

# *Selected Values of Chemical Thermodynamic Properties*

The theoretical framework of thermodynamics was well established by the time NBS was founded, and certain important applications, such as improving the efficiency of steam engines, had been demonstrated. However, the broad application of thermodynamics to the design and control of industrial processes had to await the accumulation and organization of a large amount of experimental data, as well as theoretical contributions from quantum mechanics and statistical mechanics. The appearance of *Selected Values of Chemical Thermodynamic Properties* [1] in 1952 marked a significant milestone in this process. This book represented the culmination of 20 years of work by Frederick D. Rossini and coworkers in evaluating and systematizing the data that had appeared in the world literature on thermochemistry. It tabulated accurate values of the thermodynamic properties of all inorganic and simple organic compounds that had been investigated in a format that allowed prediction of the outcome of many thousands of chemical reactions. Such calculations, which indicate whether a reaction will take place and, if so, the extent of reaction and amount of heat released or absorbed, are immensely important in research and engineering.

*Selected Values*, which was often referred to simply as “Circular 500” after its NBS publication designation, presented recommended values of the enthalpy (heat) of formation, Gibbs energy of formation, entropy, and heat capacity of individual chemical compounds in different physical states (solid, liquid, gas, or aqueous solution). All values were reduced to standard state conditions, defined by parameters such as temperature (25 °C) and pressure (one standard atmosphere). Since the laws of thermodynamics require that the change in properties such as energy and entropy cannot depend on the path followed in going from an initial to a final state—otherwise one could build a perpetual motion machine—the net change in thermodynamic properties in a chemical reaction can be calculated by addition and subtraction of the standard state values for the substances taking part in the reaction. This allows a simple prediction of whether the reaction will occur at all and, if it does, whether it will go to completion. In intermediate situations, one can obtain a quantitative measure of the extent of reaction from the equilibrium constant, which is easily calculated from the tabulated standard state



Fig. 1. Frederick D. Rossini.

values. Finally, most chemical changes involve either an absorption or release of heat, and the amount of this heat may be calculated from the same data. Thus *Selected Values* provided an extremely powerful tool for predicting the course of chemical reactions, a goal of chemists since the earliest days of the science.

The book itself was 822 pages in length and covered about 5000 chemical species. It was divided into two parts, the first dealing with the thermodynamic properties in a particular physical state and the second with the change in properties in transitions between states (such as melting and vaporization). All data were internally consistent, in the sense that all physical and thermodynamic relations existing between different properties for the same substance, or the same property for different substances, were satisfied by the tabulated values. The table layout in Circular 500 became the norm for thermodynamic tabulations throughout the world.

The preparation of *Selected Values of Chemical Thermodynamic Properties* required analyzing data from thousands of literature references appearing over the previous century, selecting the most reliable values in the judgment of the evaluators, and then optimizing this massive database to derive a “best set” of standard state values. Much of the data had to be corrected for changes in temperature scales, unit definitions, atomic weights, and other auxiliary data that can affect the thermodynamic properties. Shrewd detective work was sometimes required; for example, when a nineteenth-century chemist had failed to report the ambient temperature during a measurement, newspaper archives were consulted in order to estimate the laboratory temperature at the time. Since there was considerable redundancy in the data, related data sets were subjected to statistical analysis using weighting factors based on the evaluator’s appraisal of the accuracy of each measurement. In this way an internally consistent set of standard state values was derived that gave the best fit to the much larger database of experimental measurements. It was a remarkable achievement that Rossini and his group did this before the advent of computers and before the term “database” was even coined. They anticipated by many years the process of obtaining the best fit for a large set of data of varying accuracy—a procedure which is now commonplace in all scientific fields.

Subsets of these data had been released in loose-leaf form to universities, industrial users, and others in the 1947-1950 period. The complete tables received wide distribution as soon as they appeared in 1952 and went out of print six years later. Demand continued, and NBS reprinted the book in 1961. *Selected Values* became a standard fixture in physical chemistry laboratories. A generation of chemistry students used the book to analyze their laboratory data, and researchers in many fields used it to plan their experiments. Chemical engineers used it in various stages of process design. The late Henry Eyring, one of the major figures of twentieth century chemistry, once asserted that Circular 500 saved U.S. industry enough money to pay the entire cost of NBS since its founding. Unfortunately, it was difficult to document that claim in a way that would help NBS budget requests!

One of the early applications of *Selected Values* was in the U. S. rocket program, which went into full gear shortly after its publication. Chemical thermodynamics was the key factor in boosting the performance of rocket engines, and there was a major effort to find new fuels and oxidizers as space competition with the Soviet Union intensified. Many chemical reactions involving exotic compounds were explored in the process of searching for ways to increase rocket thrust. The data in *Selected Values* were used to screen prospective

reactions and identify those that were promising enough to warrant experimental investigation. A large DOD (and later NASA) program was started in the mid-1950s to extend the thermodynamic tables to the very high temperatures involved in rocket engines (as noted, the data in *Selected Values* are at room temperature). This spawned the *JANAF* (Joint Army-Navy-Air Force) *Thermochemical Tables* [2], a publication project in which many NBS staff members took part. The *JANAF Tables*, which are now in their fourth edition [3], have had a major impact in combustion research and many other areas of science and engineering; they have consistently been among the best sellers of the NIST Standard Reference Data program.

Rossini left NBS shortly before the publication of Circular 500 to become Chairman of the Chemistry Department at Carnegie Institute of Technology, but the work was carried on by two of the other authors, Donald Wagman and William Evans. A full update had been planned for the early 1960s, but the task proved to be far greater than expected. An explosion of the literature reporting new thermodynamic data took place as a result of greater government funding, an increase in the number of doctoral students, and, in particular, the introduction of automated instrumentation for calorimetric measurements. When the Standard Reference Data program was established at NBS in the mid-1960s, the thermodynamic tables project was designated the Chemical Thermodynamics Data Center and became a cornerstone of the new program. Partial updates to Circular 500 were issued between 1965 and 1981 in the *NBS Technical Note 270* series [4] as work was completed on specific parts of the periodic table. Digital computers became available during this period, which greatly expedited the process of fitting the reaction data to obtain the best set of standard state properties, but considerable human effort was still required to assess the accuracy of the reported measurements. A complete revision of Circular 500, entitled *The NBS Tables of Chemical Thermodynamic Properties* [5], was finally published in 1982 as a supplement to the *Journal of Physical and Chemical Reference Data*. This book has become a fixture in chemistry libraries and laboratories, and even today receives 150 or more citations each year. The data from *The NBS Tables* have now been converted to electronic form and included in the *NIST Chemistry WebBook*, which receives heavy use on the NIST Internet site [6].

Tabulation of thermodynamic data has continued as an active field at NBS/NIST and has been broadened from the primarily inorganic thrust of Circular 500 to more complex organic and biochemical substances. Extensive tables of heat capacity and entropy data on organic compounds have been published by

Eugene Domalski and colleagues. Robert Goldberg has led a program to evaluate data on the thermodynamics of enzyme-catalyzed reactions. Several data compilations on aqueous solutions have also appeared.

The data from Circular 500 and its updates and offspring have circulated widely beyond the original publications. It is fair to say that most tabulations of chemical thermodynamic properties in textbooks, popular handbooks, and online databases have been extracted from the NBS/NIST publications described here. More recently, these data have been incorporated in software packages for engineering design applications and environmental modeling.

Frederick D. Rossini came to NBS in 1928 after completing his Ph.D. at Berkeley, which was at that time the leading center for chemical thermodynamics research in the United States. He established an experimental program at NBS for measuring heats of combustion and other calorimetric properties with high accuracy. By drawing upon expertise in the Electricity and Heat Divisions of NBS, he advanced the state of the art in this type of measurement. His careful attention to the purification of his samples was another factor in achieving a new level of accuracy. Many of his measurements of the heat of formation of basic chemical compounds are still the best available. This high accuracy in calorimetric measurements provided new insights into the structure of organic compounds, for example by giving precise values for the very small energy differences between different geometric configurations of a complex molecule. Ernest Eliel, a distinguished organic chemist who used Rossini's data in studying the conformations of cyclohexane, likened this feat to measuring the mass of a boat captain by first weighing the boat with the captain aboard, then weighing it without the captain, and taking the difference [7].

In addition to his contributions to basic chemistry, Rossini had a keen interest in applying thermodynamics to industrial processes. In 1934 he became director of a project on thermodynamic properties of hydrocarbons, conducted at NBS under sponsorship of the American Petroleum Institute (API). The measurements on energy changes in isomerization of hydrocarbons carried out under this project laid the foundation for improving petroleum refining methods to give gasoline of higher quality. He initiated a program to prepare very pure samples of the pertinent hydrocarbons, which were widely distributed and used in other laboratories for a variety of physical measurements. These were, in effect, Standard Reference Materials, although there was no formal SRM program at that time. During World War II this work on hydrocarbons played a critical role in the development of high octane aviation fuels.

In parallel with his experimental research programs, he developed an early interest in organizing and systematizing thermodynamic data. In 1936 he published *The Thermochemistry of the Chemical Substances* [8], co-authored by F. R. Bichowsky, a book which was a precursor to Circular 500. The research program on hydrocarbons led to the establishment in 1942 of API Project 44, under which data sheets were prepared on the physical and thermodynamic (and later spectral) properties of hundreds on hydrocarbons and related compounds. These data were published in 1947 as NBS Circular 461, *Selected Values of Properties of Hydrocarbons and Related Compounds* [9], which became a basic source of design data for the oil industry.

After leaving NBS in 1950, Rossini served as Chairman of the Chemistry Department at Carnegie Institute of Technology until 1960. While there he continued to oversee the API tables project, which he had brought from NBS. This project evolved into the Thermodynamics Research Center (TRC), under the direction of Bruno Zwolinski, and later moved to Texas A&M University. TRC continued to provide data to the chemical and oil industries and became one of the affiliated data centers of the NBS Standard Reference Data program. In an interesting twist, TRC relocated from Texas A&M to the NIST Boulder Laboratories in 2000, thus coming full circle from its origin at NBS almost 60 years before as API Project 44.

Rossini himself moved from Carnegie to Notre Dame in 1960 as Dean of Science and later Vice President for Research. After his retirement from Notre Dame in 1971, he was given a part-time appointment at Rice University, where he returned to experimental measurements of thermodynamic properties. He later retired to Florida and died in 1990 at the age of 91.

Rossini's honors included the National Medal of Science (awarded in 1977), membership in the National Academy of Science, the Priestly Medal (highest award of the American Chemical Society), Department of Commerce Gold Medal, and countless others. He chaired the Commission on Thermodynamics of the International Union of Pure and Applied Chemistry (IUPAC) for 15 years; this service was recognized by the establishment of the Rossini Lectureship, now awarded every 2 years to an outstanding thermodynamicist. In the 1960s he was the prime mover in founding CODATA, the Committee on Data for Science and Technology of the International Council of Scientific Unions, and served as its first President from 1966 to 1970. CODATA has proved to be a valuable forum for the NBS/NIST Standard Reference Data program; many cooperative projects have been

organized under its umbrella, and two SRD Directors, David Lide and John Rumble, have followed Rossini as CODATA presidents.

Don Wagman and Bill Evans maintained the high quality of the NBS work on thermodynamic tables for another 30 years after Rossini left, culminating in the publication of the previously mentioned *NBS Tables of Chemical Thermodynamic Properties* [5]. Under the auspices of CODATA they established a fruitful collaboration with thermodynamicists in the Soviet Union. This project on Key Values for Thermodynamics [10], which included contributions from several other countries as well, led to agreement on an internationally accepted set of values for the properties of certain key compounds that play a ubiquitous role in thermodynamic calculations. In addition to the importance of the standardization effort, the project promoted significant human contacts between scientists during some of the most difficult years of the cold war.

The appearance of *Selected Values of Chemical Thermodynamic Properties* established NBS as the world authority on thermodynamic properties of chemical substances. This publication and its successors have had a broad impact on research, education, and industry. It ushered in a period of 50 years of NBS leadership in providing reliable thermodynamic data to the scientific and engineering communities.

*Prepared by David R. Lide.*

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