

This Week's Citation Classic[®]

Woolley H W, Scott R B & Brickwedde F G. Compilation of thermal properties of hydrogen in its various isotopic and ortho-para modifications. *J. Res. Nat. Bur. Stand.* 41:379-475, 1948. [Low Temperature Section, Heat & Power Division, National Bureau of Standards, Department of Commerce, Washington, DC]

This paper brought together thermal data for H_2 , HD, and D_2 in solid, liquid, and gaseous states, including distinctive properties of ortho and para forms of H_2 and D_2 . A tentative entropy diagram for $n-H_2$ in the range of experimental data was also given. [The *SCI*[®] indicates that this paper has been cited in over 405 publications since 1955, making it the most-cited publication for this journal.]

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This compilation was in some way an outgrowth of the discovery of deuterium and of Ferdinand G. Brickwedde's connection with that event, and it is a credit to his planning, direction, and joint authorship as senior author. As a junior author then in his Low Temperature Section at the National Bureau of Standards (NBS), I spent an initial period learning the rules and notations of thermochemistry and recalling my instruction in quantum mechanics, in particular, its relevance to C_p for H_2 as taught by D.M. Dennison at Michigan.

To get ideal gas functions for the ortho and para constituents of ordinary hydrogen, I calculated sums of states (or partition functions) and their temperature derivatives, involving rotational and vibrational spectroscopic data from the literature. For better extrapolation to higher temperatures, I applied a Dunham-type analysis to the potential, extending it further by my own variations of the Klein-Rydberg method. "Real gas" thermodynamic properties were obtained from ideal gas values using equations of state formulations in a form suggested by C.S. Cragoe of the bureau staff.

At lower temperatures, other local fitting procedures came into play. Ultimately, the process involved numerical smoothing along observed isotherms, interpolation to densities

of chosen spacing, drawing of smooth isochores, and interpolation to the temperatures desired for the final table. This part of the fitting with further smoothing was carried out by R.B. Scott, who died in 1967.

As to two-phase equilibria, very sensitive data of Scott and Brickwedde on the dependence of vapor pressure on ortho-para composition of liquid H_2 were included. Study of the H_2 vapor pressure data suggested that ortho-ortho interactions formed a leading source of special energy effects in the liquid. Many data items were considered in producing the T-S diagram. The overall correlation across the coexistence region was the output of the draftsman, Robert N. Schwartz, one of several student assistants, as a result of his "visual" smoothing of irregularities in the numerical estimates presented to him.

The preparation of the hydrogen compilation paper extended through the period of World War II. There were a number of unrelated interruptions. For example, sometime after Belgium had been overrun, we were visited by a Marquis du Mazuel, who hoped his technical military experience could help in developing a CO_2 propellant assist for "bazooka type" rocket launching.

Later, an extensive program began, related to hopes for production of synthetic rubber (or "rubbah" as Franklin Roosevelt seemed to say it). Our laboratory's part involved calorimetry on relevant compounds from near "helium temperatures" upward to the vapor state. This was to determine the entropy of the vapor and thereby assist us in spectroscopic assignments needed for correct calculation of thermodynamic property values for the compounds in the "ideal gas state."

The subsequent establishment of the NBS Boulder laboratories has led to further improvement in thermodynamic knowledge. Numerous publications on hydrogen have resulted^{1,2} as well as on other substances. A publication on deuterium is to appear shortly.³

The many citations to this paper in the years since its first printing are due to the timeliness of the subject matter in view of the related technologies that have blossomed under various external stimuli and temporary national needs.

1. Roder H M, Weber L A & Goodwin R D. *Thermodynamic and related properties of parahydrogen from the triple point to 100 °K at pressures to 340 atmospheres*. Washington, DC: US Government Printing Office, 1965. 112 p.
2. Weber L A. *Thermodynamic and related properties of parahydrogen from the triple point to 300 K at pressures to 1000 bar*. Springfield, VA: National Technical Information Service, 1975. 100 p. NASA Special Publication 3088 and National Bureau of Standards Interagency Report 374.
3. McCarty R D & Jung S. *Thermodynamic properties of deuterium for temperatures from the triple point (18.71 K) to 423 K with pressure to 280 MPa*. (In press.)