

# Melting Points and the Characterization of Organic Compounds

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## Question

When was melting point introduced to characterize organic compounds?

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## Answer

The Belgian physical chemist, Jean Timmermans, in his classic monograph, *On the Concept of Species in Chemistry*, attributed the first use of melting points as a means of characterizing organic compounds to the famous 1832 paper by the German chemists, Justus von Liebig and Friedrich Wöhler, on the chemistry of the benzoyl radical in which they reported the melting point of benzamide (1, 2). A year later Liebig also reported the boiling point of liquid acetal (3). From this date 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 by the last decade of the 19th century melting point determinations had become a standard introductory topic in virtually all organic laboratory manuals (4).

Liebig and Wöhler said nothing about their method for determining the melting point of benzamide. However, beginning in 1870s an increasing number of proposals for the rapid and accurate determination of melting points began to appear in the chemical literature (5). By the 1890s the most popular of these (figure 1) involved attaching a melting point capillary to the stem of a thermometer suspended in a long-necked, round-bottom flask filled with concentrated sulfuric acid or some other liquid with a high boiling point and carefully heated using a Bunsen burner – a technique which was still being used when the present writer took introductory organic laboratory in the 1960s (6). By 1900 laboratory supply catalogs

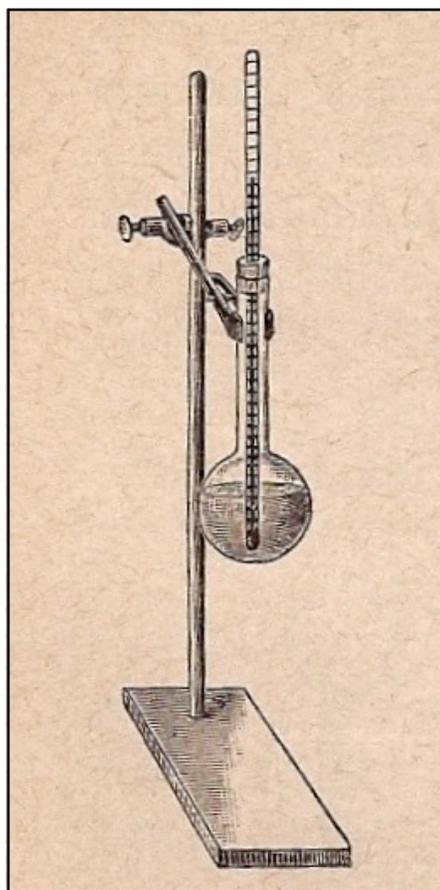


Figure 1. Simple melting-point apparatus as depicted by Gattermann in 1894 (6).

were selling several elaborated versions of this flask (known as Roth and Anschutz-Schulze flasks respectively). Though first proposed in 1907, it was not until the 1920s that supply catalogs began to offer specialized “Thiele melting-point tubes,” whose characteristic “b” shape (figure 2) allowed one to position the burner to one side rather than directly beneath the thermometer bulb (7). Early versions of electrically heated melting point devices first appear in laboratory supply catalogs in the 1930s, but dependable, inexpensive models

suitable for student use are uncommon before the late 1950s.

Liebig and Wöhler also failed to indicate their motivation in reporting the melting point of benzamide. One may, however, speculate that it 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 the analysis reported by Wöhler for silver cyanate while working in the laboratory of Berzelius in Stockholm, 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 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 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 began shortly after the explicit recognition of the concept of isomerism, since this data served as a convenient way of unambiguously detecting yet further examples of this new phenomenon.

### Literature Cited

1. 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 this does not mean that they do not exist.
2. 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.
3. J. Liebig, "Ueber Acetal (Sauerstoffäther), Holzgeist und Essigäther," *Annalen*, **1833**, 5, 25-37. Boiling point reported on p. 26.
4. See, for example, the organic laboratory manuals by Lassar-Cohen (1890), Orndorff (1893), Gattermann (1894), Hewitt (1897), Cohen (1900), and Holleman (1904).
5. For the relevant references, see E. Lassar-Cohen, *Arbeitsmethoden für Organisch-Chemische Laboratorien*, 4th ed., Voss: Leipzig 1906, p. 229.
6. For details see L. Gattermann, *The Practical Methods of Organic Chemistry*, Macmillan: New York, NY, 1901,

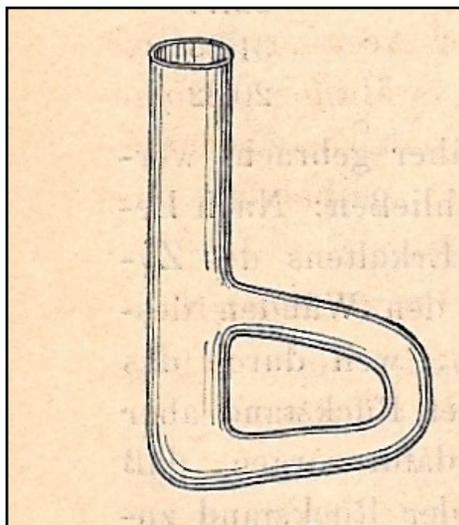


Figure 2. Thiele's original melting point tube, circa 1907 (7).

pp. 66-70.

7. J. Thiele, "Ein neuer Apparat zur Schmelzpunktbestimmung," *Berichte*, **1907**, 40, 996-997.

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.

9. J. Berzelius, "Körper von gleichen Zusammensetzung und verschiedenen Eigenschaften," *Jahres-Berichte*, **1832**, 11, 44-48. Swedish edition 1831.

*Do you have a question about the historical origins of a symbol, name, concept or experimental procedure used in your teaching? Address them to Dr. William B. Jensen, Oesper Collections in the History of Chemistry, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172 or e-mail them to [jensenwb@ucmail.uc.edu](mailto:jensenwb@ucmail.uc.edu)*

### Update

Since writing this article I have discovered an earlier survey of melting-point apparatus by Peter Morris which covers much of the same ground (1). However, in contradiction to Timmermans, Morris attributes the first use of melting points in organic chemistry to the French chemist, Michel Chevreul, who employed them to characterize various fatty acids, waxes, and oils in his famous work, *Recherches chimiques sur les corps gras d'origine animale*, first published in 1823, and which summarized work extending back as far as 1813 (2). The next year Chevreul summarized the analytical techniques used in this work in a separate monograph entitled *Considerations générales sur l'analyse or-*

*ganique*, in which he explicitly noted that, among the physical properties used to properly characterize a newly isolated solid compound, were its crystal form, its melting point, and its vaporization point (3). In neither book does he discuss the apparatus or procedures that he used to actually determine melting points in the laboratory.

1. P. J. T. Morris, "Melting-Point Apparatus," in R. Bud,

D. J. Warner, Eds., *Instruments of Science: An Historical Encyclopedia*, New York, NY, 1998, pp. 373-374.

2. 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, Carbognere 2009.

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