Thermodynamic Properties of Water and Steam for Power Generation

In the early 1900s, the electric power generation industry was experiencing rapid growth and change. The steam engines used for power in the previous century had been displaced by turbines which generated electricity as they were rotated by pressurized steam generated in boilers. Turbines and boilers were operating at higher temperatures and pressures (and also in increasingly complex cycles, which required more sophisticated thermal design and analysis) in order to attain greater thermodynamic efficiency. They were also becoming larger as the demand for electricity skyrocketed.

A major source of growing pains for the industry was the lack of accurate and standardized values for the properties of water and steam. For the design of power plants and the boilers and turbines within them, it is necessary to have accurate values of thermodynamic quantities such as the vapor pressure (pressure at which water boils at a given temperature) and the enthalpy of vaporization or latent heat (amount of heat required to generate steam from liquid water). More important, the evaluation of the performance of purchased equipment depends on the calculation of these properties. The efficiency of a turbine is measured as the fraction of the energy available in the steam that is converted to electricity, but that available energy is calculated to be a different number depending on the values used for the thermodynamic properties. A turbine might appear to be 28 % efficient with one set of properties and only 27 % efficient with another set; because of the large flows involved, these small differences could mean large sums of money. It therefore became imperative to settle on internationally standardized values for the properties of water and steam, so that all parties in the industry could have a "level playing field" on which to compare bids and equipment performance. The paper *Calorimetric Determination of the Thermodynamic Properties of Saturated Water in both the Liquid and Gaseous States from 100 to 374 °C* [1] describes the accurate measurements carried out at NBS that were essential in reaching agreement on the needed standards.

In the United States, this problem was first addressed in 1921 by a group of scientists and engineers brought together by the American Society of Mechanical Engineers (ASME). The 1921 meeting led to the formation of the ASME Research Committee on Thermal Properties of Steam. This committee, recognizing the need for reliable data, collected subscriptions from industry and disbursed the money to support experimental measurement of key properties of water and steam at Harvard, MIT, and the Bureau of Standards. Because the ASME committee was not as successful in their fundraising as they had hoped, all three institutions ended up subsidizing some of the research themselves in recognition of its importance.

The need for standard, reliable data was also recognized in other countries (notably England, Germany, and Czechoslovakia), and research efforts were coordinated internationally. In the late 1920s and early 1930s, three international conferences were held with the purpose of agreeing on standardized values for the properties of water and steam. This culminated in 1934 with the adoption of a standard set of tables, covering the range of temperatures and pressures of interest to the power industry at that time. These tables gave the vapor pressure as a function of temperature, values of the volume and enthalpy for the equilibrium vapor and liquid phases along the vapor-pressure curve, and volumes and enthalpies at points on a coarse grid of temperatures and pressures. Each value had an uncertainty estimate assigned to it. The data those tables were based on also became the basis for a book of "Steam Tables" produced by J. H. Keenan and F. G. Keyes [2]; the Keenan and Keyes tables were the *de facto* standard for the design and evaluation of steam power generation equipment worldwide for the next 30 years.

The most important data behind these new steam tables came from the laboratory of Nathan S. Osborne at the National Bureau of Standards. Through most of the 1920s and 1930s, Osborne and his coworkers painstakingly built equipment and conducted measurements. The ASME had originally hoped for data within three years of the project's 1921 start, but fortunately they were patient (and grateful to the NBS for subsidizing the work) and continued to support the project through years of pioneering, but often frustrating, apparatus development. Finally, beginning in the late 1920s, their patience was rewarded as data of unparalleled quality began coming from Osborne's laboratory.

The primary experimental technique was calorimetry, in which a measured amount of heat is added to a fluid under controlled conditions. Osborne and coworkers had previously performed calorimetric measurements on ammonia. For measurements on water, several new calorimeters were developed. One of these, constructed from copper and used for the region below 100 °C, has been preserved in the NIST museum; it is shown in Fig. 1.

The region of most industrial importance, however, was at much higher temperatures (and correspondingly higher pressures), well beyond what had been encountered in the ammonia work. Experiments at these conditions were also more difficult because water is very corrosive at high temperatures. We briefly describe the calorimeter that was built to overcome these difficulties and that was used to take the data reported in the Osborne, Stimson, and Ginnings paper [1].

The heart of the calorimeter was a heavy-walled 325 cm^3 vessel of chromium-nickel steel. The contents were not stirred to achieve thermal equilibrium; instead, heat was diffused by 30 internal silver fins. The vessel contained a heater and carried a miniature platinum resistance thermometer. The calorimeter was shielded from the environment by two concentric silver shields that were maintained at the calorimeter temperature at all times. The calorimeter had two valves. The valve at the top allowed a measurable amount of vapor to be extracted, and the bottom valve allowed extraction of a known amount of liquid water. The water simultaneously served as a pressure transfer medium to allow measurement of the saturation pressure. During extraction of either vapor or liquid, the remaining liquid would partially evaporate, and heat was supplied to the calorimeter in order to keep the temperature constant.

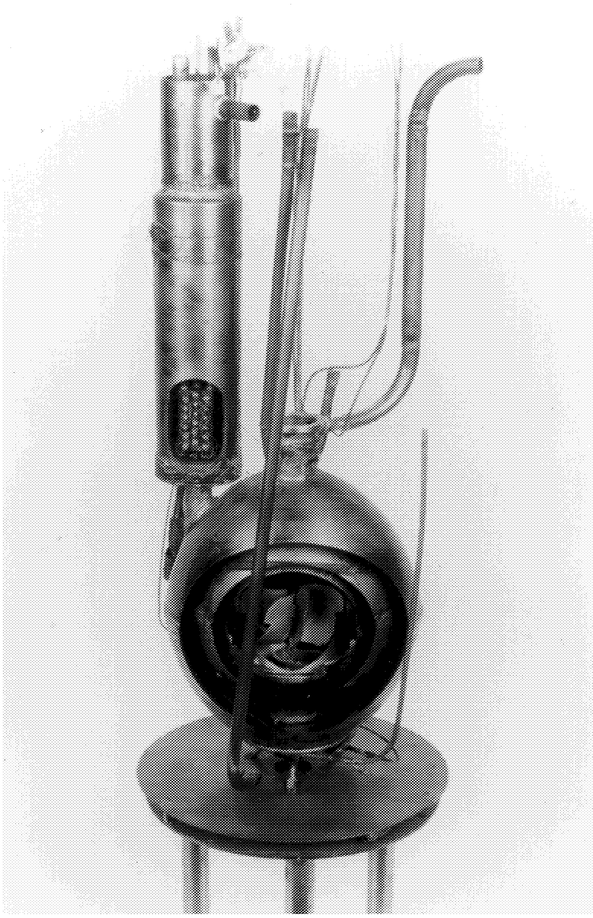

Fig. 1. Calorimeter used by Osborne et al. to study water properties at temperatures below 100 °C.

The calorimeter was operated in three different modes. The two isothermal modes in which either liquid or vapor was extracted provided information on the latent heat (enthalpy) of vaporization. The calorimeter could also be sealed and heated, giving information on the enthalpy and heat capacity of the liquid. By combining these measurements with the vapor pressure data and applying thermodynamic relationships, the specific volumes and enthalpies of the coexisting phases were calculated. The caloric properties, particularly the heat of vaporization, are the key data for the design and evaluation of steam power generation equipment because they determine the heat that must be added in the power cycle and the energy available in the steam to be converted to electricity in the turbines.

These investigations covered the range from water's freezing point (0 °C) to the end of the vapor pressure curve at the critical point (approximately 374 °C with a pressure near 22 MPa, over 200 times normal atmospheric pressure). They were reported in a series of papers [1, 3, 4, 5]. Reference [1] reports the heat of vaporization and enthalpy data at higher temperatures, which have proved to be the most industrially important of these data over the years.

The impact of this work was both immediate and enduring. As already mentioned, Osborne's data were incorporated (sometimes before they had even been published) into the steam tables desperately needed by industry at the time. Over 60 years later, much of the data, notably the heats of vaporization, are still the most accurate available. Many new steam tables have been produced through the years, including several generations of official replacements for the 1934 international standards. While these tables have taken advantage of some newer data, particularly at higher temperatures and pressures, the Osborne data have continued to be the backbone of all international water property standards. It is not an exaggeration to say that these data are fundamental to the design and operation of all steam power-generation facilities in the world today.

With the completion of Osborne's work in 1939, the most pressing industrial need for steam data had been met. However, water property standards continued to be improved as new data were taken and as better means for representing data were developed. These standards are important not only for the steam power industry, but also for other industries such as chemical processing. Accurate water property standards are also needed for scientific research, both because of the direct scientific importance of water and because water is commonly used as a calibration standard. The NBS (and later NIST) remained involved with these standards as an active participant in the international conferences that eventually evolved into the International Association for the Properties of Water and Steam (IAPWS). Howard J. White of NBS maintained the Secretariat of the Association for many years. When new international standards were adopted in the 1960s, Joseph Hilsenrath of NBS, an early leader in the application of computers to the analysis of scientific and engineering data, was involved in their development and dissemination. An improved representation of water and steam properties was adopted in 1984 under the leadership of NBS's Lester Haar, and tables from that formulation were published as the widely distributed *NBS/NRC Steam Tables* [6].

The 1990s saw a new generation of improved property formulations, taking advantage of both new data and improved computer optimization techniques. IAPWS coordinated the international development and testing efforts for these formulations. The latest state-of-the-art representation of water's thermodynamic properties was adopted by IAPWS in 1995 [7], and properties calculated from current IAPWS standards for general and scientific use are distributed in a computer program by the NIST Standard Reference Data program [8]. IAPWS also maintains a separate "industrial" standard specifically for the steam power industry [9]; this standard sacrifices some accuracy in order to meet the special requirements (computational speed and less frequent revision) of that industry. NIST, through the involvement of its personnel in the ASME subcommittee which is the U.S National Committee for IAPWS, has done much of the work in disseminating the new industrial standard in the United States [10]. All of these standards, from the 1930s to the present, have been anchored by the data of Nathan Osborne and his coworkers.

Nathan S. Osborne graduated from the Michigan College of Mines (now Michigan Technological University) in 1899. He was one of the earliest employees of the National Bureau of Standards, beginning his career there in 1903. Except for a period of two years, when he returned to Michigan to teach at his *alma mater,* he remained at the NBS until his retirement in 1939. During this time, he rose from the humble status of Laboratory Assistant to the prestigious rank of Principal Physicist. Prior to his work on water and steam, Osborne was part of an effort, funded by special Congressional appropriation at the behest of the refrigeration industry, to measure properties of interest in refrigeration. The most significant result of this work was a set of "ammonia tables" [11] that served as a standard for many years. The latter half of his career was mostly occupied by the work on water and steam; recognition for this work included honorary doctorates from his alma mater and from the Stevens Institute of Technology. Osborne died in 1943 at the age of 68.

Harold F. Stimson received a Ph.D. in physics from Clark University in 1915. His advisor, A. G. Webster, was one of the founders of the American Physical Society, and in the 1890s had been one of the first scientists to advocate the creation of a national standards laboratory. Stimson (known affectionately as "Stimmy" to his colleagues) was hired by NBS in 1916 and worked on the ammonia and water projects with Osborne. Most of his subsequent work was concerned with temperature measurement; he represented the United States in the deliberations that resulted in a new International Temperature Scale in 1948 and participated in its 1960 revision. He reluctantly retired in 1960 (later describing reaching the then-mandatory retirement age as being "fired"), but continued his interest in gas thermometry research at the NBS for many more years. He was known for giving haircuts to his colleagues; this, too, continued after retirement. He maintained a large vegetable garden, which he plowed using his station wagon, until he was well into his 80s. An active mountaineer, he also played the cello and is on record as a member of the Bureau of Standards orchestra in 1918. Stimson died in 1985 at the age of 94.

Defoe C. Ginnings began his career at NBS after receiving his Ph.D. in chemistry from the University of Illinois in 1929. He worked at NBS for the next 40 years, using calorimetry and other techniques to measure properties of fluids and solids, often at extreme conditions. The calorimeters he designed were at the leading edge of measurement technology. In addition to the work on water and steam, he took important calorimetric data on a number of hydrocarbons, which proved very valuable to the petroleum processing industries, and made high-temperature measurements of materials important in the defense and space programs. Ginnings was known for his personal modesty and for his dedication to pioneering and high-quality experimental work. He served as Chief of the Heat Measurements Section through most of the 1960s. He died in 1971 at the age of 65.

Prepared by Allan H. Harvey, with assistance from Johanna M. H. Levelt Sengers.

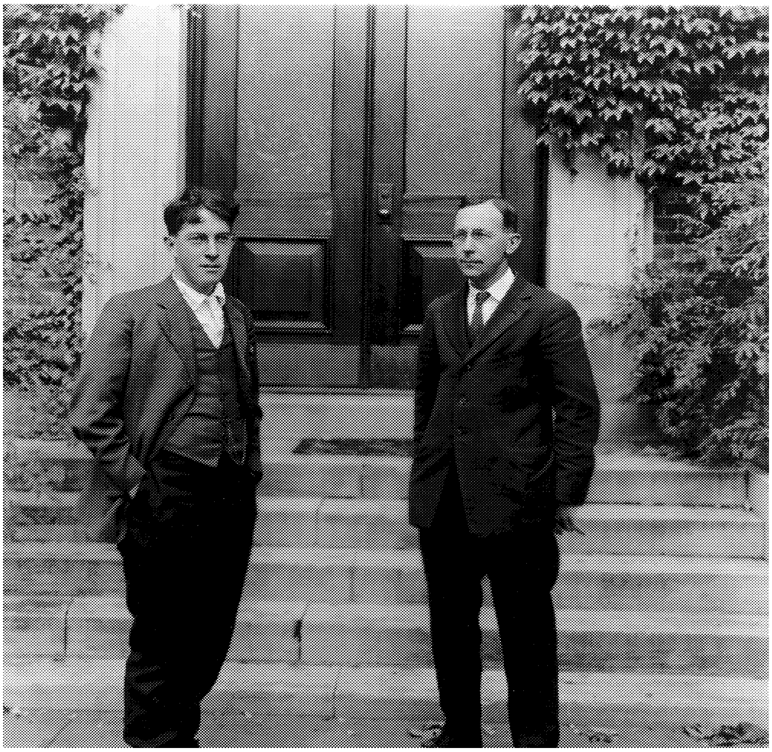

Fig. 2. Harold Stimson (left) and Nathan Osborne in 1923, roughly the time when they were beginning their experimental work on water.

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