

IAPWS Certified Research Need - ICRN

Thermal Conductivity of H₂O at Low Pressures and High Temperatures

The IAPWS Working Group “Thermophysical Properties of Water and Steam” has examined the available experimental and theoretical information for the thermal conductivity of H₂O. The Working Group has concluded that there is a need for:

- (a) New experimental measurements for the thermal conductivity of H₂O at low pressures at temperatures up to at least 600 K with an accuracy at the one-percent level
- (b) Additional theoretical studies of procedures for calculating the thermal conductivity of H₂O from intermolecular potentials

Although encouraging this work, IAPWS is not able under its statutes to provide financial support. The IAPWS contact can provide any further development information and will liaise between research groups.

**Issued by the
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Thermal Conductivity of H₂O at Low Pressures and High Temperatures

The International Association for the Properties of Water and Steam (IAPWS), in collaboration with the International Association for Transport Properties (IATP), has embarked on an initiative to develop new formulations for calculating the transport properties of H₂O replacing previous recommended formulations based on experimental information available prior to 1980, to extend the range of temperatures and densities, and to make the formulations consistent with the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use [1]. The development of a new correlating equation for the viscosity of H₂O has been completed and was recently adopted as the IAPWS Formulation 2008 for the Viscosity of Ordinary Water Substance [2,3].

The current procedure for calculating the thermal conductivity of H₂O recommended by IAPWS is based on a Revision of the IAPS Formulation 1985 for the Thermal Conductivity [4]. Research in support of the development of a new formulation for the thermal conductivity of H₂O is still being pursued. Collection of all experimental information for the thermal conductivity of H₂O has been completed [5].

Meanwhile, Hellmann *et al.* have developed a theoretical procedure for calculating the transport properties from accurate intermolecular potential energies for dilute gases of polyatomic molecules such as CH₄ [6] and H₂O [7]. Specifically, for H₂O they have calculated the shear viscosity, thermal conductivity, self-diffusion, and volume viscosity in the dilute-gas limit at temperatures from 250 K to 2500 K [7] starting from an accurate *ab initio* potential-energy surface for the H₂O pair obtained by Bukowski *et al.* [8].

The theoretical values for the dilute-gas viscosity of H₂O calculated by Hellmann *et al.* [7] are in agreement with the experimental data within their experimental accuracy. They also agree with the new IAPWS formulation for the viscosity of H₂O in the dilute-gas limit within the tolerance of the correlation in the temperature range up to 1173 K covered by the formulation, although the extrapolating behavior of the viscosity to higher temperatures differs somewhat from that obtained by extrapolating the IAPWS formulation beyond its range of validity [3,7].

On the other hand, for the thermal conductivity of H₂O in the dilute-gas limit there are some serious discrepancies between the theoretical values and the available experimental data. The percentage deviations of the experimental data (indicated by symbols) and of the current IAPWS formulation for the thermal conductivity (indicated by the solid curves) from the new theoretical values are shown in Figures 1 and 2. At temperatures above 400 K, most of the experimental data (and the IAPWS formulation that was based on these data) start to differ from the theoretical values; the discrepancy is on the order of 5% in the range from 800 K to 1200 K. Not only do the deviations at higher temperatures become larger than the tolerance of 3% of the IAPWS formulation, but the deviations are clearly systematic.

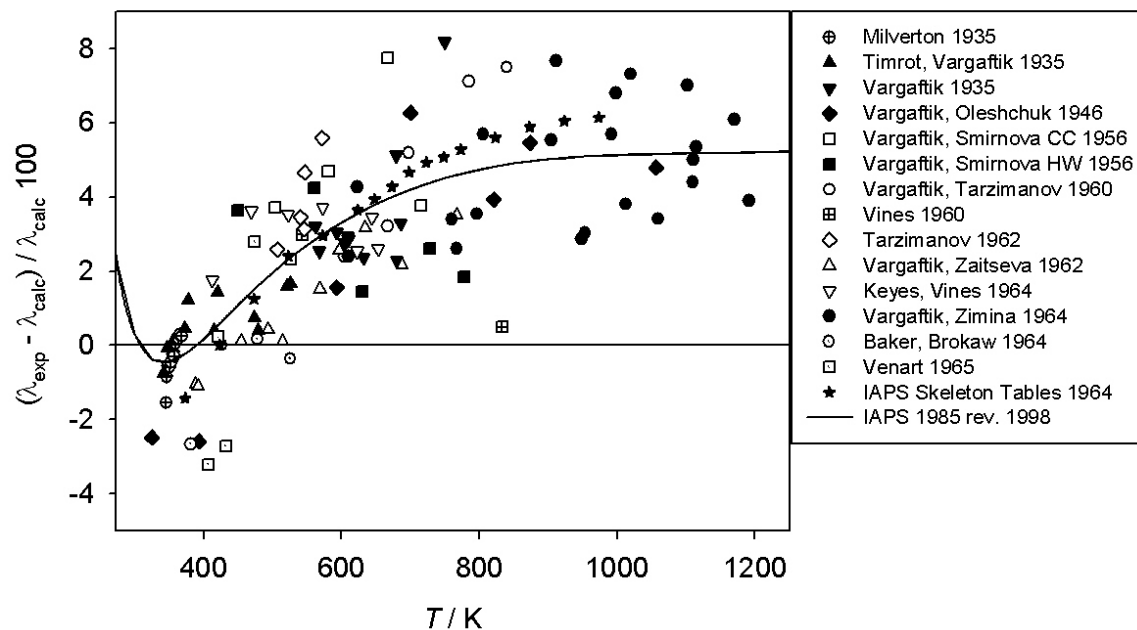


Figure 1. Percent deviation of experimental low-density thermal conductivity data (symbols) and the current IAPWS correlation [4] (solid curve) from theoretical values calculated from a high-accuracy pair potential. See Hellmann *et al.* [7] for more details.

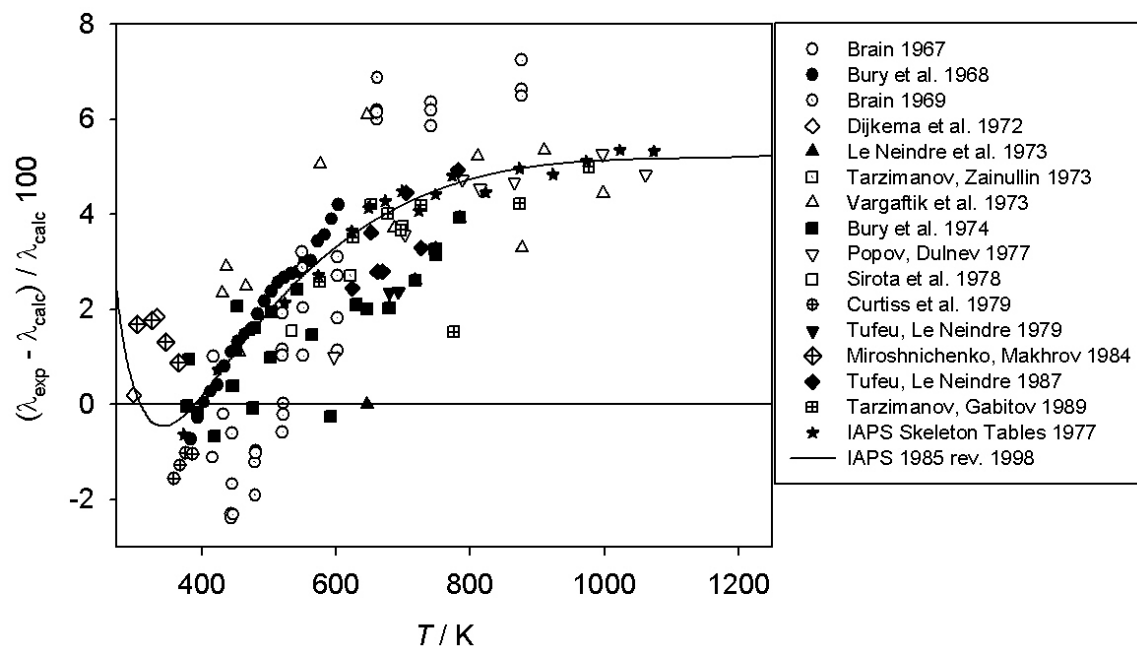


Figure 2. Percent deviation of experimental low-density thermal conductivity data (symbols) and the current IAPWS correlation [4] (solid curve) from theoretical values calculated from a high-accuracy pair potential. See Hellmann *et al.* [7] for more details.

It is not easy to obtain accurate experimental data for the thermal conductivity in the dilute-gas limit. It is not possible to measure directly the thermal conductivity at zero density. To obtain the thermal conductivity in the dilute-gas limit, one needs to extrapolate from higher pressures or densities. Moreover, some of the experimental data may not be independent from one another [7]. In other cases, one may not have enough information to assess the effect of radiation, temperature jumps, parasitic heat flow, etc. It is therefore in practice not realistic to make an assessment of the accuracies of the published experimental data different from the ones claimed by the investigators. Hence, there is a need for new experimental thermal-conductivity data at high temperatures with an accuracy at the one-percent level. It will not be necessary to measure the thermal conductivity at temperatures all the way up to 1200 K. New experimental data up to at least 600 K could suffice to establish the trend of the temperature dependence of the thermal conductivity at high temperatures.

However, the current IAPWS formulation for the thermal conductivity does give a good representation of the available experimental data which seem to be more or less internally consistent within realistic error estimates. Hence, it is not evident *a priori* that the discrepancies at high temperatures must necessarily be attributed to unreliability of the experimental information. An alternative possibility is that the theoretical thermal-conductivity values have a systematic error at the higher temperatures. There seems little reason to doubt the accuracy of the intermolecular potential surface of Bukowski *et al.* [8] for H₂O, but it should be remembered that it is a potential for the ground state of the molecule. Possible deformation of the molecule in higher rotational states at higher temperatures cannot be excluded. Moreover, use of the potential surface to calculate the thermal conductivity involves a number of additional assumptions such as a rigid-rotor assumption [7]. Hence, parallel to an experimental effort, there is also a need for additional theoretical studies to obtain an independent assessment of the actual accuracy with which the thermal conductivity can be calculated from an accurate intermolecular potential energy surface for H₂O in its ground rotational and vibrational state.

Summary of Need

In the case of the thermal conductivity of steam at high temperatures, the available experimental data are in disagreement with the best current theoretical estimates. Improved theoretical work and/or new high-temperature experiments are needed to resolve this discrepancy and reduce the uncertainty in our knowledge of this important property.

References

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