Notes from the Oesper Collections

The Parr Calorimeter

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The use of either a water or an ice calorimeter to measure the heats of chemical reactions and phase changes is a laboratory technique that dates back to the late 18th century and the work of Joseph Black and Adair Crawford in Scotland and of Antoine Lavoisier and Pierre Laplace in France. Among its most notable practitioners in the 19th century were the Russian chemist, Germain Hess, the French team of Pierre Favre and Johann Silbermann, and the Irish chemist, Thomas Andrews, in the first half of the century, followed by the Danish chemist, Julius Thomsen, and the French chemist, Marcellin Berthelot, in the second half (1).

Inspection of surviving examples of 20th-century American-made calorimeters quickly reveals that the vast majority correspond to so-called "Parr Calorimeters" and were manufactured by The Standard Calorimeter Company of East Moline, Illinois (figure 1), where the "Parr" in question refers to the American chemist, Samuel Wilson Parr (figure 2), who was both the company's founder and its first president.

Parr was born on 21 January 1857 in Granville, Illinois and educated at the University of Illinois, from which he received a B.S. degree in 1884. This was followed by a year of graduate work at Cornell University and an M.S. degree in 1885. That same year Parr was appointed as Professor of General Science at Illinois College in Jacksonville, Illinois, followed six years later by his appointment in 1891 as Professor of Applied Chemistry at the University of Illinois at Urbana-Champaign, where he would remain until his retirement in 1926 (2).

Figure 1. Label from an early Parr calorimeter, c. 1912 (Jensen-Thomas Apparatus Collection).

Figure 2. Samuel Wilson Parr (1857-1931).

As implied by his title, Parr's primary teaching responsibility at Urbana involved the training of industrial chemists and he is widely considered to be the founder of the University of Illinois Chemical Engineering Program, which was first formally listed as such in the university catalog for the 1901-1902 academic year. His research speciality was the evaluation of fuels and especially the scientific development and exploitation of the coal fields of Southern Illinois – a topic on which he published numerous books and monographs (3).

Whereas many of the chemists listed earlier were attracted to calorimetry for its theoretical importance as a possible means for quantifying the concept of chemical affinity, Parr's interest in the field was purely

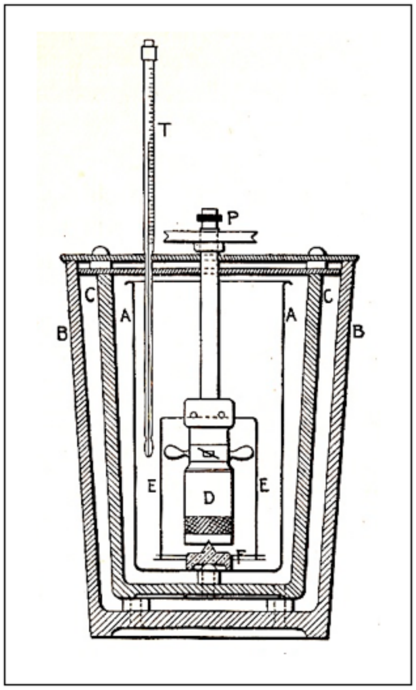

Figure 3. Diagram of the interior of Parr's original peroxide calorimeter, c. 1900.

practical and centered on its use in quantifying the heating efficiency of coal and other fuels and, more particularly, on his proposal in 1899 of a new method of measuring coal's heat of combustion using a bomb calorimeter in which, rather than directly oxidizing the coal to carbon dioxide in an atmosphere of pure dioxygen gas, it was instead indirectly oxidized by mixing the powdered coal with solid sodium peroxide and initiating the reaction by means of a potassium chlorate accelerant and an electrical ignition source (4, 5). Thus rather than:

$$C(s) + O_2(g) \rightarrow CO_2(g) + \text{heat} \qquad [1]$$

the primary reaction presumably became:

$$C(s) + 2Na_2(O_2)(s) \rightarrow Na_2(CO_3)(s) + Na_2O(s) + \text{heat} \qquad [2]$$

in which the absence of both reactant and product gases made the method both easier to perform in the laboratory and less susceptible to potential explosions.

In order to provide a commercial source of calorimeters especially tailored for use with his new peroxide method, Parr founded the Standard Calorimeter Company in Champaign, Illinois, in 1899, eventually moving it to East Moline, Illinois, in 1911. The outer double insulating walls (BB and CC of figure 3) of his early calorimeters were originally made of molded straw and glue (6). Inside these was a nickel-plated water chamber (AA) to absorb the heat from the combustion reaction and the steel combustion bomb itself with attached stirring paddles (D). This was rotated on pivot F using an external motor and pulley system (P). The Jensen-Thomas Apparatus Collection contains two early Parr calorimeters of the straw-glue variety (figures 1 and 4), both of which probably date from around 1912 and which list only the 1901 and 1902 patent dates on the attached identification plates.

Unfortunately reaction 2 ultimately proved to be more complex and less reproducible than originally thought and in order to improve calorimetric accuracy it became necessary to once again revert to reaction 1. As a consequence, by the 1920s Parr was also manufacturing his version of the traditional Berthelot high-pressure (25-30 atm) oxygen bomb calorimeter, which had been first introduced in 1881. Parr continuously improved the design of his calorimeters by incorporating new materials and conveniences as they became available. As shown in figures 5 and 6, by the 1930s the straw and glue insulating containers had been replaced by black Bakelite and the calorimeter came with the stirring motor permanently attached. Since the combustion bomb required for the solid-gas

Figure 4. An example of a later variant of the Parr peroxide calorimeter, c. 1912 (Jensen-Thomas Apparatus Collection). The water chamber is to the left and the combustion bomb and pivot support are to the right. The pulley attachment for the top of the combustion bomb and the detachable stirring wings are missing.

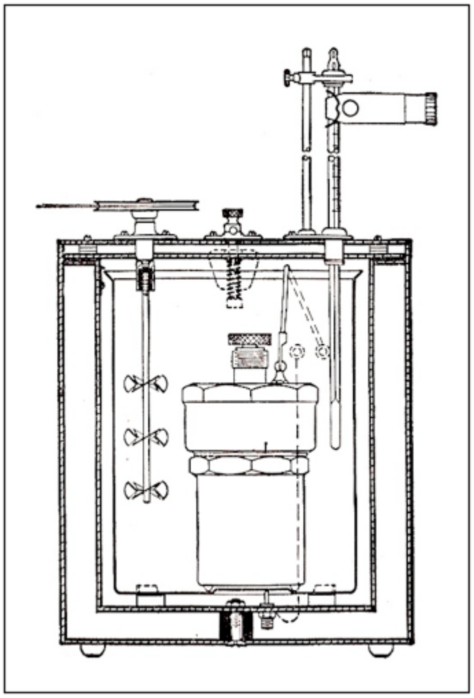

Figure 5. Diagram of the interior of an early Parr oxygen bomb calorimeter, circa 1932.

Figure 6. An example of a Parr oxygen bomb calorimeter, c. 1940 (Jensen-Thomas Apparatus Collection).

coal-dioxygen reaction was much larger and heavier than that required for the solid-solid coal-peroxide reaction, the stirring mechanism was separated from the bomb, which now remained stationary. In addition, a small sliding magnifying device was attached to the thermometer to facilitate accurate reading of its scale. A typical example of this design from the Jensen-Thomas Apparatus Collection is shown in figure 6 and probably dates from around 1940.

By the 1930s the company was also offering a larger variant of the oxygen bomb calorimeter known as an adiabatic calorimeter in which the traditional cylindrical design had been replaced by a cubic shape and a permanently attached lid that could be conveniently rotated out of the way when opened (figures 7 and 8). Rather than an insulating air gap between the outer and inner walls, the so-called adiabatic calorimeter used a wall of circulating water. As a result it had two thermometers, one as usual for the nickel-plated water chamber surrounding the combustion

Figure 7. An example of a Parr adiabatic oxygen bomb calorimeter, c. 1956(Jensen-Thomas Apparatus Collection).

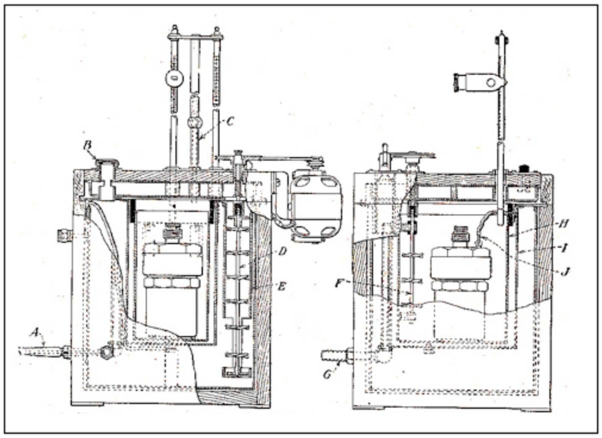

Figure 8. Diagram of the interior of a Parr adiabatic oxygen bomb calorimeter, c. 1932.

bomb and one to monitor the insulating jacket of circulating water. Likewise, it also had two stirring systems for the same purpose. When closed, the calorimeter lid could be locked down to produce a water-tight seal, as the stirring system for the water jacket served to pump water through the lid as well. Also required were external inlets and outlets (A and G of figure 8) for the entrance and exit of the water in the circulating jacket.

A typical example of a Parr adiabatic calorimeter from the Jensen-Thomas Apparatus Collection is shown in figure 7 and probably dates from around 1956. It also includes an external push button ignition system (small box to the far left) and an alternative combustion chamber for sulfur determinations (the container in front of the ignition box).

As early as 1915 the corrosion of his steel calorimetric bombs by the acidic oxides of nitrogen and sulfur produced as a necessary by-product in the combustion of coal samples had induced Parr to search for a more corrosion-resistant alloy and had led to his development of *Illium* – a tungsten alloy named after the University of Illinois that contained eight additional components (Cu, Mn, Si, Ni, Al, Fe, Cr, and Mn) and which was not only acid resistant but could be used as a substitute for such noble metals as platinum and palladium in many other laboratory devices (7). This sojourn into the field of metallurgy later led to work on the causes of the embrittlement of boiler plate and to effective remedies for its prevention which eventually produced vast savings for a wide range of industries (8).

In later years Parr was widely acknowledged as a world expert on fuel and coal chemistry and was the recipient of many awards and honors, including the Chandler Medal in 1926 and service as President of the American Chemical Society in 1928 (9). After Parr's death in 1931, his sons continued to run the Standard Calorimeter Company, which by then had branched out into other areas of chemical instrumentation. In recognition of this fact, the company was renamed the Parr Instrument Company in 1933.

References and Notes

1. L. Médard, H. Tachoire, *Histoire de la thermochimie*, Université de Provence: Provence, 1994.

2. J. M. Smith, "Samuel Wilson Parr" in W. D. Miles, Ed., *American Chemists and Chemical Engineers*, ACS Books: Washington, DC, 1976, pp. 381-382 and other biographical sources cited therein.

3. The vast majority of these were booklets of 100 pages or less published by the University of Illinois or by the Illinois State Geological Survey. Parr's only commercial book was the highly successful textbook, S. W. Parr, *The Analysis of Fuel, Gas, Water, and Lubricants*, McGraw-Hill: New York, NY, 1922, 4th ed., 1932. The first two editions, dating back to 1911 and 1916, were apparently self-published for classroom use.

4. S. W. Parr, "A New Coal Calorimeter," *J. Am. Chem. Soc.*, **1900**, *22*, 646-652.

5. A. H. White, *Technical Gas and Fuel Analysis*, McGraw-Hill: New York, NY, 1913, Chapter 17.

6. E. Child, *The Tools of the Chemist: Their Ancestry and American Evolution*, Reinhold: New York, NY, 1940, pp. 144-146.

7. S. W. Parr, "An Acid-Resisting Alloy to Replace Platinum in the Construction of a Bomb Calorimeter," *J. Am. Chem. Soc.*, **1915**, *37*, 2515-2522.

8. S. W. Parr, F. G. Stubb, "The Embrittlement of Boiler Plate," *Ind. Eng. Chem.*, **1927,** *19,* 620-622.

9. C. A. Browne, M. E. Weeks, *A History of the American Chemical Society: Seventy-Five Eventful Years*, ACS: Washington, DC, 1952, pp. 141, 485.