{d}T}\right]K^{mon}(n/v) + f(\rho^2) \qquad (4)$$

where K^{mon} is the conductivity of H_2O, considered as monatomic $B(T)$ the second virial coefficient at temperature T.

COMPARISON WITH EXPERIMENT

It may be seen that K_r is dependent on ρ the density and equation (4) can be written as

$$K_c = \alpha\rho + f(\rho^2) \qquad (5)$$

where α is a constant. Hence we have

$$K_{cal} = K_{mix} + K_r + \alpha\rho + f(\rho^2). \qquad (6)$$

We have fitted $K_{mix} + K_r$ to a series of the form

$$K_{mix} + K_r = K_o + \beta\rho + \gamma\rho^2 \qquad (7)$$

where β and γ are constants.

The second term in equation (4) is a function of ρ^2. Consequently we have

$$K_{cal} = K_o + (\alpha + \beta)\rho + F(\rho^2). \qquad (8)$$

Kestin *et al.* [1] have fitted the experimental thermal conductivity data of Keyes *et al.* [4] (denoted by the subscript M) and those of Vargaftik *et al.* [5–9] (denoted by the subscript V) to a series of the form

$$K = K - K_o = a\rho + b\rho^2. \qquad (9)$$

They have observed that although the coefficients $b_M(T)$ and $b_V(T)$ are close to each other the coefficient $a_M(T)$ and $a_V(T)$ show a wide difference in their temperature dependence. At present we have only attempted to throw light on the difference in the values of the coefficient a.

Since $F(\rho^2)$ cannot be evaluated accurately we have made the following comparison,

$$\left.\begin{aligned} K_{expt} - K_o - b\rho^2 &= a\rho \\ \text{and} \qquad K_{calc} - K_o - F(\rho^2) &= (\alpha + \beta)\,\rho \\ &= a_{calc}(T)\,\rho \end{aligned}\right\} \quad (10)$$

It is evident from the above expression that $(\alpha + \beta)$ at any temperature is comparable with a. The values of $a_{calc}(T)$ together with the values of $a_M(T)$ and $a_V(T)$ as determined by Kestin *et al.* [1] are shown in columns 2–4 of Table 1.

Table 1

T°K	$a_{calc}(T)$ W/ degC gcm^3	$a_M(T)$ W/M degC gcm^3	$a_V(T)$ W/M degC gcm^3	$a'_M(T)$ W/M degC gcm^3	$a'_V(T)$ W/M degC gcm^3
469·15	0·434	0·143	—	0·485	—
522·4	0·324	0·153	—	0·231	—
572·65	0·264	0·163	—	0·216	—
622·35	0·226	0·172	—	0·195	—
723·2	0·193	—	0·228	—	0·998
783·2	0·174	—	0·259	—	1·059
823·2	0·168	—	0·276	—	1·901
833·2	0·165	—	0·280	—	1·941

It may be seen that in contradiction to the experimental values $a_{calc}(T)$ decreases with the increase of temperature. In order to explain the difference between the theoretical and the calculated values of $a(T)$ we have determined $a_M(T)$ and $a_V(T)$ by considering the K values at the low pressures where the term $b\rho^2$ was calculated using the coefficient b as determined from the thermal conductivity data. The values of $a_M(T)$ and $a_V(T)$ calculated from low pressure data are denoted by primes.

The values of $a'_M(T)$ and $a'_V(T)$ thus determined are shown in column 5 and 6 of Table 1. It may be seen that the values of $a'_M(T)$ show a temperature variation in agreement with that of the theory. However, $a'_V(T)$ shows an increase with the increase of temperature. The quantitative agreement between $a'_M(T)$ and $a_{calc}(T)$ is remarkably good. The increase in $a_M(T)$ with the increase of temperature when fitted over the whole density range is most probably due to the failure of a second-order polynomial to represent the experimental data. A higher order polynomial may show a decrease of $a_M(T)$ with the increase of temperature. The variation of $a_V(T)$ may be due to errors in experimental measurements.

ACKNOWLEDGEMENT

The authors wish to express their thanks to Prof. B. N. Srivastava, D.Sc., F.N.I., for his kind interest and encouragement.

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