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EARLY THERMOMETRY AND DIFFERENTIAL THERMOMETRY

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ABSTRACT

A review is given of some highlights in the history of thermometry and differential thermometry, with special reference to the developments made in Florence in the mid 17th century and in St. Andrews in the mid 18th century.

INTRODUCTION

Although most thermoanalytical experiments are performed in the pyrometric or the cryometric region, thermometry forms the basis of thermal analysis, as the degrees in which temperature is measured are those of thermometry in their upward and downward extensions. Moreover, differential thermometry is the basis of DTA and, indeed, of heat-flux DSC.

THERMOMETRY

The origins of thermometry are lost in the mists of antiquity, as pneumatic experiments that could have led to a thermoscope (an ungraduated thermometer) were described in the 2nd and 1st centuries BC by Philo of Byzantium and Hero of Alexandria. Hero's work was known in the west before that of Philo, as it was published in Latin and Italian translations in the late 16th century, whereas Philo's treatise did not appear until 1882 [1] - although manuscript copies of a Latin translation existed in several libraries [2]. Thermoscopes were probably produced independently on both sides of the Alps about the beginning of the 17th century, but it is now generally conceded [1-3] that the earliest was that of Galileo (Fig. 1A), possibly based on the observations of Hero. Sanctorius, shortly after, marked changes in the liquid level by two moveable

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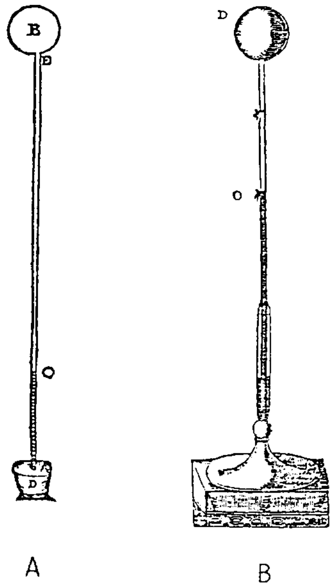

Fig. 1. An early thermoscope (A) and the thermoscope of Sanctorius with threads (B) [1].

threads (Fig. 1B) before adding a scale to form a thermometer. One can only assume that the use of 'degrees' on the scale arose from the Galenic concept of four *degrees of heat* and four *degrees of cold* - an assumption supported by the fact that the earliest known illustration of a thermometer, in a manuscript dated 1611 [4], has a scale of 8 degrees.

All early instruments were of the gas-thermometer type and, having reservoirs open to the atmosphere, were affected by pressure. About 1630, an unsealed liquid(water)-in-glass instrument was used for clinical purposes by the French physician Jean Rey, who was unaware of all previous work [1]. This was not followed up, however, and for the next advance we must turn to Florence, where Grand Duke Ferdinand II and his brother Prince (later Cardinal) Leopold, who were both intensely interested in science, collected around them a coterie of scientific excellence and founded the *Accademia del Cimento* (Academy for Scientific Studies) in 1657. This Academy, which was active for ten years, had no written constitution or membership list but seems to have comprised some nine or ten scientist-courtiers in addition to the two brothers. Its activities consisted of scientific experimentation, rather than paper-reading or debate, and its work is fully recorded in the *Saggi di Naturali Esperienze fatte nell'Accademia del Cimento*, edited by the Secretary, Lorenzo Megalotti, and published in 1667 [5].

In the first section of the Saggi, which is devoted to thermometers, their construction and use, appears the first certain depiction of sealed liquid-in-glass types. The earliest of these, the floating-ball type (Fig. 2 V), was invented by Ferdinand himself about 1640 [1] and depended on density change rather than expansion and contraction. The hollow glass balls floating in the 'spirit of wine' (alcohol) were of different colours and different

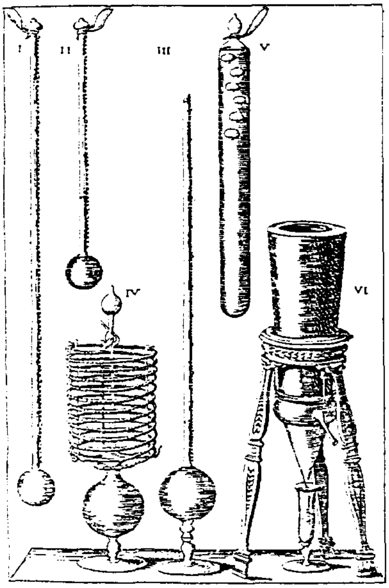

Fig. 2. Various thermometers (I-V) depicted in Plate I of the Saggi.

densities so that the higher the temperature, the greater the number of balls that sank. By using only balls of similar densities [5], a number of these instruments were constructed to within reasonable limits of tolerance. Because of their slow response, such thermometers were known as 'the lazy ones' and a clinical version was, from its shape, termed a 'tadpole' [6]. About 1654 [1], Ferdinand devised what is now the conventional type (Fig. 2 I,II), which was also filled with spirit of wine, as water, it was realised, would have cracked the bulb when it froze and also expanded near the ice-point. These, the celebrated 'Florentine thermometers', took two forms - the 100- and 50-degree types, the 100-degree simply being more sensitive than the 50-degree. Despite the fact that the original scales were somewhat arbitrary, each one of the large number constructed was made to conform (at least when Antonio Alamanni, Ferdinand's superb glassblower, was alive), within narrow tolerance limits, with all the others of its type by careful adjustment of the dimensions of the bulb and tube and of the amount of liquid [5]. The accuracy of the 50-degree thermometers was shown in 1829, when the ice-point on several tested was found to be uniformly at 13½ degrees, the zero point at $-19^{\circ}C$ and the 50-degree point at $55^{\circ}C$: the ice-point on the 100-degree instrument was at $20^{\circ}C$, but this may not have been so accurate on all [5].

The instruments in Fig. 2 III,IV were not really practical. Indeed, the Saggi states that IV was "made ... through curiosity to see the liquid run through tens of degrees when it is simply breathed on" [5]. Yet more than one of each was made and these, as well as many other items of fine glassware testify to the skill of Alamanni: when he died, the Academicians lamented that "now he is gone, we not only have not found his equal, but do not even hope for this, nor think it be possible" [6].

The 50- and 100-degree instruments were particularly important because (a) they were the first thermometers of conventional type to appear, (b) they were produced in considerable quantity and with a good degree of accuracy, and (c) they were widely distributed by Ferdinand and Leopold both in Italy and in Europe generally. They therefore presented the first opportunity of validly comparing temperatures at different places and at different times. Surprisingly, in view of the many upheavals since the 17th century, 223 of the 547 instruments used by the Academicians are still extant [6] and many, including thermometers of the types illustrated in Fig. 2, are on display in the Museo di Storia della Scienza in Florence. Any scientist inspecting this exhibition cannot but appreciate the extent of our debt to Ferdinand, Leopold and Alamanni.

The many thermometers that appeared during the next half century were usually peculiar to their constructors/users and temperatures measured on one could not be compared with those on another. This difficulty was overcome in 1713, when Daniel Gabriel Fahrenheit made the first precision sealed mercury-in-glass thermometers calibrated with the ice-point at 32 degrees and blood heat at 96 degrees, later changed to boiling water at 212 degrees [1]. Although this two-fixed-point calibration was soon universally accepted as a standard, a lacuna was left, as many meteorological and other measurements made earlier on individual instruments could not be compared and were essentially lost. In 1739, however, George Martine of St. Andrews noted, on studying the literature, that certain relatively fixed points were recorded on various scales and, using this observation, was able to correlate no fewer than 14 earlier thermometers with the Fahrenheit in a diagrammatic manner [7], thus ensuring continuity. Corrections for the irregular expansion of the spirit of wine used in the early instruments were introduced by Jean André de Luc late in the 18th century [8], with consequent further increase in precision. It is interesting to note that de Luc also constructed two thermometers with non-standard scales - one for correcting barometer readings for expansion of the mercury column with temperature and the other for determining heights from the boiling point of water [8].

DIFFERENTIAL THERMOMETRY

Differential thermometers appeared during the very early days of thermometry and may even date back to before 1610 [2]. The two-

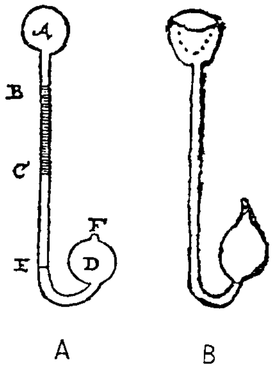

Fig. 3. Two two-bulbed thermometers, one (A) with a perforation in the lower bulb and the other (B) sealed [2].

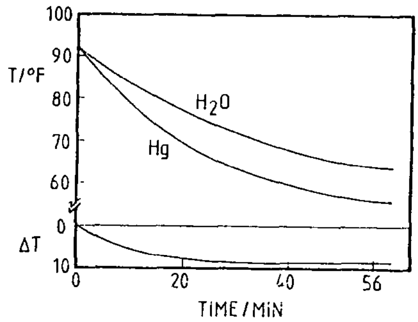

Fig. 4. A plot of the data of Martine for the cooling of equal volumes of water and mercury [7] and the ΔT curve derived therefrom.

bulbed "Dutch" thermometer, usually attributed to Cornelis Drebbel, seems to have had a perforation on the lower bulb (F, Fig. 3A), but if this bulb were sealed as some may have been, a differential thermometer would result. Certainly, the instrument with a cup for liquid in the upper bulb (Fig. 3B), dating from 1664, was of this type [2]. Many other differential thermometers were devised over the years, perhaps the most sensitive being that described by William Ritchie of Tain, Scotland, in 1827 [9]. This consisted of two squat cylindrical thin-metal bulbs coated in lamp-black and sealed on to a graduated glass U-tube containing a tinted liquid. Its extreme sensitivity was found ideal in the study of radiant heat transfer.

None of these instruments seems to have been used to give DTA information and the first use of the DTA principle appears to be due to Martine [7]. In his time, Boerhaave's view that the amount of heat required to heat a body over a given range was proportional to the density of that body was generally accepted. On this basis mercury would require 13½ times as much heat as water - a supposition doubted by Martine for very good reasons [7]. He therefore placed roughly equal volumes of mercury and water in two thin-walled glass flasks, "set them down ... *almost close to one another*, before a great fire ... *so that the heat should equally set upon them* [my italics]" [7] and measured, by two identical sensitive thermometers, the temperature of each as they heated up. He found that the mercury heated more quickly than the water and, on placing the flasks side-by-side in a cool place once they were at the same temperature, that the mercury also cooled more quickly. The experiments were then repeated with more carefully measured quantities and the results tabulated. Martine's results for the second cooling experiment (the heating ones are vitiated by the heat being applied to only one side) are plotted in Fig. 4 together with the curve for ΔT (i.e. $T_{Hg} - T_{H_2O}$) against time. Although Martine himself did not derive ΔT, this would seem to be the first recorded use of the DTA principle and the $\Delta T/t$ plot is clearly of the type from which heat capacity and specific heat can be calculated [10]. Martine also recorded results for other pairs of liquids heated and cooled under identical conditions - data that were used by Joseph Black in his lectures [11] to develop the concept of heat capacity, which later led to specific heat [12].

REFERENCES

1. W.E.K. Middleton, A History of the Thermometer and its Use in Meteorology, Johns Hopkins, Baltimore, MD, 1966.
2. F.S. Taylor, Ann. Sci., 5 (1942) 129.
3. P.E. Ariotti, Ann. Sci., 31 (1974) 457.
4. J.A. Chaldecott, Ann. Sci., 8 (1952) 195.
5. W.E.K. Middleton, The Experimenters: A Study of the Accademia del Cimento, Johns Hopkins, Baltimore, MD, 1971.
6. M.C. Cantu and M.L.P. Bonelli, The Accademia del Cimento, Nardini, Firenze (no date: *ca* 1980).
7. G. Martine, Essays on the Construction and Graduation of Thermometers and on the Heating and Cooling of Bodies (1738-1740), 2nd Edition, Alex. Donaldson, Edinburgh, 1772.
8. J.A. de Luc, Recherches sur les Modifications de l'Atmosphere ...., 2nd Edition (4 Vols), Duchesne, Paris, 1784.
9. W. Ritchie, Phil. Trans. R. Soc. Lond., (1827) 129.
10. M.I. Pope and M.D. Judd, Differential Thermal Analysis, Heyden, London, 1977, p. 39.
11. J. Robison (Editor), Lectures on the Elements of Chemistry Delivered in the University of Edinburgh by the Late Joseph Black M.D., Creech, Edinburgh, 1803.
12. E.L. Scott, Ann. Sci., 38 (1981) 141.