# Accurate measurements of thermodynamic and transport properties of industrial gases with acoustic resonators

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Acoustic resonators have been developed at NIST as tools to measure the thermodynamic and transport properties of gases. High Q cylindrical acoustic resonators are routinely used to measure the speed of sound in gases with uncertainties of 0.01% or less. Model intermolecular potentials are fitted to the acoustic data to obtain virial coefficients, gas densities r?and heat capacities  $C_P$  with uncertainties of 0.1% as well as estimates of the viscosity h and thermal conductivity l with uncertainties of less than 10%. The viscosity is measured directly with uncertainties of less than 1% using the Greenspan acoustic viscometer, a novel acoustic resonator developed at NIST. A novel resonator is used to measure the Prandtl number ( $Pr = hC_P/l$ ) with uncertainties of about 2%. This paper summarizes our work with these resonators and their applications to numerous gases including very reactive gases used in semiconductor processing.

## **OVERVIEW**

The National Institute of Standards and Technology (NIST) has an on-going research program to obtain accurate thermodynamic and transport property data of industrial gases. The gases that we study include ones that may be toxic, corrosive, reactive, flammable, or unstable at high temperature. We have studied more than 20 gases including refrigerants, chlorine, boron trichloride, tungsten hexafluoride, hydrogen bromide, carbon monoxide, and carbon tetrafluoride. These data are part of the Database of the Thermophysical Properties of Gases Used in the Semiconductor Industry accessible over the web at *http://properties.nist.gov/SemiProp/*. The success of this program has required the development of special gas-filled resonators and dosing systems to overcome the difficulties associated with the measurement and safe handling of these gases.

In order to obtain the desired data, this work exploits fundamental relationships between the acoustic and thermodynamic properties of gases through the use of high precision acoustic resonators [1]. We measure the frequency response of the resonators and its dependence on temperature and pressure. The results are analyzed with detailed acoustic models of gas-filled resonators, together with a calibration with argon.

In practice, the high precision of this technique is overshadowed by the uncertainty in the gas composition. This uncertainty is due to the presence of unknown impurities in the commercial sample and/or impurities that are generated during the scope of the study. Impurities of the latter type are particularly troublesome because their concentration may change with time and the rate of change may depend on the temperature. Therefore, materials compatibility is a primary consideration. For this work, we have constructed acoustic resonators and gas handling systems in which stainless steel or Monel and gold are the only materials that the test gas touches [2].

With a low loss (high Q) cylindrical resonator, we obtain speed of sound, heat capacity, and density data over a wide range of temperature and pressure. The uncertainties in these data are typically  $\pm 0.01\%$  for speed of sound,  $\pm 0.1\%$  for the ideal gas heat capacity, and  $\pm 0.1\%$  for the density. For some gases, we can also measure the average relaxation time of internal degrees of freedom [1].

Two other resonators developed in this program have geometries that are optimized for measuring the transport properties of gases. These "lossy" resonators exhibit greater thermal and viscous damping making them more suitable for accurately measuring the viscous or thermal diffusivity. The Greenspan acoustic viscometer [3] is a double Helmholtz resonator with which we have measured gas viscosity with a root-mean-squared (RMS) uncertainty of less than 0.5%. The other resonator is used for measurements of the Prandtl number, which is the ratio of the viscous and thermal diffusivities, with an uncertainty of about 2% [1].

# **RESONATOR DESIGNS**

For our measurements of thermodynamic properties, we use a cylindrical resonator (65 mm

diameter and 140 mm length), as shown in Fig. 1 [2]. Sound is transmitted between the resonator and two remote electro-acoustic transducers (near room temperature) through argon-filled waveguides. Thin diaphragms transmit the sound between the test gas



**FIGURE 1.** (a) The cylindrical resonator with remote transducers (Source and Detector). (b) Measured speed of sound in  $WF_6$  (upper) and deviations from a surface fit (lower) [2].

and the pressure-balanced argon in the waveguides. Thus, the test gas never contacts the elastomers and other non-metal parts of the transducers. Also shown in Fig. 1 are the measured sound speeds in tungsten hexafluoride (WF<sub>6</sub>) and the deviations from a surface fit [2].

The Greenspan acoustic viscometer (shown in Fig. 2) is a double Helmholtz resonator formed by two identical chambers with volume  $V_{c,s}(29 \text{ cm}^3)$  connected by a small duct of radius  $r_d$  (2 mm) and length  $L_d$ .(31 mm). Again, the transducers are isolated from the test gas by thin diaphragms.



**FIGURE 2.** A double Helmholtz resonator (Greenspan acoustic viscometer) used for viscosity measurements.

Figure 3 shows a comparison of the viscosity measured using the Greenspan viscometer with high quality data from the literature. These measurements have an RMS scatter of about 0.18% [3].



**FIGURE 3.** Deviations of the measured viscosity of several gases from known values. RMS deviations for all the data are about 0.18%.

A third resonator (shown in Fig. 4) is designed for Prandtl number  $Pr=D_v/D_T$  measurements [1]. This is a cylindrical resonator containing an array of ducts in the center region. Odd numbered longitudinal modes are damped primarily by viscous drag in the ducts and even numbered modes are damped primarily by thermal conduction to the duct walls.



**FIGURE 4.** A resonator designed for Prandtl number measurements.

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## REFERENCES

- Moldover, M.R., Gillis, K.A., Hurly, J.J., Mehl, J.B., Wilhelm, J. "Acoustic Measurements in Gases," in *Handbook of Elastic Properties of Solids, Liquids, and Gases, Vol IV*, edited by Levy, Academic Press, San Diego, 2000, Ch. 12.
- 2. Hurly, J., J., Int. J. Thermophys. 21, 185-206 (2000).
- 3. Wilhelm, J., Gillis, K.A., Mehl, J.B., and Moldover, M.
- R., Int. J. Thermophys. 21, 983-996 (2000).