On the History of Caloric

The play of ideas in human minds searching for truth is ever an interesting spectacle. Here a new thought flashes upon the intellect, there a new interpretation of our universe suggests itself. Thought clashes against thought. New hypotheses dispel the old. The intellectual panorama of successive theories of nature is most magnificent to behold.

In this article a few efforts of the human mind to secure a philosophical insight into some of the most common phenomena of nature will be discussed. Three topics will be considered : (I) the place of Lucretius in material theories of heat; (II) the interrelation of phlogiston and caloric; (III) the views on heat held by early American scientists.

Histories of science refer to different views on the nature of heat set forth by the Greek philosophers HERACLITUS, PARMENIDES, EMPEDOCLES and ARISTOTLE, but make no reference to the interesting views found in the *De rerum natura* of the Roman philosophical poet LUCRETIUS. Like HERACLITUS, LUCRETIUS believed in the existence of a material substance called « heat » and another material substance called « cold ». Thus LUCRETIUS says (1) : « Smells too incessantly stream from certain things; as does cold from rivers, heat from the sun, spray from the waves of the sea. » LUCRETIUS refers to the interaction between heat and air as follows : « Heat draws air along with it; there being no heat which has not air too mixed with it; for since its nature is rare, many first-beginnings of air must move about through it » .(2) Lightning and fire are materials of different degrees of fineness : « You may say that the heavenly fire of lightning subtle as it is formed of smaller shapes and therefore passes through openings which this our fire cannot pass born as it is of woods and sprung from pine ».(3)

(1) LUCRETIUS, *De rerum natura*, Bk. IV, line 223; also Bk. VI, lIne 925.
(2) *Loc. cit.*, Bk. III, line 235.
(3) *Loc. cit.*, Bk. II, lines 387-392

In celestial physics LUCRETIUS teaches : « that heat which the sun emits and that bright light pass not through empty void, and therefore they are forced to travel more slowly, until they cleave through the waves so to speak of air. Nor do the several minute bodies of heat pass on one by one, but closely entangled and massed together; whereby at one and the same time they are pulled back by one another and are impeded from without, so that they are forced to travel more slowly. » (1)

LUCRETIUS touched upon a topic which greatly agitated chemists and physicists of the XVIIIth century, the question whether this heat substance has weight. He says (2) : « Now methinks is the place, herein to prove this point also that no bodily thing can by its own power be borne upwards and travel upwards; that the bodies of flames may not in this matter lead you into error. For they are begotten with an upward tendency, and in the same direction receive increase, and goodly crops and trees grow upwards, though their weights, so far as in them is, all tend downwards. And when the fires leap to the roofs of houses and with swift flame lick up rafters and beams, we are not to suppose that they do so spontaneously without a force pushing them up. » It follows from this that LUCRETIUS believed heat to be a substance possessing weight; heat was ponderable. Thus we see that this Roman poet who has been credited with a pre-vision of many modern theories believed in the material character of heat and cold.

We pass to our second topic, the historic relation of caloric to phlogiston. It has been stated in a prominent American publication that the caloric theory is an eighteenth century offspring of the phlogiston theory, that phlogiston « before it quitted the world », retarded the progress of physics « by generating an offspring especially inimical to the true ideas about radiant heat », called « caloric ». (3).

As a matter of fact, the actual historic sequence makes phlogiston follow in the wake of caloric theories. That heat was a material substance, had been held by philosophers of antiquity and also by the alchemists and scientists of the sixteenth century. Some European medieval writers divided the chemical elements into light and

(1) *Loc. cit.*, Bk. II, lines 150-156.

(2) *Loc. cit.*, II, lines 156 ff.

(3) S. P. LANGLEY, in *Proceedings Am. Association Advanc. Science* for 1888, vol. XXXVII, p. 7. Salem 1889.

heavy. As light they designated fire and air, fire being regarded absolutely light, air only relatively light. (1)

The empirical period of the seventeenth century brought with it a new conception, according to which heat was a motion or vibration of some sort. This view was held by FRANCIS BACON, RENÉ DESCARTES, JOHN LOCKE, ROBERT HOOKE, CHRISTIAN HUYGENS, ISAAC NEWTON, and others. Nevertheless, at this time, the old view was far from being abandoned generally. That heat is a substance was adhered to at the close of the sixteenth and in the seventeenth centuries by WILLIAM GILBERT, PIERRE GASSENDI, ROBERT BOYLE and SEBASTIAN BASSO. H. CARDAN, TELESIUS (1565) and GILBERT followed the course of medieval writers in assuming this heat-substance to be imponderable (without weight).

About 1700 we behold the creation of the phlogiston doctrine by JOHANN J. BECHER and GEORG ERNST STAHL. BECHER replaces the four elements (earth, water, air and fire) of EMPEDOCLES by the three elements (earths), the « mercurial », « vitrifiable », and « combustible ». The combustible, called *terra pinguis,* escapes from bodies when they burn and from metals when they are calcined or oxidized. STAHL called this substance *phlogiston.*

In some ways, phlogiston trespassed upon the territory previously occupied by the older heat-substance; in part it occupied new territory. The exact relation of these two substances to each other was not clearly explained by STAHL and his followers.

The ancients looked upon ordinary combustion as a separation of the material of fire from the burning substance; PLINY regarded the ease with which sulphur burns as a proof of its being largely composed of the material of fire. Believers in the phlogiston theory considered combustion as a process of decomposition during which phlogiston escapes and the other constituent of the substance remains behind. Thus in ordinary combustion, phlogiston now took the place of the substance of fire.

Burning and the appearance of fire is according to STAHL only a special condition of the escaping phlogiston during which its smallest parts are in rapid upward motion designated by him *motus verticillaris.* (2) Phlogiston is not the material fire but the means for the

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(1) H. KOPP, *Geschichte der Chemie*, 2. Theil, p. 271. Braunschweig, 1844.
(2) H. KOPP, *Geschichte der Chemie*, Dritter Theil, p. 138, 1845.

formation of flames of fire; that is, when phlogiston escapes, it does so in the form fire.

The daily fluctuations of temperature were not explained by the aid of phlogiston. Here the heat-substance was without a rival. But the two theories were in sharp conflict with each other in explaining the oxidation of metals — « calcination » as the process was called. This process, leading to an increase in weight, had been explained by the aid of a ponderable heat-substance as a *synthetic* process; the greater weight was due to heat material penetrating the metal. STAHL, on the other hand, explained this phenomenon as a process of *decomposition;* phlogiston was driven out of the metal regarded as a compound, leaving behind the more primitive earths. On the question of the increase in weight during oxidation, STAHL remained silent. Says KOPP (1) : « Probably STAHL hesitated to accept the explanation of BECHER, BOYLE and N. LEMERY which assumed explicitly a ponderable material fire, for he perceived that absorption of fire cannot be harmonized with his hypothesis of the phlogiston in the form of fire ». STAHL did not explain how a metal could lose phlogiston and at the same time gain weight. Apparently this greater weight was regarded as incidental. The Frenchman LEMERY (1675) made combustion of metals a double phenomenon in which phlogiston escapes from the burning metal and a ponderable fire material simultaneously unites with that metal. (2)

The result is greater weight. JEAN REY in France and JOHN MAYOW in England suggested the effect as resulting from an absorption of air, but this happy guess remained unheeded at that time.(3) BOERHAAVE made the pertinent observation that weighing the same piece of metal when hot and when cold disclosed no change in weight. Hence the increase in weight could not be due to the entry of a ponderable heat-substance. He and URBAN HIAERNE (1712) suggested the entry of some foreign substance from the coal or wood or the containing vessel, but did not test their suggestions experimentally. Still others advanced the notion that phlogiston possessed negative weight. GUYTON DE MORVEAU (1772) assumed simply that phlogiston is lighter than air, that therefore its escape from the metal results in greater

(1) H. KOPP, *Geschichte der Chemie*, Dritter Theil, p. 127, 1845.

(2) H. KOPP, *Loc. cit.*, Dritter Theil, p. 123, where quotations from the original sources are given.

(3) H. KOPP, *Loc. cit.*, Dritter Theil, p. 140.

weight of the parts left behind — thus confounding specific and absolute gravity. All these explanations, except LEMERY's are conducted without the aid of a ponderable heat-substance. None of them was generally accepted. The increase in weight of metallic calx remained a great paradox in the chemistry of the eighteenth century.

A few eighteenth century scientist took the view advocated the preceeding century by NEWTON, HUYGENS and others, that heat was due to vibratory motion. During the eighteenth century heat was a ponderable substance with the Swedish chemist KARL WILHELM SCHEELE, the Dutch physicist PIETER VAN MUSSCHENBROEK and others; it was an inponderable substance with JOHANN TOBIAS MAYER of Göttingen, HERMANN BOERHAAVE of Leyden and others. Evidently, extreme lack of unanimity prevailed on the nature of material heat and the rôle it played in the most common everyday phenomena of combustion. Hardly was there room in eighteenth century science for both phlogiston and material heat. Were we permitted to personify the two, then phlogiston would be represented as a big boy suggesting to the little boy caloric : « If one of us were to get out of here there would be more room *for me.* » For a while little caloric was down and out most the time. Later the big boy Phlogiston was killed by a giant and the little boy, Caloric, occupied the field alone, and himself grew big.

This giant was the French chemist LAVOISIER. He destroyed the phlogiston theory, but permitted the theory of material heat to remain. In his time the word « caloric » was coined. In 1787 four French chemists, LAVOISIER, DE MORVEAU, BERTHOLLET and DE FOURCROY began to revise and simplify chemical nomenclature. As a result, LAVOISIER, in his *Traité élémentaire de chimie,* 1789, used the word « calorique ». While stating that calorique need not be considered as really material, LAVOISIER nevertheless included « calorique », along with light, in his list of chemical elements. With phlogiston out of the way the doctrine of caloric became firmly established. The new school of chemists had found a satisfactory way of explaining the increase in weight of metals during oxidation; hence heat as a ponderable substance passed away and heat as an imponderable remained and flourished until the middle of the nineteenth century. It enjoyed this long life notwithstanding the ingenious experiments of Count RUMFORD and Sir HUMPHRY DAVY, which really disproved the caloric theory.

We pass to our third topic, the views on heat held by early American scientist. As Count RUMFORD's epoch-making experiments are so well known and as they were carried on abroad, we shall omit description of them. On November 16, 1770, before RUMFORD had begun his experiments, a physician, HUGH WILLIAMSON, read before the American Philosophical Society in Philadelphia a paper on comets containing also conjectures on the origin of heat (1).

He considers heat as a mode of motion. « Whatever produces a tremulous motion in the particles of any body, excites heat in that body, and *vice versa*... Does heat therefore consist in nothing else than the rapid vibrations of the minute particles of any body ? »

In a communication addressed to DAVID RITTENHOUSE and dated June 20, 1788, entitled « New and curious theory of Heat and Light » (2), BENJAMIN FRANKLIN uses language which is very strange, if one considers that it was written at a time when the corpuscular theory of light and the material theory of heat were at their height. Says FRANKLIN : « Universal space, as far as we know of it, seems to be filled with a subtle fluid, whose motion or vibration is called light. » He did not consider heat to be due to the motion of small particles or molecules as did WILLIAMSON but rather to be vibrations of the ether. How close FRANKLIN was to the more modern views on radiant energy is shown by the following passage : « This fluid may possibly be the same with that which being attracted by and entering into other more solid matter, dilates the substance by separating the constituent particles and so rendering some solids fluid, and maintaining the fluidity of others; ...as there may be a continuity or communication of this fluid through the air quite down to the earth, is it not by the vibrations given to it by the sun that light appears to us; and may it not be, that every one of the infinitely small vibrations, striking common matter with a certain force, enters its substance, is held there by attraction, and augmented by succeeding vibrations, till the matter has received as much as their force can drive into it ? Is it not thus that the surface of this globe is continually heated by such repeated vibrations in the day, and cooled by the escape of the heat when those vibrations are discontinued in the night or intercepted and reflected by clouds ? »

These and other passages that we might quote illustrate the truth of

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(1) *Transactions Am. Philos. Society*, vol. I, p. 138. Philadelphia, 1789.
(2) *Transactions Am. Philos. Society*, vol. III, p. 5, 1793

the remark made by the Harvard professor JOHN WINTHROP, that FRANKLIN possessed extraordinary ability of starting big game for the natural philosophies to pursue and run down.

A few years later we find printed in the same Transactions a paper by the aged English chemist, JOSEPH PRIESTLEY, who spent the sunset years of his life in America. PRIESTLEY states on February 5, 1796 : « ...light and heat are almost universally allowed to be *substances,* though no person has been able to weigh them. »

More curious than convincing is a guess advanced by JAMES T. WATSON of New York on May 8, 1824 (1), relating to the heat produced by friction. « In rubbing two bodies together it is evident that the air in their pores, and interstices will be compressed, and as air readily yields heat by pressure, it is possible that the heat excited by friction may be thus explained. » Experiments on friction in the open and under the receiver of an air pump rendered partial support to this view. This explanation has the advantage of dispensing with a special heat substance; and it is really a mechanical or kinetic theory.

But the general sentiment among chemists and physicists crystallized in favor of the materialistic theory of heat. America's noted chemist, ROBERT HARE of Philadelphia, in 1822, gave his reasons (2) for rejecting the kinetic theory of RUMFORD and DAVY.

With the purpose of controverting the argument of DAVY he boldly entered upon the discussion of the mechanism of the motions of molecules in a body. According to the laws of (inelastic) impact he concluded that if equal weights of matter be mixed, the temperature ought to be the mean; and if equal bulks are mixed, the temperature ought to be as much nearer the previous temperature of the heavier substance as the weight of the latter is greater; but the opposite is in most instances true. This argument given at a time when not even the kinetic theory of gases had been worked out mathematically, marks an early attack of a problem which is not solved even at the present day. It was not difficult to criticize HARE's argument.

DENISON OLMSTED of Yale says (3) : « Little as I am disposed to

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(1) B. SILLIMAN'S, *American Journal of Science and Arts*, vol. VIII, p. 276. New Haven, 1824.

(2) *American Journal of Science and Arts*, vol. IV, p. 142, 1819.

(3) *American Journal of Science and Arts*, vol. XI, p. 358, 1826.

adopt the views of Sir HUMPHRY DAVY, I cannot but think that Dr. HARE has here suggested an answer which is not altogether unobjectionable. The application of his rule or test makes it necessary to suppose that the particles subjected to impact are all moving in the same direction — that they all actually come into collision, each upon each and that they are non-elastic; none of which conditions are capable of being proved actually to exist. »

Moreover, « it by no means establishes the doctrine of the materiality of heat, to prove that DAVY has failed of showing that it is a product of motion. Both parties in my view, evince how idle it is to reason respecting chemical phenomena upon mechanical principles. » This attack directed by OLMSTED against the reasoning of chemists drew from HARE a rejoinder (1) in which he re-affirms his argument and challenges OLMSTED to explain DAVY's experiment « in which a thermometer in the focus of one mirror is influenced by a hot body in the focus of another mirror the whole being within an exhausted receiver, ...if the cause of it is not material. » OLMSTED replied that DAVY's mirror experiment simply shows that radiation is not dependent on the presence of air; it does not prove that heat is a material substance. He pointed out that DAVY's molecular motions were conceived to be both rotatory and vibratory, while HARE considered them simply rectilinear and in one continued direction. It must be noted that this controversy is not between representatives of two rival schools but is between men who are both adherents of the materialistic school. At this time the mechanical or kinetic theory of heat had few friends in America. OLMSTED said in 1826 (2): « A few maintain that we have sufficient reason to deny its materiality, while a greater number think that its materiality is capable of being established by proof. »

In 1830 BENJAMIN SILLIMAN (3) spoke of light, heat and galvanism as « imponderable agents », evidently hesitating to call heat a « substance ». This is substantially the position taken by the Swede chemist BERZELIUS who spoke of light, heat, electricity and magnetism as « properties of bodies » (4), yet used the term « imponderable ».

(1) *American Journal of Science and Arts*, vol. XII, p. 52. New Haven, 1827.

(2) *American Journal of Science and Arts*, vol. XI, p. 356, 1826.

(3) B. SILLIMAN, *Elements of Chemistry*, vol. I, p. 1. New Haven, 1830.

(4) J. J. BERZELIUS, *Lehrbuch der Chemie*, übers. v. WÖHLER, 3 te Ausgabe, p. 11. Dresden und Leipzig, 1833.

However, twenty-nine years later, in SILLIMAN'S *First Principles of Physics*, 1859, heat is said to be « due to the vibratory movements of the molecules ». The earlier view of it as an « imponderable agent » is found in other American texts. (1)

But there were books printed in America which did not hesitate to use the phrase « imponderable substance », even as late as 1856 and 1863. (2)

In Europe the widely used text on chemistry of the Heidelberg professor LEOPOLD GMELIN spoke of heat as an imponderable substance (3). J. S. T. GEHLER takes the same stand in 1841. (4). In 1862 JOHN TYNDALL (5) stated in a lecture delivered at the Royal Institution in London, « till very lately ... the material theory had the greater number of adherents, being opposed by only a few eminent men ». TYNDALL'S book was reviewed favorably in the *American Journal of Science and Arts*, Vol. 86, 1863, page 310.

One consideration which delayed the acceptance of the kinetic theory of heat was the confusion which prevailed between heat and radiant energy. The two were assumed to be the same, to the extent that an argument against the one was taken to be an argument against the other. We read in a work of 1829, « the strongest argument in favor of the material nature of heat is probably that which is derived from its radiation ». (6)

PICTET suspended in an exhausted receiver a thermometer and found it capable of changing its temperature. From this he concluded that heat was capable of passing through a vacuum, hence must be an imponderable substance.

Time has shown that caloric and phlogiston were false keys for unlocking the secrets of nature. Nevertheless they were better than

(1) For instance, ALONZO GRAY'S, *Elements oJ Chemistry*, 2nd Ed., p. 22 New York, 1841.

(2) See E. TURNER, *Elements of Chemistry*, American edition, p. 5. Philadelphia, 1840. — JOHN A. PORTER, *Principles of Chemistry*, p. 27. New York, 1856. — JOHN JOHNSTON, *Manual of Chemistry*, 6th Ed., p. 17. Philadelphia, 1863.

(3) L. GMELIN, *Handbuch der Theoretischem Chemie*, vol. I, 1827, and later editions.

(4) J. S. T. GEHLER, *Physikalisches Wörterbuch*, Bd. 10, « Wärme », 1841.

(5) J. TYNDALL, *Heat as a Mode of Motion*, p. 37, 1866.

(6) *Natural Philosophy*, Library of Useful Knowledge, p. 1, « Heat ». London, 1829.

no keys, for they fitted well enough to assist JOSEPH BLACK, JOSEPH PRIESTLEY, KARL W. SCHEELE and others to wrest from nature several of her guarded secrets. Our brief story again exemplifies the truth expressed in Locksley Hall :

> Science moves, but slowly slowly,
> Creeping on from point to point.

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