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GOMENIUS AND BLACK: PROGENITORS OF THERMAL ANALYSIS

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ABSTRACT

Comenius and Black lived a century apart, yet each made contributions to the study of heat - the former qualitatively and the latter quantitatively. These advances are detailed and critically considered as steps in the pre-history of thermal analysis.

INTRODUCTION

Although developments in any branch of science stem logically from earlier findings and observations, there are times when individuals endowed with more incisive minds than their fellows leave their own stamp on the subject. The manner in which Gomenius and Black fit into this category in relation to their work on heat is assessed below.

Alchemists laid much stress on the control of heat, but it was only with the development of the thermoscope and thermometer in the 17th century (the thermoscope of Philon of Byzantium, *ca* 225 BC, having been forgotten) that measurement of the intensity of heat through the thermal expansion of liquids or gases became possible[1]. The 16th-17th centuries proved indeed a very fertile period for science generally, as they saw the rise of a new generation of scientists remarkable for their criticism of Aristotelian theories, their refutation of mediaeval scolasticism, their return to and reconstruction of atomic theories, and their recognition of the importance of experiment. Among these were the Italians Bernardino Telesio (1508-1588) - who introduced two active principles (heat and cold) acting on a third passive principle (matter) - Francesco Patricio (1529-1597), Giordano Bruno (1547-1600) and Tomanaso Campanella (1568-1639), the Englishman Francis Bacon (Lord Verulam, 1561-1626) and the Welshman Robert Fludd (1574-1637). All these considered the sun to be the source of heat - as, indeed, did the geocentrists - thus giving rise to the term 'philosophical heliocentrism'.

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JOHANNES AMOS COMENIUS (1592-1670)

Among those who furthered natural science by opposing Aristotelian and scholastic doctrines was Johannes Amos Comenius, born in Nivnice, Moravia, as Jan Amos, the youngest of the five children of Martin Komenský and his wife, a devout Moravian Brethren family, on 28 March 1592. Despite his father's death in 1604, Jan was able to attend school in Přerov from 1608, proceeding thence to study theology at the University of Herborn and later at Heidelberg. Returning to Moravia in 1614, he was ordained a pastor in 1616. After the unfortunate battle of White Mountain (Bila Hora) in 1620 life became very difficult and he had to go in hiding from place to place before emigrating to Leszno, Poland, in 1628. There he became a bishop and rector of the Gymnasium and wrote several educational and pansophic treatises, including the celebrated *Porta* (later *Janua*) *linguarum reserata* (1631), which became so well known internationally that, in 1641, he accepted an invitation from Samuel Hartlib (1600-1662) to assist in reforming the school system in England. In the next year, however, on receiving two similar requests - one from Cardinal Richelieu in France and the other from Chancellor Oxenstierna in Sweden - he preferred the latter and moved to Sweden, where he remained until 1648, when, disappointed with the Treaty of Westphalia, he returned to Leszno. At the invitation of Zigmund Rakoczy, he spent 1650-1654 in Hungary, where he created his first pictorial encyclopedia *Orbis sensualium pictus* (1658). Again he returned to Leszno, but, on the destruction of his valuable library in the Swedish-Polish war, he made his home in Amsterdam, where he died on 15 November 1670.

Despite his troubled and peripatetic life, Comenius was a prolific author, whose writings reflect nothing of his own sufferings but rather reveal a kind optimistic man endowed with a deep sense of justice and with profound wisdom. His tendency to be a perfectionist is illustrated by the fact that he revised *Janua rerum* (1681) no fewer than thirty times in his attempt to explain physics (then embracing all natural sciences) by "relating causes to their immediate effects". He kept constantly abreast of scientific developments by extensive reading and by correspondence with other scientists, such as Marin Mersenne (1588-1648), the French mathematician and physicist. A supporter of atomism and somewhat sceptical of earlier theories, he never doubted the Bible as a source of knowledge and, although a geocentrist, did not reject all Copernicus' views. A

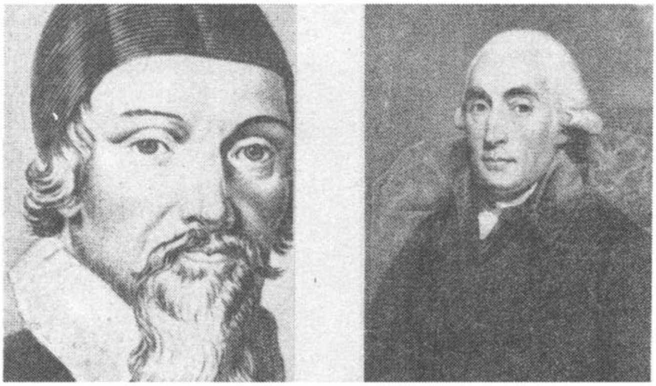

Plate 1. J.A. Comenius (*left*) and J. Black (*right*).

meeting near Leyden in 1642 with Rene du Perron Descartes (1596-1650), who had fought on the opposite side at the battle of White Mountain, led to no agreement between the two philosophers, Descartes complaining that Comenius "confused philosophy with theology".

As well as his educational and pansophic books, Comenius wrote several scientific works. *Physicae ad lumen divinum reformatae synopsis* (1642)[2,3] - i.e. 'Survey of Physics Reformed by Divine Light' - was immensely successful and is reputed to have introduced Robert Boyle (1627-1691) to Campanella's atomistic theory. In all his writings, Comenius stressed the importance of experiment and direct observation, and he is reputed to have constructed parts of his 'perpetuum mobile' with his own hands.

In *Physicae synopsis*[2,3] he considers all stars to be spheres composed of light and heat, the cause of different kinds of motion to be heat, and motions directly related to heat and cold to be "expansion" and "contraction". Thus,

> the motion of expansion arises when a substance thinned by heat seeks to occupy a larger space and expands beyond its limits; the motion of contraction occurs when a substance is densified so that it should occupy a smaller space.

As examples, he mentions the vaporization and condensation of water vapour. Moreover, to prove that "heat applied to matter can both expand and densify it", he cites the ingenious experiment:

> Take a flask empty of matter but filled with air [which, of course, also contains water vapour]. Join some smaller bottle to the long protruding neck and seal it around the joint so that no air can escape. Put the air thus enclosed over a fire and thus

> force it to become rarified. You will see that the air, feeling that it cannot expand further, will densify in the farthest, and consequently coldest, spot as water. Remove the fire and you will see that the water drops disappear slowly and return to the form of air.

This experiment, although carefully observed, unfortunately led Comenius to the false conclusion that cold can arise through the action of heat. Vaporization he believes to be caused by heat diluting the matter of bodies, converting it into vapour, and condensation of vapour to be caused by cold; ice is water contracted by frost. Attempts to measure the volume increase on vaporization of water led him to a value of about 100, compared with Aristotle's estimate of 10. His explanation of the water cycle in nature - i.e. water evaporated from oceans being returned by rivers - is correct.

The most important work of Comenius on heat is his *Disquisitiones de caloris et frigoris natura* ... (1659)[3,4] - i.e. 'Discourses on the Nature of Heat and Cold, true knowledge of which is the key to many secrets of nature' - probably written at Leszno but revised for publication at Amsterdam. This didactic treatise is not without its faults. Thus, although, following the ideas of Francis Bacon, the main purpose of the book is to establish that heat and cold are forms of motion (outwards and inwards, respectively), yet Chapter 12 speaks of "spicules" of heat and cold, the former being "thin and sharp" and the latter "thick and blunt". Moreover, cause is sometimes confused with effect (e.g. "When matter begins to densify and contract, cold issues") and some erroneous deductions are drawn (e.g. the breaking, on freezing, of a glass flask nearly filled with water and tightly sealed is attributed to the creation of a vacuum, "which nature does not tolerate".)

Despite these shortcomings, there is much of interest in this book. Thus, Comenius rejects the Aristotelian theory that materials have a mixture of hot and cold (still adhered to in his time by, e.g., Jean Baptiste Morin, 1583-1656[5]) and the argument of the astrologers that Saturn is the source of cold, arguing that the sun is the source of both, "through opposite librations", and later commenting on the warmth of sunlight and the cold of shadow. Thermometers in his time were in an embryonic state and no standard scales existed[1], so it is not surprising that Comenius never mentions them; his observations are therefore qualitative. He recognizes three "degrees of heat" (*calor, fervor* and *ardor*) above ambient (*tepor*) and three "degrees of cold" (*frigus, algor* and one unnamed) below.

The hottest, *ardor*, represents the temperature at which a combustible substance "collapses inwardly and is dispersed into atoms", whereas the unnamed coldest is "the cold at which a substance breaks up by constriction (just as the heat of fire decomposes it by burning)", thus essentially envisaging absolute zero.

From the thermoanalytical viewpoint, the most interesting part of the book is Chapter 3, which commences:

> To observe clearly the effects of heat and cold, let us take a visible object and let us observe the changes that occur on heating and cooling, so that the effects of heat and cold are apparent to our senses

- surely the aim of all thermoanalytical experiments. As a subject for this study, Comenius chose water and, taking some in a kettle, he brought it closer and closer to a fire, noting, as he did so, that it began, sequentially, to swirl, to expand, to evaporate and to boil. He then deduces, correctly, that the bubbles formed on boiling are "vesicles in the water, full of 'air'" and that this 'air' must be water "resolved into vapour". On cooling, particularly in winter when conditions are more favourable, the boiling water first stops boiling, then evaporating, then swirling, decreases in volume and, "finally, if the force of cold is strong, it freezes" to a body "solid, immobile and dense as stone". The same processes occur reversibly on all heating and cooling cycles. To show that other bodies behave similarly, he goes on to consider the behaviour of a lit candle and of air in a thermoscope (*vitrum caldarium*) bulb enveloped alternately by sponges soaked in hot and cold water. These observations reveal an acuity of observation above that of most of his contemporaries.

Finally, in Chapter 4, Comenius makes another observation that brings us naturally to the work of Black:

> By a well burning fire we can melt ice to water and heat it to very hot water very quickly - in about a quarter of an hour. There is, however, no means of converting hot water to ice very quickly. Even when exposed to very intense frost, water takes several days to be converted completely to solid ice.

Unfortunately, Comenius never considered *why* freezing (or boiling) should take so long: that was probably beyond the limitations of his time and had to await solution by Black some 100 years later.

Despite the fact that Comenius' works on natural science had less impact than his educational and philosophical treatises, they should not be underestimated. Indeed, Comenius was, in some respects, a true precursor to Black.

JOSEPH BLACK (1728-1799)

The 'Auld Alliance' of 1295 led to centuries of close ties between Scotland and France - so close, indeed, that Louis XII, in 1498, even granted Letters of Naturalization to the whole Scottish nation, a statute that has never been repealed[6]. For a long period, therefore, French quality wines found a ready market in Scotland (by 1762, 'excellent claret', directly imported, was even obtainable in some country inns[6]) and it is not surprising that some families engaged in the wine trade should take up residence in France. One such family in Bordeaux consisted of John Black, who hailed from Belfast but was of Scots extraction, his wife, an ex-patriate Scot from Aberdeenshire, and their thirteen children, their fourth son[7] Joseph having been born on 16 April 1728. As the family owned a farm, a country house and a vineyard, in addition to their town residence[8], Joseph was brought up in comfort. But his surroundings were not entirely commercial, as John Black numbered among his close friends Charles Montesquieu, Baron de la Brede (1689-1755), an eminent jurist and then President of the Parlement of Bordeaux, while his wife was closely related to several academics. Taught English by his mother, Joseph was sent to school in Belfast in 1740 and then to the University of Glasgow in 1744, matriculating in 1746 but never graduating there[7]. In 1752 he moved to Edinburgh to complete his medical training, which he did in 1754 with his famous MD thesis on mild alkalis and 'fixed air'. Appointed professor of botany and anatomy in Glasgow in 1756, he transferred the next year to chemistry and medicine, where his heart lay, to succeed his erstwhile teacher, William Cullen (1710-1790), who was the first to teach chemistry systematically at Glasgow (1747)[7] and who had just moved to Edinburgh. He again succeeded Cullen in the chair at Edinburgh in 1766 and remained there until he retired in 1797. He died on 10 November 1799.

In addition to his classes in chemistry and medicine, Black maintained a private medical practice, acted as consultant, took an active part in societies such as the Royal Society of Edinburgh, of which he was a founder member[9], and even enjoyed social occasions. If one adds to this his voluminous correspondence, his continuous update of his lectures to keep abreast of research[10], the care he had to take of his health, which was never robust, and his meticulous and perfectionist nature, it is easy to see why he never succeeded, despite at least one attempt[11], to prepare his lectures for publication. Black, however, was by no means unworldly, as he apparently weighed carefully the guineas received from students in class fees[12]! His keen commercial sense is also revealed in his correspondence with James Watt (1736-1819), the improver of the steam engine[13].

In passing, it may be mentioned that a student visiting the professor of chemistry (James P. Kendall, FRS) in Edinburgh in the early 1940s was usually invited to sit in 'Black's chair', then in his room. This chair is still housed in the department.

Unlike Comenius, Black published very little - and nothing on heat - but he fully described his work in his class lectures, of which at least 89 versions (covering the years 1766-1796) are still extant in the form of student notes[7]. A definitive edition, compiled from his own notes by his close friend, academic colleague and biographer, John Robison (1739-1805), and published posthumously in 1803[11], represents fairly accurately his lectures as delivered in the mid 1790s, although Robison may occasionally have tinted the text with his own views when he had to fill in gaps in the notes[7]. Despite the lack of publications, the international repute of his lectures[7], his own records[11], student notes and correspondence[7,13] allow events to be fairly closely dated[5,7] and ensure that he can be granted priority where this is due.

Black's work on heat was all conducted in Glasgow in 1756-1766, although he later supervised several theses on the subject[7] and maintained a correspondence on it with James Watt until his death. He may first have become interested in heat during his studies on the slaking of lime (pp. 525-526*), but his interest was stimulated by other general observations and the trigger may have been Cullen's observation that ether boiling under vacuum caused water in a surrounding vessel to freeze[7]. According to a letter dated 5 March 1780[13], he first lectured on latent in 1757 or 1758.

His definition of chemistry (p. 11) is illuminating:

> The science or study of those effects and qualities of matter which are discovered by mixing bodies together ... and by exposing them to different degrees of heat, alone, or in mixture with one another, in order to enlarge our knowledge of nature and promote the useful arts,

as, like the statement of Comenius quoted above, it would cover all thermoanalytical studies. He also defined chemistry briefly as the "Study of the Effects of heat and mixture"[14], so it is easy to see

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* All page numbers refer to Volume 1 of the 1803 edition of the *Lectures*[11].

why 225 pages out of the 1222 in the two volumes of the *Lectures*[11] should be devoted to heat.

As to the nature of heat, Black was rather non-commital and, even when he supported the phlogiston theory[7], always urged extreme caution[14], as he distrusted all hypotheses not based on observable facts. After 1780, despite his gradual conversion to the theory of Lavoisier[7], he was still non-commital. In the *Lectures* (pp. 31-34), he dismisses several theories, including those used by Comenius, as unlikely and seems to favour the opinion of William Cleghorn (*fl.* 1779) that heat is a (pp. 34-35)

> subtile fluid elastic matter ... [with] a strong attraction for the particles of the other kind of matter in nature, which have in general more or less attraction for one another, ... [whereas] the particles of heat have a strong repulsion for one another,

which bears a considerable similarity to, but is not identical with, the 1789 definition of Lavoisier[15] that heat is

> un fluide très subtil qui s'insinue à travers les molécules de tous les corps et qui les écarte; ... nous avons désigné ... ce fluide éminemment élastique ... par le nom de 'calorique'... [mais] nous ne sommes pas même obligés de supposer que le calorique soit une matière réelle [et] il suffit ... que ce soit une cause répulsive quelconque qui écarte les molécules de la matière.

Black, however, still urges caution, as (p. 35) "our first business must be to *study the facts*, ... which will lead us to more adequate knowledge and information".

Black's main contributions to the study of heat, the concepts of specific and latent heats[5,7,16], were derived by pure thought from established facts. Implicit in both terms is the distinction between 'quantity' (or 'capacity' - Black uses both terms of heat and its 'intensity'. While Hermann Boerhaave (1668-1738) probably appreciated the difference[7], he had no way of measuring quantity and believed it to be "in proportion to the space occupied by a body" (p. 81): Black, on the other hand, clearly expressed the difference and devised a method. Black argued (p. 78) that all materials at equilibrium in a constant-temperature environment have the same temperature (i.e. intensity of heat), yet,

> if we have one pound of water in one vessel and two pounds of water in another, the two pounds of water must contain twice the *quantity* of heat that is in the one pound.

From an experiment carried out by Daniel Gabriel Fahrenheit (1686-1736) for Boerhaave (pp. 79-81), in which equal amounts of water and mercury were mixed, he draws the logical conclusion that mercury has a smaller heating power (and therefore capacity for heat) than does water. This he confirms (p. 82) using the observation of George Martine (1702-1741) that mercury heats or cools much more quickly than water when equal amounts of each at the same temperature are placed side by side in front of a fire - surely one of the earliest uses of the principle of DTA. Black therefore concludes that each material has its own individual capacity for heat and that this value must be experimentally determined; moreover, as bodies expand differently on being heated, the temperature of determination should always be noted along with the value. He does not detail an experimental method, but Robison (p. 506) says that Black mixed

> two bodies of equal masses but of different temperatures, and then stated *their capacities as inversely proportional to the change in temperature of each by the mixture*.

Thus, if a pound of gold at 150°F raises the temperature of a pound of water at 50°F to 55°F, the capacity of gold to an equal weight of water is as 5:95 or 1:19. Although Robison (p. 504) claims that Black, assisted by William Irvine (1743-1787), used this method before 1756, there is no evidence that Black himself made such measurements at Glasgow[7]; however, Watt, with Black's guidance, later made many accurate measurements. It is now universally acknowledged that Black devised the concept of specific heat[5,16] but that the name, in the form 'chaleur specifique', was first used by Jean Hyacinthe de Magellan (1722-1790) in 1780; Magellan also published the first table of specific heats.

Despite the fact that Robert Hooke (1635-1703) in 1665, Ole Christensen Rømer (1644-1710) in 1702 and Rene-Antoine Ferchault de Reaumur (1683-1757) in 1730 had all, independently, used the ice-point, because of its stability, for thermometer calibration[1] and despite the observations of Comenius on the time taken to freeze water, it was generally considered, before Black's time, that any small increment of heat would convert a solid at its melting point into a liquid. Black, however, from a consideration of various phenomena (pp. 112-118), including the slow melting of ice and snow, concluded that, on the contrary, ice requires much heat to induce melting. To check this (pp. 120-122), he suspended by fine wires two identical flasks, each containing equal amounts of water but with one frozen and the other at 33°F, in a large room (i.e. a constant-temperature environment) at 47°F. In half an hour the water was at 40°F, whereas the ice had barely started to melt, thus confirming his deductions. By measuring the time it took for all the ice to melt, he was able to calculate that the amount of heat required to melt the ice would have raised the temperature of an equal amount of water by 139-140°F. By plunging a known weight of ice at 32°F into an equal amount of water at 190°F and measuring the temperature once the ice had melted, he calculated the amount of heat to be equivalent to 143°F, allowing, in this instance, for the water equivalent of the glass container. The mean of these two figures (which were obtained before 23 April 1762[5]), 141°F, is equivalent to 78 cal - remarkably close to the modern value (79.77 cal).

Black then turned his attention to the vaporization of water, arguing that, if any small increment of heat at the boiling point converted water into steam, boiling should be explosive. He could think of no sufficiently uniform source of heat for an experiment until (p. 157) he was "told by a practical distiller that, when his furnaces were in good order, he could tell to a pint the quantity of liquor he would get in an hour". Using "a cast-iron plate, having a furnace of burning fuel below it, taking care that the fire should be regular", he checked, by replicate heating and boiling off of quantities of water in flat-bottomed tin-plate vessels, that his heating was indeed regular. He then measured the time for water to go from 50°F to 212°F and the time taken to boil off. Assuming the temperature rise occurred uniformly, he calculated that the heat required to vaporize water was, in three experiments, that equivalent to the amount required to raise the temperature of an equal amount (if that were possible) by 810, 830 and 750°F, the last low figure probably "arising from irregularity in the fire". Again, it is interesting that the mean of the first two figures gives 455 cal/g, compared with the modern 539 cal/g - remarkably good, considering the various possible sources of error. Black concludes (p. 157):

> As [in melting] the ostensible effect of the heat consists, not in warming the surrounding bodies, but in rendering the ice fluid, so, in boiling, the heat absorbed does not warm surrounding bodies, but converts the water into vapour: ... the heat, therefore, is concealed, or latent, and I gave it the name of LATENT HEAT.

In addition to the doctrines of specific heat (or heat capacity) and latent heat (or enthalpy of transformation), both of great importance in thermal analysis, Black's lectures also contain other noteworthy features. The first is the emphasis laid on calibration. Thus, he not only checked the uniformity of his thermometer tubes, using the mercury-thread technique of Hooke[1], but he also confirmed the scale accuracy between 32 and 212°F by mixing equal amounts of water at different temperatures, taking the means of readings when warm was poured into cold and *vice versa*. For the expansion of water on conversion to steam he obtained the figure of 1664 times and quotes Watt as having obtained 1720 times - as compared to the 100 of Comenius. Black clearly envisaged an absolute zero, as (p. 64) he comments that ingenious experiments made "to determine the lowest possible degree, or beginning of heat" had not proved satisfactory. He also discusses thermal conductivity at considerable length and, in his experiments on the latent heat of vaporization, was the first to check quantitatively that he had an accurately controlled source of heat.

But the most interesting point is that he used, or at least envisaged - from the phraseology, it is difficult to say which - the method of cooling curves. Thus (p. 126), he suggests taking two identical flasks with equal amounts of water, equally hot and each with a sensitive thermometer, but one containing some salt to prevent it freezing. If these are placed side by side "in cold air, in a sharp frost", both cool equally to 32^{o}F, but, while the salted water continues to cool, the pure water

> will begin to change into ice, ... but with a slow progress ... and during all this time it will continue at the 32d degree of Fahrenheit's scale ... until it be totally frozen; after this it will again become colder.

If the temperature of the surroundings were constant during the experiment, this would conform with the ICTA definition[17] - so do we now have to backdate the first true thermoanalytical experiment from 1829[18] to about 1764?

CONCLUSIONS

Both Comenius and Black were intensely interested in heat and, although the former was bound by the restrictions of his time, he at least experimented and made some interesting observations worthy of record. Black, in a more sophisticated age, was a masterly experimenter, who contributed enormously to our knowledge of heat and may even have carried out an early thermoanalytical experiment.

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