

Oesper Museum Booklets on
the History of Chemical Apparatus

No. 2

MELTING POINT APPARATUS

William B. Jensen
University of Cincinnati

Photography by Jay Yocis



Oesper Collections
University of Cincinnati
2014

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SERIES INTRODUCTION

Like most museums, only about 25% of the holdings of the Oesper Collections in the History of Chemistry are on public display at a given time. In order to make the remaining 75% available in some form, it was decided to initiate a series of short museum booklets, each dedicated to a particular instrument or laboratory technique of historical importance to the science of chemistry. Each booklet would include not only photographs of both displayed and stored museum artifacts related to the subject at hand, but also a short discussion of the history of the instrument or technique and of its impact on the development of chemistry as a whole. Several of these booklets are expansions of short articles which have previously appeared in either the bimonthly series *Museum Notes*, which is posted on the Oesper website, or the series *Ask the Historian*, which appeared in the *Journal of Chemical Education* between 2003 and 2012.

William B. Jensen
Cincinnati, OH
April 2014

MELTING POINT APPARATUS

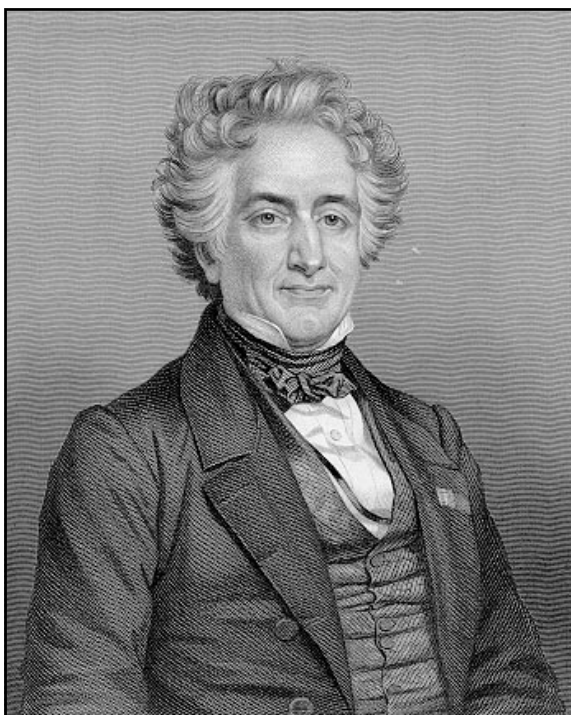


Figure 1. Michel Eugène Chevreul
(1786-1889)

The Origins of Melting Point Determinations

The use of melting points as useful physical constants for the characterization of chemical substances rests on a recognition that every pure solid substance has its own characteristic melting point and latent heat of fusion – concepts which, in turn, may be traced back to the late 18th century and the work of Joseph Black in Scotland, Johan Wilcke in Sweden, and Antoine Lavoisier in France.¹ One of the earliest sources to advocate the explicit use of these constants in the newly emerging field of organic chemistry was the 1824 monograph, *Considerations générales*

sur l'analyse organique, by the French chemist, Michel Eugène Chevreul (figure 1).^{2,3} In this often overlooked classic, which summarized many of the laboratory techniques introduced by Chevreul in his earlier, well-known, studies of the chemistry of organic fats, oils and soaps,⁴ he recommended not only the measurement of melting points as a valuable technique for the characterization of organic species, but also the measurement of boiling points and crystal form, as well as use of both elemental combustion analysis and the systematic study of chemical reactions. Regrettably, in keeping with the book's title, Chevreul did not include the details of either the laboratory apparatus or the procedures he used to make these measurements.

Writing in 1963, and unaware of Chevreul's earlier work, the Belgian physical chemist, Jean Timmermans, in his classic monograph, *On the Concept of Species in Chemistry*, mistakenly attributed the first use of melting points as a means

OESPER MUSEUM BOOKLETS

of characterizing organic compounds to the famous 1832 paper by the German chemists, Justus von Liebig (figure 2) and Friedrich Wöhler (figure 3), on the chemistry of the benzoyl radical, in which they reported the melting point of benzamide.^{5, 6} This was followed a year later by a paper in which Liebig also reported the boiling point of liquid acetal.⁷

Like Chevreul before them, Liebig and Wöhler failed to report the details of their melting point apparatus. In

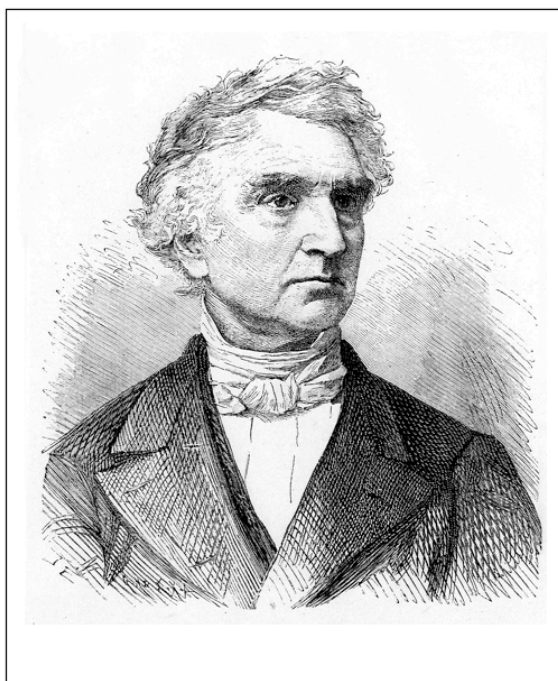


Figure 2. Justus von Liebig
(1803-1873)

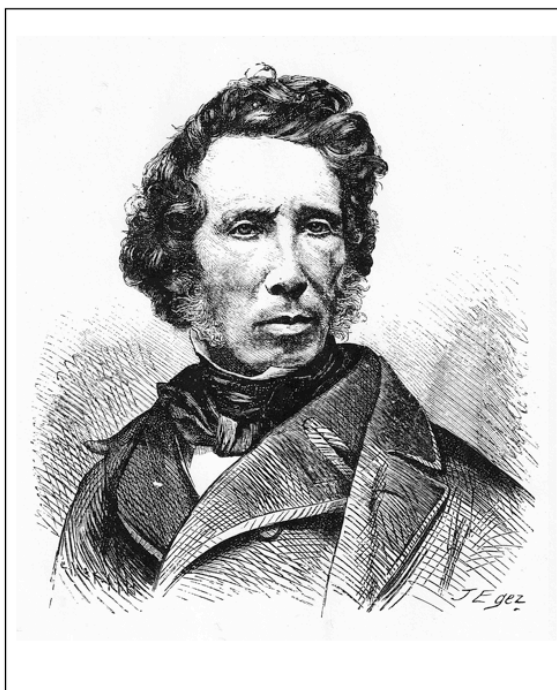


Figure 3. Friedrich Wöhler
(1800-1882)

addition, they also failed to record their motivation for measuring the melting point of benzamide in the first place, since similar measurements were not reported for the various other benzoyl derivatives described in their paper. One may speculate, however, that their interest in the technique had its origins in their first encounter with one another eight years earlier in 1824. That year Liebig, working in Gay-Lussac's laboratory in Paris, had reported his analysis of the compound silver fulminate, only to discover that it was identical to

MELTING POINT APPARATUS

the analysis that Wöhler had reported for the compound silver cyanate later that year while working in the laboratory of Berzelius in Stockholm, even though the two compounds had radically different properties (most notably that silver fulminate was explosive whereas silver cyanate was not).⁸ Since these results violated the then accepted postulate that all differences in properties were ultimately traceable to differences in composition, Liebig initially claimed that Wöhler's analysis was faulty, though this was soon shown to be incorrect.

This encounter not only led to a life-long friendship between Liebig and Wöhler but, ultimately, to the formulation of the concept of isomerism by Berzelius in 1831.⁹ It is probably not a coincidence that the practice of supplementing compositional analytical data for organic compounds with melting and/or boiling point data became increasingly common after the explicit recognition of the concept of isomerism, since this data, when coupled with elemental analysis, served as a convenient way of unambiguously detecting yet further examples of this new phenomenon.

From the 1830s on, the practice of reporting not only the analytical composition, but also the melting and/or boiling points, of newly isolated organic compounds seems to have rapidly spread, not only in the pages of Liebig's *Annalen*, but in other chemical journals as well, so that, by the last decade of the 19th century, melting-point determinations had become a standard introductory topic in virtually all organic laboratory manuals.¹⁰

Functional Group Analysis

Whereas the use of melting points in the research literature was a matter of properly characterizing newly synthesized compounds, their use in the introductory organic laboratory, where students were merely replicating the synthesis of already established compounds, was more closely related to the issue of purity, since any contamination of the desired product by excess reactants and/or undesirable by-products would automatically result in a characteristic lowering of the melting point relative to the value reported in the literature for the pure product. In addi-

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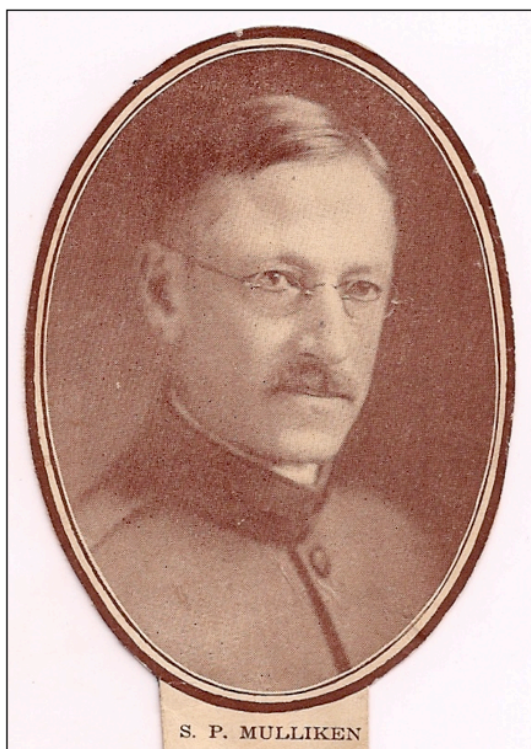


Figure 4. Samuel Parsons Mulliken (1864-1934), one of the founding fathers of functional group analysis.

tion, by the early decades of the 20th century, yet a third major use of melting points in organic chemistry would come into existence with the rise of systematic qualitative organic analysis.

By 1900 over fifty thousand organic compounds had been prepared and characterized and the number known today is well over a million. When properly classified in terms of their functional groups and relative positions within a given homologous series, this vast array of compounds formed an impressive interlocking system which greatly facilitated the identification and characterization of any newly discovered compounds. By the first decade of the 20th century, these consequences had resulted in the development of a systematic scheme for the rapid characterization of organic com-

pounds whereby the position of an unknown compound within this vast organizational array could be determined by means of a series of quick qualitative tests based on its solubility in various solvents, certain characteristic functional group reactions, the preparation of various solid derivatives and, most importantly from the standpoint of this booklet, via the determination of the melting points of these derivatives.

Largely the work of the American chemist, Samuel Parsons Mulliken (figure 4), whose massive four-volume reference work, *A Method for the Identification of Pure Organic Compounds*, was published between 1904 and 1922,¹¹ and the American chemist, Oliver Kamm, whose introductory laboratory manual, *Qualitative Organic Analysis*, first appeared in 1922,¹² systematic qualitative organic

MELTING POINT APPARATUS

analysis or functional group analysis, as it came to be known, would become a standard university course for the training of organic chemists by the late 1920s, and over the next few decades would spawn countless laboratory manuals and reference compilations of melting points.¹³ As such, it continued to be taught in American universities at least through the late 1970s, when it was gradually displaced by newer instrumental methods of analysis.

While of tremendous importance in the field of organic chemistry, the determination of melting points never attained a similar degree of importance in the field of inorganic chemistry for the simple reason that the vast majority of organic compounds contain discrete molecules, whereas most solid-state inorganic compounds are nonmolecular. As a consequence, the melting of an organic compound requires only the disruption of relatively weak intermolecular attractions, whereas the melting of an inorganic compound requires the disruption of far stronger intramolecular bonds. Thus, while most organic compounds that are solids at RTP have melting points lying between 30°C and 350°C, most solid-state inorganic compounds either have extremely high melting points, sometimes approaching several thousand degrees, or else thermally decompose before melting.

Simple Apparatus for Melting-Point Determinations

Though, starting in the 1870s, an increasing number of proposals for the rapid and accurate

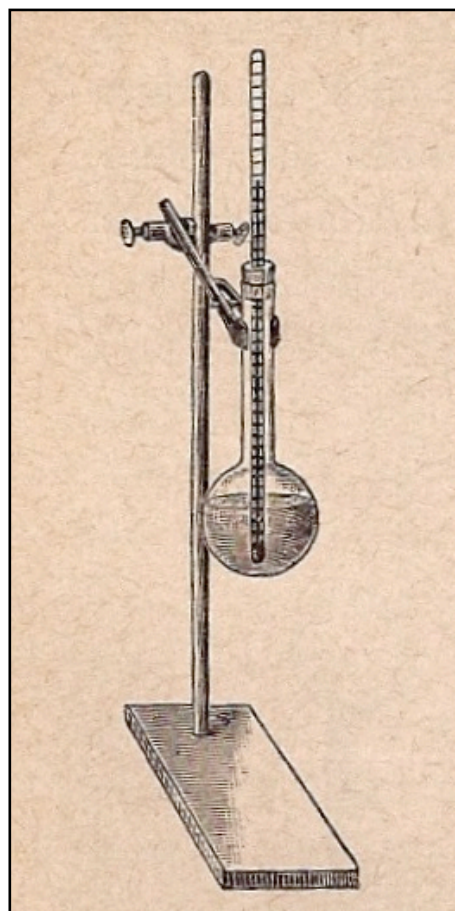


Figure 5. A simple melting-point apparatus as depicted in the 1901 edition of Ludwig Gattermann's *The Practical Methods of Organic Chemistry*, which first appeared in German in 1894.

OESPER MUSEUM BOOKLETS



Jensen-Thomas Apparatus Collection

Figure 6. A simple melting point apparatus (23" x 7" x 4") similar to that pictured in figure 5.

determination of melting points began appearing in the chemical literature,¹⁴ by the 1890s the dominant method (figures 5 and 6) involved attaching a melting point capillary, containing the compound in question, to the stem of a thermometer suspended in a long-necked, round-bottom flask containing a high-boiling point liquid bath. This was carefully heated using a Bunsen burner until sample melting was visually observed¹⁵ – a technique which was still being used when the present writer took introductory organic laboratory in the 1960s.

Since many organic compounds have melting points greater than 100° C, the liquid in the flask had to be something other than water. Though mineral oil could be used in a few cases, the most common choice was concentrated sulfuric acid, which could be heated to around 300°C before decomposition began and higher if mixed with salts such as sodium sulfate. Unfortunately, this would gradually attack the rubber band used to hold the capillary tube to the thermometer and required the use of caution when removing the thermometer and capillary after completing the measurement, not to mention the seriousness of any accident involving the breaking of the flask. In addition, corrosion of the rubber band gradually caused the sulfuric acid bath to

MELTING POINT APPARATUS

become dark brown and thus inhibited observation of the melting point.

To mitigate some of these problems, by 1900 laboratory supply catalogs were selling several elaborated versions of this flask, known respectively as Anschütz-Schultze and Roth flasks (figure 7), in which the capillary and thermometer were separated from direct contact with the sulfuric acid bath by means of a glass sleeve sealed into the neck of the flask. The

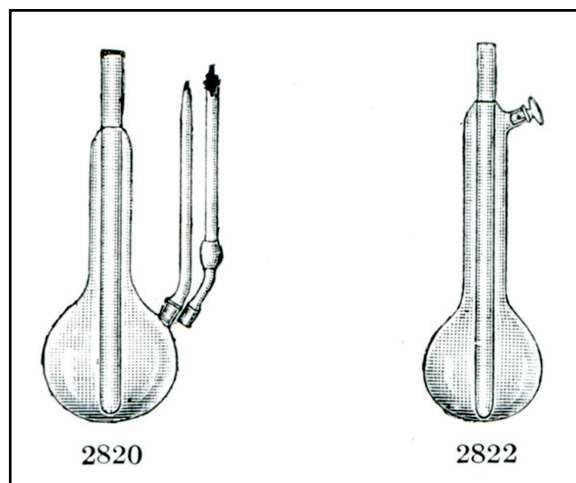


Figure 7. Special Anschütz-Schultz (left) and Roth (right) flasks for use in melting point determinations as depicted in the 1912 catalog for the E. H. Sargent Company of Chicago.

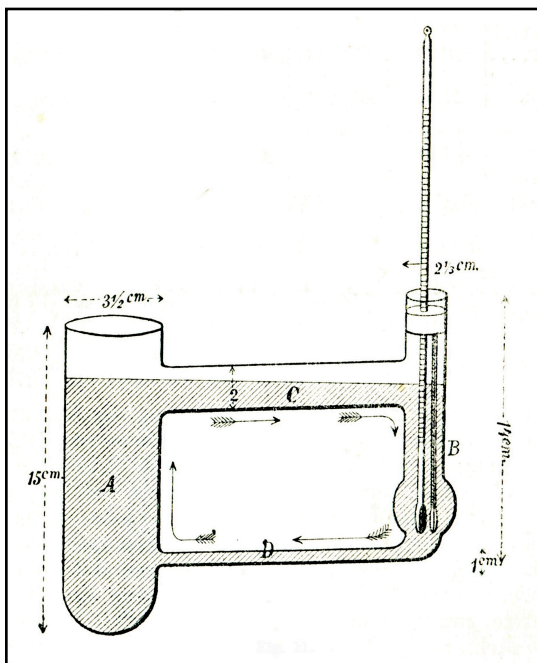


Figure 8. Olberg's 1886 convection tube for melting-point determinations. Heating tube A produced convection currents which supposedly eliminated localized hot spots in tube B.

latter also had a separate side-opening for the addition or removal of the sulfuric acid. In addition, by the 1960s several grades of silicone oil with high-boiling points were commercially available as potential replacements for the sulfuric acid. However, like the special flasks, such luxuries were relatively expensive and seldom made it into the typical undergraduate organic laboratory, which tended instead to rely on the simple arrangement shown in figures 5 and 6.

Convection Tubes

The corrosive properties of sulfuric acid



Figure 9. Johannes Thiele
(1865-1918)

configuration was replaced by a single large test tube having a side-loop fused to one wall (figure 10) so as to give it the overall appearance of a lower-case letter “b.”¹⁷ Rather than placing the Bunsen burner directly below the thermometer bulb, as in the flask arrangement, where it could give rise to localized hot spots, it was instead placed beneath the bend in the side loop where it could generate a convection current that would help to more evenly distribute the heat in the surrounding liquid.

were not the only problem with the conventional flask arrangement in figures 4 and 5; the development of localized hot spots due to poor circulation in the liquid bath was yet another. This led to the proposal of a number of devices which employed convection in order to eliminate transient thermal gradients. One of the earliest of these devices was proposed by the German chemist, Gustav Olberg, in 1886 (figure 8), but this appears to have never caught on.¹⁶ However, in 1907 the German chemist, Johannes Thiele (figure 9), proposed a simplified version of Olberg’s apparatus in which the double-tube

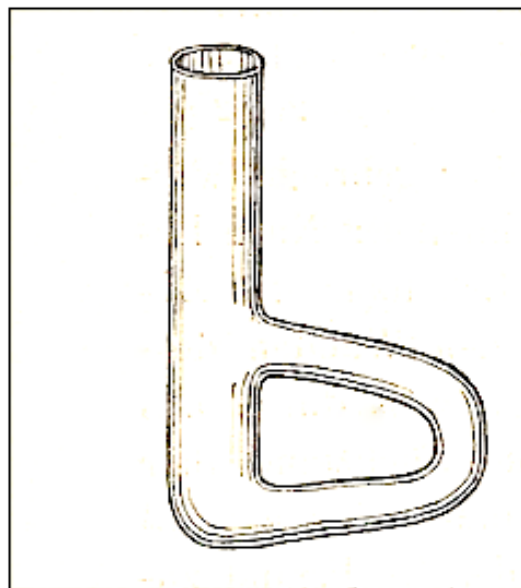


Figure 10. Thiele’s original melting point tube as depicted in his 1907 article in the *Berichte*.

MELTING POINT APPARATUS

Though first proposed in 1907, it was not until the 1920s that most laboratory supply catalogs began offering inexpensive “Thiele melting-point tubes,” which soon displaced the specialized Anschütz-Schultze and Roth flasks. Indeed, by then Thiele’s original tube had, in turn, been modified by the American chemist, L. M. Dennis, so as to improve circulation of the heated liquid by allowing the side-loop and the bottom of the test tube itself to sag downwards so as to create a more exaggerated and effective heating loop (figure 11).^{18, 19}

Electric Melting-Point Apparatus

The 1920s also saw the first attempts to introduce electrically heated melting-point devices, though they did not become common in laboratory supply catalogs until the 1930s. In most of these devices, both the capillary and thermometer bulb were inserted into holes drilled in a block of either copper or aluminum that was, in turn, electrically heated. This had the advantage that it eliminated the problems associated with working with corrosive liquid baths and uneven heat distributions. More elaborate versions even included a mag-



Jensen-Thomas Apparatus Collection

Figure 11. A typical setup (24” x 5.25” x 5.25”) for melting-point determinations using a Thiele-Dennis tube. Note the greater droop to the side loop in comparison with the original tube shown in figure 10.

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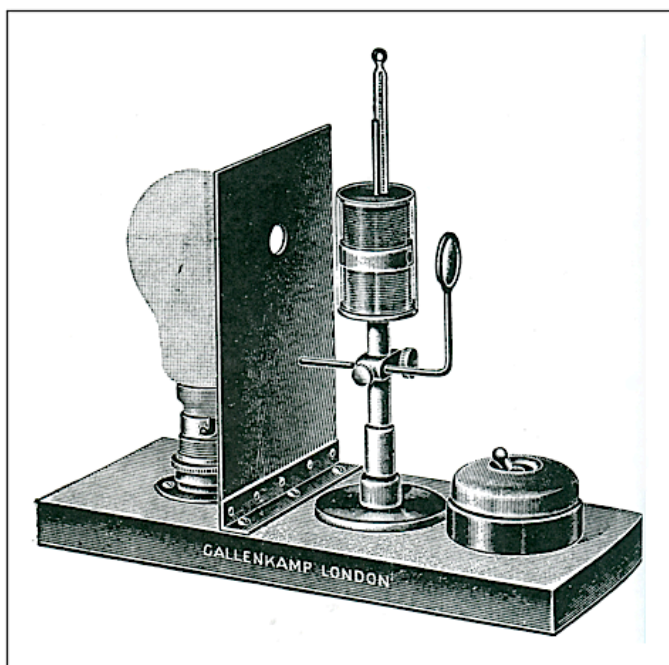


Figure 12. An electric melting-point apparatus designed by Frederick Mason, as depicted in the 1929 laboratory supply catalog of A. Gallenkamp & Co. of London. Its construction and operation are virtually self-evident from the engraving.

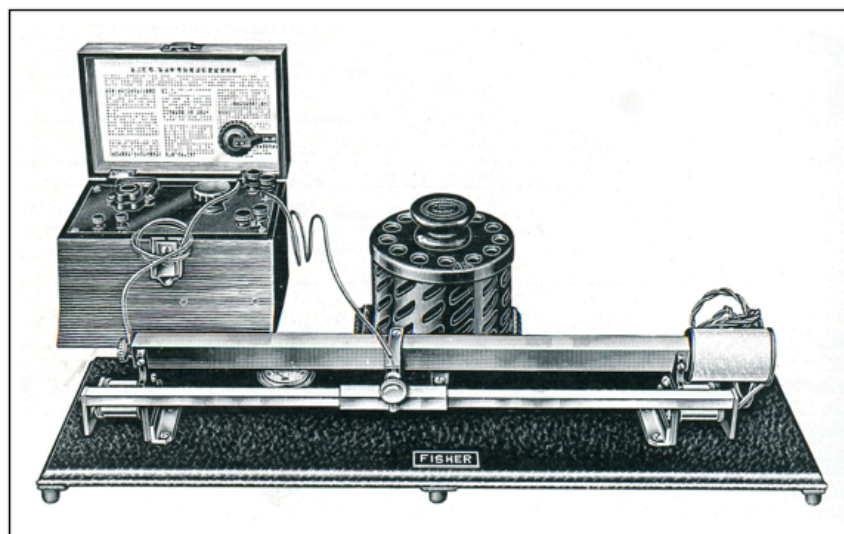


Figure 13. An electric melting-point apparatus designed by L. M. Dennis and R. S. Shelton¹⁹ of Cornell University as depicted in the 1934 catalog of the Fisher Scientific Co. of Pittsburgh. The rheostat controls an electric heater at one end of a copper bar. This produces a thermal gradient along the bar. The finely powdered sample is distributed along the length of the bar and the temperature of the position above which it melts is determined by means of a thermocouple and the potentiometer shown on the left.

MELTING POINT APPARATUS

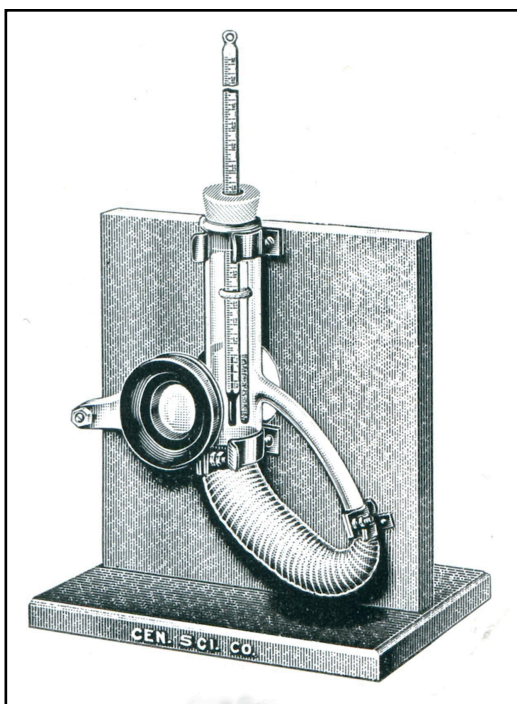


Figure 14 (left). An electric melting-point apparatus designed by J. D. Burchard of the State Teachers College of San Diego,²⁰ as depicted in the 1936 catalog for the Central Scientific Company (CENCO) of Chicago. It consists of a standard Thiele-Dennis melting point tube mounted on asbestos board, the lower end of which has been wrapped in brass-band heating coils. A magnifying lens has been added for easy viewing of the capillary. To operate, the heating unit must be connected to a standard rheostat and power source.

nifying lens and backlighting to aid in viewing the capillary. Once again these devices were relatively expensive and thus appear to have had little impact on the undergraduate organic laboratory. Indeed, very few of these early models seem to have survived and made their way into museums and, in lieu of this, we have instead included etchings of several examples taken from period catalogs (figures 12-14).

The Mel-Temp Apparatus

By the mid-1950s the dependability and ease of use of electric melting-point de-

MEL-TEMP . . . an integrated capillary melting point apparatus reaches 400°C effortlessly in only 6 minutes.

MEL-TEMP is useful to 500°C and renders obsolete the usual combination of hazardous fluid-type bath plus sluggish high temperature block. Heater is controlled by variable transformer and excellent viewing is provided by built-in light and lens. Attractive gray hammertone base occupies only 4" x 5".

**Accurate
Fast
Safe
Convenient**

Write for Bulletin 60.

LABORATORY DEVICES
P. O. BOX 68, CAMBRIDGE 39, MASS.

Figure 15. An ad for the “Mel-Temp” which appeared in the *Journal of Chemical Education* in 1957.

OESPER MUSEUM BOOKLETS

VICES had increased to the point that they finally began to make significant inroads into the introductory organic laboratory course. Though still relatively expensive, they were now efficient enough that several students could share the same instrument rather than each constructing their own individual setup. Among the most successful of these devices in the United States was the compact electric “Mel-Temp” (figure 16) produced by Laboratory Devices Inc. of Cambridge, Massachusetts, which began marketing to chemical educators in the late 1950s (figure 15) and which is still sold today in modified form.

The Fisher-Johns Apparatus

Not to be outdone by small independent instrument companies, several of the larger laboratory supply houses commissioned their own in-house electric melting-point devices for the undergraduate market in the mid 1950s and early 1960s. Among these was the Fisher Scientific Co. of Pittsburgh, which, by 1955, had repackaged and streamlined (figures 17-18) an earlier modular device (figure

Figure 16 (left). A circa 1960 “Mel-Temp” (22.25” x 5” x 4”) electric melting-point apparatus with capillary and thermometer.



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MELTING POINT APPARATUS

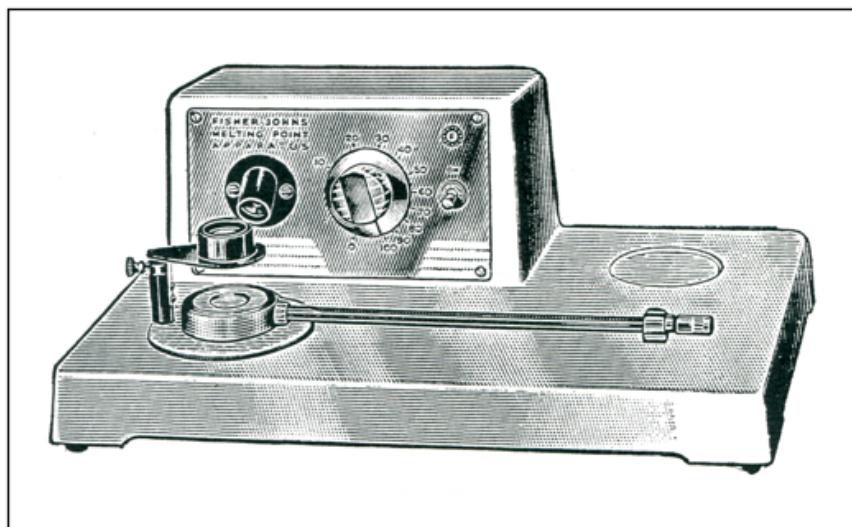


Figure 17. An etching of the refurbished Fisher-Johns horizontal melting-point apparatus as depicted in the 1967 catalog of the Fisher Scientific Co. of Pittsburgh.



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Figure 18. A surviving example of a circa 1960 horizontal (14" x 8.75" x 5.75") electric Fisher-Johns melting-point apparatus similar to that shown in figure 17.

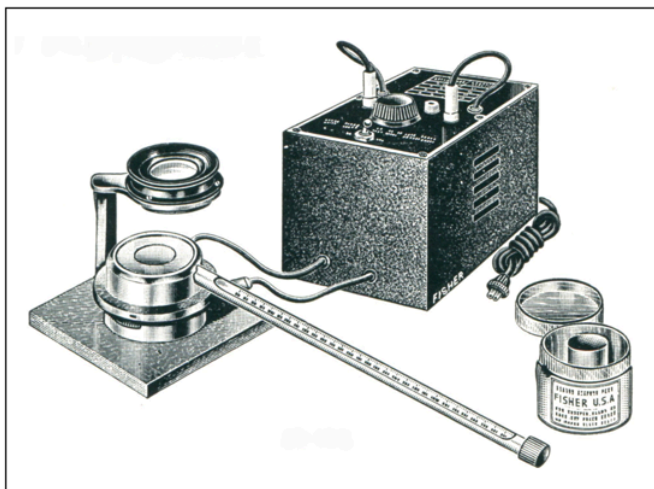


Figure 19. An earlier and more modular prototype of the Fisher-Johns horizontal electric melting-point apparatus as depicted in the 1949 catalog of the Fisher Scientific Co. of Pittsburgh.

19) designed by Dr. I. B. Johns of Iowa State College in the late 1940s. This was unique in not using the traditional vertical glass capillary-thermometer configuration. Rather the sample was instead placed on a circular glass cover-slip and positioned directly over the heating block, where it was illuminated from above and observed using a magnifying lens. Likewise, the temperature was monitored using a horizontally, rather than a vertically, positioned thermometer.

The Thomas-Hoover Apparatus

A competing device, known as the Thomas-Hoover “Uni-Melt” capillary melting-point



Jensen-Thomas Apparatus Collection

Figure 20. A surviving circa 1960 intermediate model Thomas-Hoover Capillary Melting-Point Apparatus (25.5” x 7.75” x 6.25”).

MELTING POINT APPARATUS

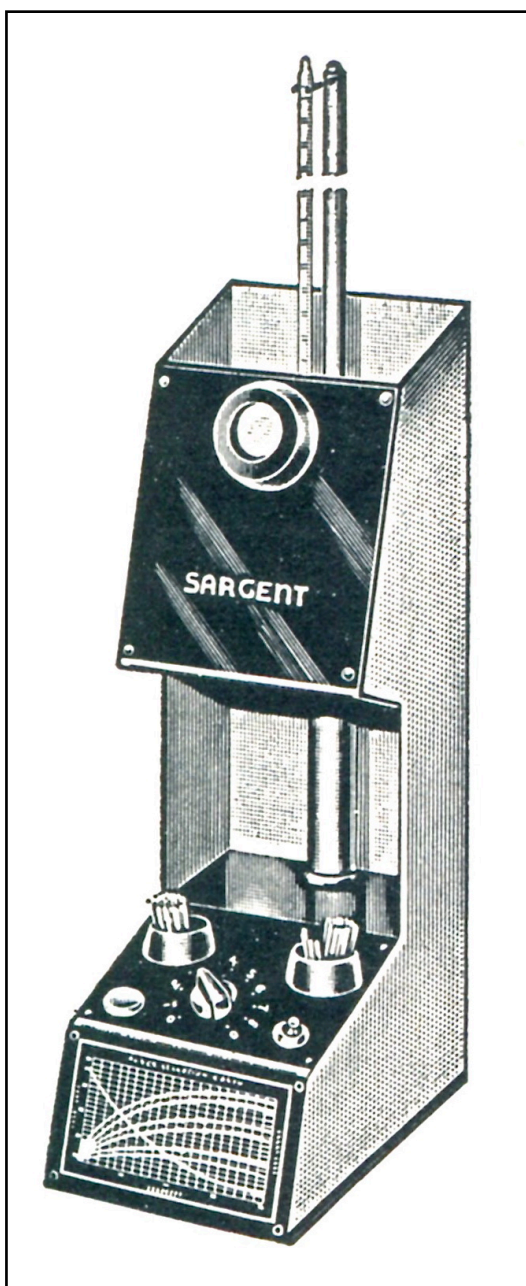


Figure 21. The Sargent electric melting-point apparatus as depicted in the 1967 catalog of the E. H. Sargent Co. of Chicago, IL.

apparatus, was introduced in the 1960s by the Arthur H. Thomas Co. of Philadelphia (figure 20). This came in three varieties. The basic model sported a magnifying lens and an electrically heated silicone oil bath with backlighting, as well as a stirrer to eliminate thermal gradients. The intermediate model added on a thermometer guard with an adjustable periscope and hairline for accurate thermometer readings, and the deluxe model added additional backlighting for the thermometer itself.

The Sargent Apparatus

Yet a third electric melting-point device was introduced around 1967 by the E. H. Sargent Co. of Chicago (figure 21). Though similar in concept to the Mel-Temp, it appears not to have been as successful as its competitors and the author has as yet to come across a surviving example.

The Büchi-Tottoli Apparatus

Yet a fourth contender from the 1960s was the Tottoli melting-point apparatus introduced by the Büchi Labortechnik of Flawil Switzerland in 1957 (figure 22). Like the

OESPER MUSEUM BOOKLETS

Thomas-Hoover apparatus, it used a stirred electrically heated silicone oil bath rather than a heating block and came with the usual magnifying lens and backlighting. Not marketed through standard laboratory supply houses, it tended to be a speciality item that was targeted more at research laboratories than at undergraduate teaching laboratories.

Further Developments

Though now more than 50 years old, the original Mel-Temp, Fisher-Johns and Thomas-Hoover melting-point devices are still being used in many undergraduate teaching laboratories, at least if we are to judge from various postings on the internet. Nevertheless, they are rapidly being displaced by yet another generation of melting-point devices which sport programmable heating rates, electronic temperature detection, and liquid crystal displays. Despite the fact that they are even more expensive than the previous generation, their widespread adoption is being driven not only by their greater convenience but also by an irrational fear of mercury which



Jensen-Thomas Apparatus Collection

Figure 22. A surviving, circa 1960, Büchi-Tottoli (25" x 8.25" x 7") electric melting-point apparatus.

MELTING POINT APPARATUS

has led to a virtual ban on the use of the traditional thermometer in both teaching and research chemical laboratories.

References and Notes

1. D. Roller, "The Early Development of the Concepts of Temperature and Heat," in J. Conant, Ed., *Harvard Case Histories in Experimental Science*, Vol. 1, Harvard: Cambridge, MA, 1963, Case 3.

2. Brief histories of the use of melting points in chemistry include P. Morris, "Melting Point Apparatus," in R. Bud, D. J. Warner, Eds., *Instruments of Science: An Historical Encyclopedia*, Garland: New York, NY, 1998, pp. 373-374; and W. B. Jensen, "Melting Points and the Characterization of Organic Compounds," *J. Chem. Educ.*, **2009**, *86*, 23-24.

3. M. E. Chevreul, *Considerations générales sur l'analyse organique et sur ses applications*, Levrault: Paris, 1824, p. 33.

4. Summarized in M. E. Chevreul, *Recherches chimiques sur les corps gras d'origine animale*, Levrault: Paris, 1823. English translation available as M. E. Chevreul, *A Chemical Study of Oils and Fats of Animal Origin*, Dijkstra-Tucker: Carbougnere 2009.

5. J. Timmermans, *The Concept of Species in Chemistry*, Chemical Publishing Co: New York, NY, 1963, p. 33. In a footnote Timmermans indicates that he was unable to locate any earlier examples, though his failure to note the work of Chevreul is puzzling.

6. J. Liebig, F. Wöhler, "Untersuchungen über das Radikal der Benzoessäure," *Annalen*, **1832**, *3*, 249-287. The melting point is reported on p. 270. An English translation is available in O. T. Benfey, Ed., *Classics in the Theory of Chemical Combination*, Dover: New York, NY, pp. 15-39. Neither melting nor boiling points were reported for the other benzoyl derivatives discussed in the paper.

7. J. Liebig, "Ueber Acetal (Sauerstoffäther), Holtzgeist und Essigäther," *Annalen*, **1833**, *5*, 25-37. Boiling point reported on p. 26.

8. J. Liebig, J. L. Gay-Lussac, "Analyse du fulminate d'argent," *Ann. chim. phys.*, **1824**, *25 (series 2)*, 285-311; F. Wöhler, "Recherches analytiques sur l'acide cyanique," *Ibid.*, **1824**, *27 (series 2)*, 196-200.

OESPER MUSEUM BOOKLETS

9. J. Berzelius, "Körper von gleichen Zusammensetzung und verschiedenen Eigenschaften," *Jahres-Berichte*, **1832**, *11*, 44-48. Swedish edition 1831.
10. See, for example, the organic laboratory manuals by Lassar-Cohen (1890), Orndorff (1893), Gattermann (1894), Hewitt (1897), Cohen (1900), and Holleman (1904).
11. S. P. Mulliken, *A Method for the Identification of Pure Organic Compounds by a Systematic Analytical Procedure Based on Physical Properties and Chemical Reactions*, 4 Vols., Wiley: New York, NY, 1904-1922.
12. O. Kamm, *Qualitative Organic Analysis: An Elementary Course in the Identification of Organic Compounds*, Wiley: New York, NY, 1922.
13. See, for example, W. Utermark, *Schmelzpunkt-Tabellen organischer Verbindung*, Akademie: Berlin, 1951 and later American editions in translation.
14. For the relevant references, see E. Lassar-Cohen, *Arbeitsmethoden für organisch-chemische Laboratorien*, 4th ed., Voss: Leipzig 1906, p. 229.
15. For details see L. Gattermann, *The Practical Methods of Organic Chemistry*, Macmillan: New York, NY, 1901, pp. 66-70.
16. G. Olberg, "Apparat für Schmelzpunktbestimmungen," *Repert. anal. Chem.*, **1884**, *6*, 94-95.
17. J. Thiele, "Ein neuer Apparat zur Schmelzpunktbestimmung," *Berichte*, **1907**, *40*, 996-997.
18. L. M. Dennis, "Apparatus for the Determination of Melting Points," *J. Ind. Eng. Chem.*, **1920**, *12*, 366-368.
19. Special flasks and tubes continued to be proposed long after the Thiele tube. Thus in 1945 McElvain described a long-necked, round-bottom flask which eliminated the rubber band by instead inserting the capillary at an angle to the thermometer via a second opening near the neck, and flasks of this type were sold by the E. H. Sargent Co. in the 1960s. See S. M. McElvain, *The Characterization of Organic Compounds*, Macmillan: New York, NY, 1945, p. 13 and *Scientific Laboratory Instruments, Apparatus and Supplies*, E. H. Sargent & Co: Chicago, IL, 1967, p. 664. Likewise, in the 1940s Fisher Scientific introduced a nested double test tube device in which the wall of the inner tube, containing the thermometer and capillary, was perforated with small holes. Heating the outer tube supposedly generated convection currents in the inner tube which eliminated

MELTING POINT APPARATUS

hot spots. See *Modern laboratory Appliances*, Fisher Scientific Co: Pittsburgh, PA, 1949, p. 619.

20. L. M. Dennis, R. S. Shelton, "An Apparatus for the Determination of Melting Points," *J. Am. Chem. Soc.*, **1930**, 52, 3128-3132.

21. J. D. Burchard, "An Electrically Heated Thiele Tube," *The Chemist Analyst*, **1930**, 19(5), 23.

Oesper Museum Booklets on the History of Chemical Apparatus

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Polarimeters

No. 2
Melting Point Apparatus

No. 3
Refractometers

No. 4
Colorimeters

No. 5
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No. 6
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Spectroscopes

Voltaic Cells

