CHAPTER IX

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

Abstract.

The coefficient representing the density
dependence of the thermal conductivity of superheated
steam have been analysed theoretically. The results show
that a higher degree polynomial than that used recently
by Kestin, Whitelaw and Zien is necessary for represent­
ing properly the density dependence.

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, Whitelaw and Zien [1], have attempted
to represent the density dependence of the thermal conduc­
tivity of superheated steam by a second order polynomial
in the densities. Such representation of viscosity and
thermal conductivity has been tried by Curtiss, McElory
and Hoffman [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, 6, 7, 8, 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

$$2 \text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{O})_2$$

... (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

$$K_p = K_{mix} + K_T + K_C \quad \ldots (2)$$

where $K_{mix}$ is the thermal conductivity of a binary mixture of monomers and dimers of $H_2O$. $K_T$ 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 ref. [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 the calculations. The force constants for $H_2O$ for this model were determined from the experimental values.
of $K_0$ and applying Suckin correction \cite{14}. $K_0$ is the value of thermal conductivity corresponding to zero pressure. The force parameters thus obtained are $\sigma = 2.845 \, \text{Å}$, $\epsilon/k = 1042^{\text{O}} \text{K}$. These should be compared with the values $\sigma = 2.71 \, \text{Å}$, $\epsilon/k = 506^{\text{O}} \text{K}$ as determined from viscosity data \cite{10}. This difference in the two sets of parameters may be due to the neglect of resonance exchange in the calculation of $K_0$. 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 \cite{13}.

(ii) Calculation of $K_T$.

On the local chemical equilibrium assumption the heat transfer due to reaction $2 \text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{O})_2$ may be written as \cite{13}

$$K_T = \left(\frac{nD_{12}}{\nu}\right)(\Delta H/RT)^2 x_2 + \ldots \ldots (3)$$

where $n$ is the number of moles, $\nu$ the volumes, $D_{12}$ the diffusion coefficient between monomers and dimers, $\Delta H$ is the heat of reaction and $x_2$ the mole fraction of dimers. $\Delta H$ was determined from the table given in ref. \cite{13}.
(iii) Calculation of $K_c$

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

$$K_c = \left(\frac{\varepsilon}{4d}\right) \left[ B(T) + \frac{\partial \ln \phi}{\partial T} \right] K_{\text{mon}}(n/V) + f(e) \quad \ldots (4)$$

where $K_{\text{mon}}$ 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 $\rho$, the density and eqn. (4) can be written as

$$K_c = \alpha e + f(e^2) \quad \ldots (5)$$

where $\alpha$ is a constant. Hence we have,

$$K_{\text{cal}} = K_{\text{mix}} + K_r + \alpha e + f(e^2) \quad \ldots (6)$$

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

$$K_{\text{mix}} + K_r = K_0 + \beta e + \gamma e^2 \quad \ldots (7)$$

The second term in Eqn. (4) is a function. Consequently, we have

$$K_{\text{cal}} = K_0 + (\delta + \rho) e + f(e^2) \quad \ldots (8)$$
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

\[
K = K - K_0 = a \rho + b \rho^2 \tag{9}
\]

They have observed that although the coefficients \(b_(M)(T)\) and \(b_(V)(T)\) are close to each other the coefficients \(a_(M)(T)\) 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,

\[
K_{\text{expt}} - K_0 - b \rho^2 = a \rho \tag{10}
\]

and

\[
K_{\text{calc}} - K_0 - F(\rho^2) = (\alpha + \beta) \rho = a_{\text{calc}}(T) \rho
\]

It is evident from the above expression that \((\alpha + \beta)\) at any temperature is comparable with \(a\). The values of \(a_{\text{calc}}(T)\) 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.

It may be seen that in contradiction to the experimental values \(a_{\text{calc}}(T)\) decreases with the increase of temperature. In order to explain the difference between
Table 1.

<table>
<thead>
<tr>
<th>T °K</th>
<th>a_{calc}(T)</th>
<th>a_M(T)</th>
<th>a_V(T)</th>
<th>a'_M(T)</th>
<th>a'_V(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>watt/M°C/gm. cm³</td>
<td>watt/M°C/gm. cm³</td>
<td>watt/M°C/gm. cm³</td>
<td>watt/M°C/gm. cm³</td>
<td>watt/M°C/gm. cm³</td>
</tr>
<tr>
<td>469.15</td>
<td>0.434</td>
<td>0.143</td>
<td>...</td>
<td>0.485</td>
<td>...</td>
</tr>
<tr>
<td>522.4</td>
<td>0.324</td>
<td>0.153</td>
<td>...</td>
<td>0.231</td>
<td>...</td>
</tr>
<tr>
<td>572.65</td>
<td>0.264</td>
<td>0.163</td>
<td>...</td>
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</tr>
<tr>
<td>622.35</td>
<td>0.226</td>
<td>0.172</td>
<td>...</td>
<td>0.195</td>
<td>...</td>
</tr>
<tr>
<td>723.2</td>
<td>0.193</td>
<td>...</td>
<td>0.223</td>
<td>...</td>
<td>0.998</td>
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<tr>
<td>783.2</td>
<td>0.174</td>
<td>...</td>
<td>0.259</td>
<td>...</td>
<td>1.059</td>
</tr>
<tr>
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<td>...</td>
<td>0.276</td>
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<td>1.901</td>
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<tr>
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<td>0.165</td>
<td>...</td>
<td>0.280</td>
<td>...</td>
<td>1.941</td>
</tr>
</tbody>
</table>

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 ρ^2 is very small from the eqn. (9). The term b ρ^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 $a_Y(T)$ thus determined are shown in column 5 and 6 of Table I. It may be seen that the values of $a_M(T)$ show a temperature variation in agreement with that of the theory. However, $a_Y(T)$ 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 $a_Y(T)$ may be due to errors in experimental measurements.

References.


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