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Robert James Morris, Jr.

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EIGHTEENTH-CENTURY THEORIES OF THE NATURE OF HEAT

A DISSERTATION

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BY

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Norman, Oklahoma

1965

EIGHTEENTH-CENTURY THEORIES OF THE NATURE OF HEAT

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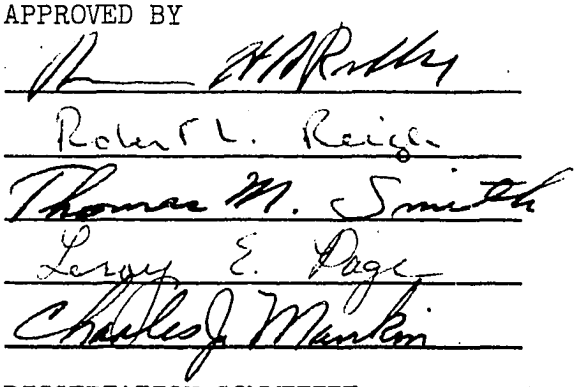

DISSERTATION COMMITTEE

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EIGHTEENTH-CENTURY THEORIES OF THE NATURE OF HEAT

INTRODUCTION

At the beginning of the eighteenth century, there were two primary theories regarding the nature of heat. One school of thought considered the subtle matter of fire as the cause of heat. This theory is discussed in Chapter I. Fire matter can be either free or imprisoned within the pores of substances. Fire particles are in constant motion, although this motion is suppressed when fire is confined. The theory derived from a strong seventeenth-century tradition. Its chief advocate and most influential supporter during the first half of the eighteenth century was Herman Boerhaave, although many of his ideas had been stated earlier in the century by such men as Wilhelm Homberg, Louis Lémery, and Willem Jacob van 's Gravesande. This theory of heat was dominant throughout the first half of the century, and it found expression in works by Petrus van Musschenbroek and the Abbé Jean Antoine Nollet.

About the middle of the century, Boerhaave's ideas concerning fire began to fuse with the phlogiston theory of Georg Ernst Stahl. This is described in Chapter II. The central figure in this development was Stahl's French disciple, Guillaume François Rouelle. Examples of the changing view are found in articles by Paul Henri Thiry, baron d'Holbach, and Gabriel François Venel in the Diderot Encyclopédie. French phlogistonists identified phlogiston with Boerhaave's concept of fire, and

they added the idea that fire is found chemically combined with other principles in inflammables and in metals and that fire is released during combustion and calcination. Rouelle's synthesis was expounded by his pupils, particularly Pierre Joseph Macquer, and it quickly superseded the older theory of heat. This newer concept is expressed in many of the more popular dictionaries and texts published during the last half of the century, for example those of Aimé Henri Paulian, Joseph Aignan Sigaud-Lafond, and François Para du Panjas, as well as in most of the articles dealing with heat theory which appeared in the Observations sur la physique prior to 1780.

Expressions of another theory of heat appeared from time to time throughout the century. This theory considered heat to be the vibratory motion of the particles of ordinary matter, and it is discussed in Chap-III. An early exponent of the vibratory concept was Isaac Newton, and explanations involving this view are found in the writings of John Harris, Stephen Hales, John Theophilus Desaguliers, and Benjamin Martin. Many of the advocates of this theory were Englishmen. During the 1770's and 1780's, Henry Cavendish and Joseph Priestley used explanations based upon this concept, and during the 1780's and 1790's, Stephen Dickson and James Keir offered the view in opposition to the caloric theory. Yet most English dictionaries and encyclopedias published after 1730 expressed belief in Boerhaave's theory of fire-matter-in-motion, and advocates of the opposing view appear more as conservative traditionalists rather than as proponents of a strong, virile scientific concept. Only a few persons attempted to establish a detailed theory of heat based upon the idea of vibration: the Russian, Mikhail Vasil'evich Lomonosov and the

Frenchman, Pierre Joseph Macquer. Despite the fame of some members of this school of thought, the vibratory theory remained the minority point of view throughout the eighteenth century.

During the 1770's, a different material theory of heat appeared. This new concept is described in Chapter IV. Emphasis upon the inherent motion of fire particles declined, and in the new theory, this feature of the older view is completely absent. The new concept of heat is intimately associated with the oxidation theory of Antoine Laurent Lavoisier. Lavoisier transformed combustion from a process of decomposition to one of combination, and he transferred the source of heat from the combustible substance to oxygen gas.

To account for the presence of fire matter in oxygen gas, he claimed that gases are the vaporous state of liquids which have boiling points far below common temperatures. The fire matter contained in oxygen gas is in the form of latent heat, and the release of heat during combustion is the same process as the release of heat during the condensation of steam. In the revised nomenclature, which appeared in 1789, the matter of heat was given the name "calorique," or "caloric" as translated into English. According to the older view, changes of state are brought about by fire matter acting as an agent to separate the particles of substances. In the caloric theory, these changes are caused by caloric chemically combining with the particles of substances. This explanation accounts for caloric becoming latent during changes of state.

In general, acceptance of the caloric theory of heat paralleled the acceptance of Lavoisier's theory of oxidation, and most eighteenth-century advocates of the caloric theory were Frenchmen. The most prolific

writers who supported the caloric theory were Armand Séguin and Antoine François de Fourcroy whose works are examined in Chapter V. Although they initially disagreed with some specific elements of Lavoisier's views, both came to accept his theory almost completely. Jean Antoine Claude Chaptal de Chanteloup, however, denied the analogy between gases and vapors and claimed that the state of caloric in oxygen gas bears no relationship to the state of caloric in vapors. Chaptal's explanation parallels a tendency in the later writings of Séguin and Fourcroy and even in the writings of Lavoisier to give less emphasis to explanations of changes of state in terms of the chemical combination of caloric and to give greater emphasis to physical explanations involving pore-space and a balance of forces.

Opposition to the caloric theory had no necessary connection with belief in phlogiston. Adair Crawford, whose work is discussed in Chapter VI, believed that phlogiston is different from caloric and that these substances tend to replace each other in chemical combinations. He agreed with Lavoisier that vital air is the source of caloric released during combustion, but he denied that heat is combined in substances. Absorption and release of heat is due to concomitant changes in specific heat. Crawford's ideas bear a striking similarity to Lavoisier's general theory. Crawford was able to incorporate in his theory many of the experimental data used to support the new chemistry, and hence his view tended to become a rallying-point for those who were impressed by these data and yet were reluctant to banish phlogiston from the realm of existence.

Crawford's views received substantial support from his contemporaries and created considerable controversy. Lavoisier himself felt it necessary to argue against some of Crawford's views and Séguin devoted a considerable portion of his writings to refuting various elements of Crawford's theory. Some of Crawford's ideas were used by phlogistonists and antiphlogistonists alike in supporting their own views and in arguing against their opponents.

Another group of critics equated phlogiston with fire matter and attacked the caloric theory directly. Among these were Jean Claude de Lamétherie, editor of the Observations sur la physique, and the geologist James Hutton. Their writings are examined in Chapter VII. Lamétherie and Hutton believed that the concept of heat associated with the new chemistry was the single foundation stone upon which the entire oxidation theory rested. Both thought that the crucial assumption in the caloric theory was that there is no fundamental difference between gases and vapors. Both emphatically denied that the caloric contained in oxygen gas resembles in any way the caloric contained in vapors. In their view, this argument vitiated the caloric theory of heat as well as the theory of oxidation based upon it.

Lavoisier's critics had little influence on him personally, although the tendency of some of his followers to deny the analogy between gases and vapors may have been due to the criticisms of such men as Hutton and Lamétherie. Claude Louis Berthollet even denied that the assumption of a material caloric was an essential feature of the new chemistry. Nevertheless, throughout these controversies and the wide range of proffered theoretical explanations, there was surprisingly

little argument concerning the nature of heat itself. Most agreed that heat is a material substance.

CHAPTER I

THE SUBSTANCE "FIRE" AND ITS MOTION AS THE CAUSE OF HEAT

Throughout the first three quarters of the eighteenth century the predominant heat theory explained heat as the result of the motion of a peculiar kind of matter, the matter of fire. Seventeenth-century foundations of this theory are found in the ideas of Pierre Gassendi (1592-1655) and Réné Descartes (1596-1650).[1] Descartes believed that heat phenomena are due to the movement of the earthy particles which make up ordinary substances. The motion of these particles is communicated to them by the motion of a more tenuous, subtle matter which fills the pore spaces within ordinary substances. Cartesians called this subtle, penetrating matter the "first element" and equated it to the matter of fire or light. Fire matter differs from ordinary matter in the smallness and the inherent motion of its particles.[2]

This Cartesian view was expressed in the eighteenth century by Jean Bernoulli (1667-1748). Bernoulli described sunlight as consisting

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[1]Gassendi believed heat is due to the rapid motion of small, spherical heat atoms; see James R. Partington, A History of Chemistry (3 vols.; London, 1961-1964), II, 463-464.

[2]Nicholas Malebranche, "Réflexions sur la lumière et les couleurs et la génération du feu," Mémoires de l'Académie Royale des Sciences, 1699 (1702), p. 33. For a more detailed discussion of Cartesian "elements," see Partington, History of Chemistry, II, 433-439; Hélène Metzger, Les doctrines chimiques en France du debut du XVIIe à la fin du XVIIIe siècle, première partie (Paris, 1923), pp. 362-372.

of streams of tiny particles which he called "massules."[3] The light and heat of the sun itself is due to the unbelievably violent agitation and perpetual collision of these particles.[4] Because of their extremely small size, these particles easily penetrate into the pores of the substances they strike. Bernoulli stated that heat

> est causée par le frottement continuel que souffrant les pores intérieurs ou leurs parois, quand les rayons y passent & agitent les petits filaments qui avancent hors de ces parois; il est clair que les parties des corps opaques, en étant ébranlées en diverses manieres, reçoivent cette qualité qu'on apelle chaleur.[5]

In the eighteenth century, one of the earliest attempts to apply the theory of fire-matter-in-motion to explain chemical phenomena was made by Wilhelm Homberg (1652-1715), German physician to the Duke of Orléans. Homberg's discussions of combustion and calcination also contain his ideas concerning the nature of fire. He thought that calcination is caused by the introduction of "particles ignées" or the "matiere du feu" into substances.[6] The increase in the weight of substances when calcined shows that fire matter has weight.[7] As calcination also occurs when sunlight is concentrated by a burning glass, fire matter is the same

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[3]Jean Bernoulli, "Essai d une nouvelle physique céleste, servant à expliquer les principaux phénomènes du ciel, & en particulier la cause physique de l'inclinaison des orbites des planètes par raport au plan de l'equateur du soleil, [1735]," Opera omnia, tam antea sparsim edita, quam hactenus inedita (4 vols.; Lausannae, 1742), III, 289. For Bernoulli's general Cartesian sympathies, see Pierre Brunet, L'introduction des théories de Newton en France au XVIIIe siècle avant 1738 (Paris, 1931), pp. 186-200, and passim.

[4]Bernoulli, Opera, III, 284. [5]Ibid., p. 289.

[6]Wilhelm Homberg, "Observations sur la quantité d'acides absorbés par les alcalis terreux," Mémoires de l'Académie Royale des Sciences, 1700 (1703), p. 69.

[7]Ibid.

as the matter of light. This fire has the ability to derange the particles of substances or fuse them. Flame, he said, is a fluid, lighter than air, composed of the matter of light mixed with volatile oil. Both the fire and the oil come from the burning object. The only difference between solar fire and terrestrial fire is that solar fire is "la simple matiere de la lumiere" not mixed with oil. Thus particles of solar fire are smaller than terrestrial ones.[8]

In a series of essays published in the memoirs of the French Academy of Sciences, Homberg attempted to establish a theoretical system to explain chemical phenomena. He listed salt, mercury, water, earth, and sulfur as the principles of matter.[9] Among these principles, the "souphre principe" is the only active one.[10] The sulfur principle is the matter of light or fire which becomes sensible only when joined to other principles.[11] The entire universe is filled with this fire matter and it is always acting and continually moving.[12] The sulfur principle may attach itself only superficially to the other principles or it may "entre dans la substance même de ces principes. . . ."[13]

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[8]Wilhelm Homberg, "Observations faites par le moyen du verre ardant," Mémoires de l'Académie Royale des Sciences, 1702 (1704), pp. 145-146.

[9]Wilhelm Homberg, "Essays de chimie," Mémoires de l'Académie Royale des Sciences, 1702 (1704), pp. 34, 37.

[10]Wilhelm Homberg, "Suite des essays de chimie, article troisième, du souphre principe," Mémoires de l'Académie Royale des Sciences, 1705 (1706), p. 88.

[11]Ibid., pp. 89-90, 95. [12]Ibid., pp. 89, 91.

[13]Wilhelm Homberg, "Suite de l'article trois des essais de chimie," Mémoires de l'Académie Royale des Sciences, 1706 (1707), p. 261.

Some of Homberg's ideas are echoed in the writings of another Cartesian Louis Lémery (1677-1743), son of Nicholas Lémery (1644 or 1645-1715) who had authored a very popular chemical textbook. The views of the younger Lémery concerning the nature of heat are contained in the memoirs of the French Academy for the year 1709.[14] Lémery believed in the existence of a particular matter which he called the matter of fire or of light. The particles of this matter are small enough to penetrate the pores of substances, these particles have a shape peculiar to themselves, and they are endowed with a tendency to perpetual movement.[15] This fire matter may traverse substances, and in certain instances it may be retained by them or unite with them.[16] Lémery thought that fire matter is nothing more than the matter of light itself, for the same effects can be produced by placing a substance in the focus of a burning glass as by placing it directly in a fire.[17]

Fire matter is the primary and the strongest dissolvent of terrestrial substances. It is the

> principe veritable de la chaleur, de le la lumiere, & même de la fluidité ou de la fusion de plusieurs corps terrestres, qui sans le mélange & l'action de cette matiere, conserveroient toûjours une forme solide.[18]

Thus solidity is the natural state of terrestrial bodies. Ice is the natural state of water, and the melting of ice into water is a true

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[14]Louis Lémery, "Conjectures et réflexions sur la matière du feu ou de la lumière," Mémoires de l'Académie Royale des Sciences, 1709 (1711), pp. 400-418.

[15]Ibid., pp. 406, 409. [16]Ibid., pp. 409-410, 415.

[17]Ibid., p. 413; cf. Homberg's views, p. 8, above.

[18]Lémery, p. 400.

fusion, in no way different from the fusion of metals except for the amount of fire necessary.[19]

In addition to producing fusion, the matter of light may be retained within substances or unite with them. The properties of fire depend upon the rapidity with which its particles move. If these particles are contained within an object, they may lose all or part of their motion.[20] Posing the question as to how substances should come in retain this fire matter if they are so porous and so easily traversed by fire, Lémery explained that when bodies are heated, their pores open and dilate. When heat agitation ceases, however, the pores contract and thus can imprison some fire in them.[21] Calcination is caused by this kind of imprisonment of fire matter. This is shown by the increase in weight of bodies when calcined and also by the release of fire matter when the bonds of the prison are broken as, for example, when a calx like quick-lime is dissolved in water.[22]

Light also may unite with substances to form combustibles. The difference between calces and combustibles is that combustibles need more external fire than calces do in order to break the bonds of the imprisoned light. Lémery said that the reason most calces do not burn is that the quantity of light contained in them is less than that contained in combustibles.[23]

Lémery was not precise in his discussion of heat itself, beyond stating that it is caused by the matter of fire or light. He stated that

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[19] Ibid., p. 414.

[20] Ibid., pp. 406, 409.

[21] Ibid., pp. 409-410.

[22] Ibid., pp. 401-403, 405.

[23] Ibid., pp. 410, 415-416.

the retention of fire matter within the pores of substances stops or at least retards the natural motion of the fire particles. This retained or imprisoned fire is not sensible, that is, it does not cause apparent heat phenomena; but fire or light matter can become sensible when it is released from its imprisonment.[24] This is what happens when quick-lime is dissolved in water and the water becomes heated. Although he was not explicit, Lémery implied that sensible heat phenomena are related to the degree of motion of the particles of fire matter and not necessarily related just to the quantity of this matter present.

According to Lémery, fire or light matter has weight, as evidenced by the increase of weight of substances when they are calcined. Combustion and calcination are opposite reactions, fire escaping during the former process and fire being absorbed during the latter.[25]

A shorter but a more detailed exposition on the nature of heat was published by the Newtonian popularizer Willem Jacob van 's Gravesande (1688-1742), professor of mathematics and astronomy and later professor of philosophy at Leyden.[26] 's Gravesande opened his discussion of fire

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[24]Stephen Hales (1677-1761), although denying the existence of a peculiar fire matter, employed the idea of imprisonment and release to explain the same phenomenon; Vegetable Staticks, or an Account of Some Statical Experiments on the Sap in Vegetables, Being an Essay towards a Natural History of Vegetation, Also a Specimen of an Attempt to Analyse the Air by a Great Variety of Chymico-Statical Experiments Which Were Read at Several Meetings before the Royal Society (London, 1727), pp. 285-286. See p. 68, below.

[25]Cf. Homberg's views, pp. 8-9, above. The explanation of combustion and calcination as being opposite reactions had been stated earlier by Robert Boyle (1627-1691), Isaac Newton (1642-1727), and others; see Hélène Metzger, Newton, Stahl, Boerhaave et la doctrine chimique (Paris, 1930), pp. 70-71, 75; Partington, History of Chemistry, II, 480-481, 530-532.

[26]Willem Jacob van 's Gravesande, Mathematical Elements of

by stating its general and most characteristic properties. Fire easily penetrates all substances, "however dense and hard they are."[27] But it does not merely pass through them, for some of the fire remains in the substance to make it grow hot. Thus, "Fire unites itself to Bodies."[28] When this happens, the substance expands, and aeriform fluids, for example, whose particles lack cohesion, acquire an increased elasticity. In some instances fire may be even attracted by objects when it is a certain distance away from them. This is shown by reflection and refraction phenomena.[29]

's Gravesande seems close to considering fire as an element which may enter into the chemical composition of substances. In describing the relation between fire and the ordinary matter of which a substance is composed, he wrote that fire "unites" with substances, or that in some cases it "coheres firmly with the Parts of Bodies." Thus smoke and vapor are parts of a substance separated from the more solid mass and agitated by the fire "that is join'd with them."[30]

's Gravesande cited the heat observed when two objects are rubbed together as demonstrating that "all Bodies contain Fire in them: for, by rubbing, Fire may be put in Motion, and separated from Body, but can by no means be generated that way."[31] Thus the heat of friction is not generated de novo within objects; but it is caused by the increased

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Natural Philosophy, Confirmed by Experiments, or an Introduction to Sir Isaac Newton's Philosophy, Written in Latin, trans. J. T. Desaguliers (2d ed., corrected; 2 vols.; London, 1721-1726), II, 1-22.

[27] Ibid., p. [1]. [28] Ibid., p. 2. [29] Ibid.

[30] Ibid., pp. 2-3. [31] Ibid., p. 2.

motion of the fire particles already present and by the motion of the particles of the objects themselves which are agitated by the moving particles of fire. Indeed motion is the essential, immediate cause of most heat phenomena, and not the cause of frictional heat alone.

The only difference between heat and light, he said, is in the nature of their motions:

> Heat and Light are to be attributed to the different Motions of Fire. Heat, in a hot Body, is the Agitation of the Parts of the Body and the Fire contained in it, by which Agitation, a Motion is produced in our Bodies, which excites the Idea of Heat in our Mind. Heat, in respect of us, is nothing but that Idea, and in the hot Body is nothing but Motion. . . .
>
> When Fire enters our Eyes in Right Lines, . . . it excites the Idea of Light. . . . A rectilinear Motion is the Motion of Light. . . . On the contrary, such a Motion is not requir'd in Heat: and that an irregular Motion is more for it, may be proved, because the Rays, that come directly from the Sun to the Top of a Mountain, produce no sensible Heat; whilst in the Valley, where the Rays are agitated with an irregular Motion by several Reflexions, there is often produced a very intense Heat.[32]

's Gravesande explained combustion as being the end result of the agitation of fire particles. In combustion, the agitation has reached a degree such that the parts of the burning object are separated from each other and carried off by the motion of the fire particles attached to them. The difference between inflammation caused by friction and inflammation caused by an externally applied flame is that in the case of friction, inflammation is produced by the fire contained within the inflammable substance itself, whereas in the latter case, inflammation is produced by the combined effects of the internal fire and the fire applied externally. This shows that sensible heat is not always proportional to the quantity of fire involved; for in the case of friction,

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[32] Ibid., pp. 13-14.

the quantity of fire remains constant, only its movement is changed; and in the case of the externally applied flame, both the quantity and the motion are changed.[33] In comparing the effects caused by a change in the quantity of fire as opposed to a change in the degree of motion of the fire particles, the latter would seem to be the most effective:

> All Bodies are dilated by the Action of Fire; but that Dilatation changes as the Heat changes; so that it seems to depend rather upon the Motion than the Quantity of the Fire; for Bodies are expanded as well by rubbing as by applying Fire to them externally.[34]

Expansion phenomena also show that, due to fire, the particles of a substance "acquire a repellent Force, by which they endeavour to fly from each other."[35] This force, which varies according to the degree of heat of the substance, is opposed to the force of cohesion which causes the particles of the substance to move towards each other. 's Gravesande explained changes of state as due to the balance between these opposing forces. When these two forces are almost equal and the particles of a substance scarcely cohere, the particles "yield to any Ipression [sic], and are easily mov'd one among another; whence we see that a Solid Body is chang'd into a Liquid by Heat. . . ."[36] Substances commonly considered to be natural fluids are fluid only because of the heat they contain. Water is melted ice; and in this respect water is no different from fused metals.[37] If the heat be increased so that the repellent force is

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[33] Ibid., p. 15; cf. Lémery's views, pp. 11-12, above.

[34] 's Gravesande, Natural Philosophy (2d ed.), II, 18.

[35] Ibid., p. 20. [36] Ibid.

[37] Cf. Lémery's ideas, pp. 10-11, above.

greater than the attraction of cohesion, the particles separate completely, "that is, [they] acquire an elastic Force, as the Particles of Air have, which Elasticity is encreased even in the Air by Heat."[38]

Many of the ideas of Lémery and 's Gravesande concerning fire are found in the works of Herman Boerhaave (1668-1738), one of the most widely known eighteenth-century writers on chemistry. Boerhaave's ideas concerning heat phenomena and even his manner of presentation are found in chemical literature over fifty years after the publication in 1732 of his text, the Elementa chemiae.[39]

Boerhaave devoted a lengthy section of his chemistry text to discussing fire. He began by assertively purging himself of any preconceived notions on the nature of fire so that he might examine the subject with an open mind:

> It is necessary, therefore, if we would keep clear of mistakes, to act with the utmost caution in our searches after a thing whose nature is so hidden and mysterious. And for this reason we must absolutely disengage our selves from all mere speculations, nor tive into any precarious hypothesis. . . . When we set about therefore to inquire what Fire really is, we must begin perfectly as though we knew nothing of the matter, and must intirely lay aside every notion that we had formed of it before.[40]

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[38]'s Gravesande, Natural Philosophy (2d ed.), II, 20.

[39]For a discussion of Boerhaave's influence and fame see Metzger, Newton, Stahl, Boerhaave, pp. 5-6, 191-193; Archibald Clow, "Hermann Boerhaave and Scottish Chemistry," An Eighteenth Century Lectureship in Chemistry: Essays and Bicentenary Addresses Relating to the Chemistry Department (1747) of Glasgow University (1451), ed. Andrew Kent (Glasgow, 1950), pp. 41-48; Partington, History of Chemistry, II, 749-751. The Scottish chemist Joseph Black (1728-1799) recommended his students to read Boerhaave's text, especially the section dealing with fire; Douglas McKie, "On Thos. Cochrane's MS Notes of Black's Chemical Lectures, 1767-8.," Annals of Science, I (1936), 102. For a discussion of Boerhaave's treatise on fire, see Metzger, Newton, Stahl, Boerhaave, pp. 209-228.

[40]Herman Boerhaave, Elements of Chemistry, Being the Annual

To determine the nature of fire, Boerhaave asserted that we must first examine the signs produced by fire which alone and universally prove its presence. Phenomena which are commonly cited as proving the presence of fire are heat, light, color, expansion or rarefaction, burning, and fusion. Heat, said Boerhaave, is a sensation and as such is too subjective and relative to be an absolute indicator of fire. Light also suffers from such acute examination; for although heat and light together indicate the presence of fire, an intense heat can exist without light, and conversely light can exist without heat.[41] Thus light is no sure indicator of the presence of fire, and as color is only a form of light, the criticisms of light apply also to color. An examination of the other possible signs, he continued, presents us with equal uncertainty.[42]

> It may be asked then, is there no effect of this wonderful cause [fire] which obtains always, and every where the same, being also utterly inseparable from fire, and not variable by objects? I should believe there is such a one; and . . . there is only one. For on a careful inquiry, I do not find any body, to which we may not apply that which all men call fire; . . . and all such bodies to which fire is thus applied, without one exception, are hereby render'd bigger, swell, and rarify, yet without any observable difference in their weight.[43]

Lectures of Herman Boerhaave, M. D., Formerly Professor of Chemistry and Botany, and at Present Professor of Physick in the University of Leyden, Translated from the Original Latin, trans. Timothy Dallowe (2 vols.; London, 1735), I, 79; hereafter cited as Dallowe Translation (1735).

[41]This same argument, used to show that heat and light are different, was made in the seventeenth century; see Muriel A. Bentham "Some Seventeenth Century Views concerning the Nature of Heat and Cold." Annals of Science, II (1937), 433.

[42]Boerhaave, Dallowe Translation (1735), I, 81-84.

[43]Herman Boerhaave, A New Method of Chemistry, Including the History, Theory, and Pracitce of the Art, Translated from the Original

Expansion then, is the "true, certain, individual and proper mark of Fire. . . ."[44] He added that in general, the degree of expansion substances will undergo when heated is proportional to their degree of rarefaction or inversely proportional to their densities.[45]

In the lengthy discussion which follows, Boerhaave confined himself mostly to an examination of heat phenomena and their explanation; and he postponed his consideration of fire matter itself to the end of his discussion. Although he was avowedly proceeding as if he "knew nothing of the matter" of fire, his explanations reveal certain definite assumptions regarding the nature of this substance, specifically that it is a kind of matter in motion.

One of the more striking features of his discussion is his emphasis upon motion and agitation:

> . . . [It] is not only possible, but really true in fact, that the most fix'd and solid Body, may be so continually agitated in its constituent Elements, that there sha'n't be any one Particle of the whole Mass, tho' ever so small, that will be absolutely at rest.[46]

He stated that "the last effect of cold, therefore, upon the particles of Bodies, would be their most intimate union and absolute rest: That

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Latin of Dr. Boerhaave's Elementa chemiae as Published by Himself to Which Are Added Notes and an Appendix Shewing the Necessity and Utility of Enlarging the Bounds of Chemistry, with Sculptures, trans. Peter Shaw (3d ed., corrected; 2 vols.; London, 1753), I, 212-213; cited hereafter as Shaw Translation (1753). This translation contains copious notes added by Shaw. These are mostly quotations from other authors. He quotes largely from Homberg, Lémery, and 's Gravesande, and he credits them with agreeing in general with Boerhaave. He also quotes Bacon, Boyle, and Newton, who Shaw said are opposed to Boerhaave's ideas and are supported by most English authors.

[44] Dallowe Translation (1735), I, 85.

[45] Ibid., p. 84.

[46] Ibid., p. 89.

of Fire, their dissolution, and perpetual agitation."[47] Again he said that, "I can't but infer, that in every solid Body that exists in our World, there is a constant peristaltic or oscillatory motion of all the particles that enter into its composition,"[48] and that "Air can never be at rest, but must suffer a perpetual agitation in all its parts, by which even its very ultimate particles must be kept in a constant oscillation."[49]

At this point in his exposition, Boerhaave committed himself to the extent that he would call by the name "Fire" that "Being, however otherwise unknown," whatever it may be, which can penetrate all substances and expand them.[50] Fire, he said, is contained in all space, "tho' not always discoverable by us," and it is continually in motion. It is present even at the lowest temperatures, although many persons mistakenly suppose that there is no fire left when the thermometer registers zero degrees.[51]

> And hence it appears probable, that fire is always contained, as well as it is always in motion or action, both in vacuo, and in the void spaces of solid bodies, as in so many vessels, and thus contunually produces certain operations inseparable from it; all which principally aim at this, viz, to remove the elements from one another. . . .[52]

Boerhaave stated that "fire is never lodg'd in the proper substance of bodies, but only in the interstices, which are left between the particles, even of the most solid bodies."[53] The separation of the

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[47] Ibid., p. 91. [48] Ibid., p. 93.

[49] Ibid., p. 96. [50] Ibid., p. 106.

[51] Shaw Translation (1753), I, 245-246.

[52] Ibid., p. 246. [53] Ibid., p. 247.

particles of substances by the interstitial fire is opposed by the mutual attraction of these particles for each other. This attraction tends to decrease the void spaces among particles and to extrude the fire contained in them.

> Thus there would be a perpetual action and re-action between the fire in the pores, endeavouring to expand the particles, and the natural endeavours of bodies, which tends to make them contract more closely. . . . Thus the two principles, the one expansive, the other contractile, prevail through all bodies, and become the causes of a multitude of corporeal actions, whose power or energy, therefore, can hardly be conceived from the idea we have hitherto had of them, and is thoroughly known by none but God himself.[54]

The action of friction is to alternately compress and expand the particles of matter. In this movement all parts are pressed, loosened, and rapidly moved.[55] Boerhaave thought that Newton was incorrect in assigning to vibration alone the sole cause of heat. Percussion and friction do indeed cause the particles of an object to vibrate rapidly, and these vibrations will last some time and are more pronounced in elastic substances. But Boerhaave argued that even vibrations of elastic substances "quickly cease among us;" and in addition, fire is never generated de novo.[56] The initial cause of the heat of attrition is indeed vibration, but it is primarily vibration of the particles of fire lodged within the pores.

> . . . hence in bodies under this attrition, and in fire equably distributed through the pores thereof, we may suppose a great degree of motion produced, and long continued: but this cannot be without the neighbouring and ambient air being equally agitated by both the

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[54] Ibid., pp. 246-247, cf 's Gravesande's views. pp. 15-16, above.

[55] Shaw Translation (1753), I, 249.

[56] Ibid., pp. 254, 296.

> said means. . . . But since by the motive causes of the rubb'd bodies, a new motion is added to the fire, besides that common one which it had before, the power of the fire must hereby be increased, which, as it tends to expand bodies, will presently discover itself by this sign; and hence the power of fire may be understood, as excited by friction. . . .[57]

The heat of percussion is produced in the same manner as frictional heat. Percussion causes the particles of an object to vibrate, "after the same manner as a cord, once struck, will continue its tremors, or a bell its sonorous undulations a long time."[58] This vibration in turn increases the motion of the interstitial fire.

In some instances the act of rubbing may concentrate fire from the surroundings.[59] But in the cases of both friction and percussion, the important process is the increased agitation produced in the fire already contained within the substance. The effects of fire are not due to its quantity alone. A burning glass causes an increase in the quantity of fire in a substance, but the same effects may be produced by percussion which increases the motion of the fire already present.[60] It is the amount of fire <u>in movement</u> which is important.

Boerhaave's emphasis on movement is almost overwhelming. He said that "water only becomes water, by virtue of the motion of the fire lodged in it."[61] And as agitation produces heat, so fire produces agitation, for

> fire, in entering dense bodies, shakes the particles thereof, and thus causes vibrations, which will be greater according to the degree of expansion, and more durable according to the density; which also,

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[57] <u>Ibid</u>., pp. 249-250.

[58] <u>Ibid</u>., p. 254.

[59] <u>Ibid</u>., p. 252.

[60] <u>Ibid</u>., p. 254, 274, 277, 281.

[61] <u>Ibid</u>., p. 365.

> so long as they continue, will agitate the contained fire, in the same manner as attrition has before been observed to do in elastic bodies.[62]

Motion is also essential in the production of heat by combustion.[63]

In Boerhaave's theory, the flame of combustion is not composed of the pure matter of fire. Flame depends upon the presence of an aliment or pabulum for its existence. This pabulum forms only a small part of the substence of combustibles; but this does not mean that the non-pabulum portion takes no part in the production of heat or in intensity of the flame. The intensity of the flame depends upon the gross amount of matter which is set to vibrating; and it is by increasing the total amount of vibrating matter that the non-pabulum portion of combustible substances increases the force. The role of air in combustion is to hold the fire and pabulum together by its pressure so that the other two can react and vibrate.[64]

Boerhaave explained changes of state by the action of fire which separates the particles of matter and "hinders the particles, as they touch one another, from clinging, or cohering. . . ."[65] To account for the time required for a heated body to cool, he assumed that fire "may be united with all solid bodies" and adhere to them for some

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[62] Ibid., p. 253.

[63] For a discussion of the role of motion and attrition in Boerhaave's explanation of animal heat see Everett Mendelsohn, Heat and Life: The Development of the Theory of Animal Heat (Cambridge, Mass., 1964), pp. 71-74.

[64] Shaw Translation (1753), I, 332. For a detailed discussion of Boerhaave's theory of combustion, see Metzger, Newton, Stahl, Boerhaave, pp. 228-245.

[65] Shaw Translation (1753), I, 217; see p. 20, above.

time.[66] The power of retention of fire is somehow related to the density of the body involved. He thus explained the long time required to freeze water as being due to the density difference between air and water.[67]

He was aware that the boiling point of liquids is constant, and he cited Guillaume Amontons (1663-1705) as having first shown this. He also cited Gabriel Daniel Fahrenheit (1686-1736) as having demonstrated that this temperature is modified by the pressure of the air, although the temperature is constant for a given pressure.[68] Boerhaave explained the effect of the air as holding the particles of the liquid together thus requiring more or less fire to separate them.[69] His explanation of the constancy of boiling points makes it clear that he was aware of the constancy of freezing points also:

> . . . it seems probable, that when the Fire has so disposed Bodies, that it can pass, and exert itself equably through their Pores, then, no more Fire can be united with them, than what is actually in them at that time; and this seems to be the case in Fluids as soon as ever they begin to boil; in Solids, when the force of the Fire has perfectly melted them. . . .[70]

Among the properties common to matter, weight is the principle one; and Boerhaave inquired whether fire, being a substance, also has weight.[71] He weighed a large mass of iron when heated to redness and

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[66] Ibid., p. 284.

[67] Ibid., p. 288.

[68] See Martin K. Barnett, "The Development of Thermometry and the Temperature Concept," Osiris, XII (1956), 298-299.

[69] Ibid., pp. 233-234; cf. Dallowe Translation (1735), I, 104. Cf. Isaac Newton, Opticks, or a Treatise of the Reflections, Refractions, Inflections, and Colours of Light, (2d ed., enlarged; London, 1718), pp. 318-319 [Query 11].

[70] Boerhaave, Dallowe Translation (1735), I, 158; cf. Shaw Translation (1753), I, 289.

[71] Shaw Translation (1753), I, 285.

when cold, and he found no difference between the two weights.[72] As fire has no weight, it can not be due to the presence of fire that calces weigh more than the substances from which they are formed. The increased weight is due to some other matter which is introduced.[73]

Toward the end of his discussion, Boerhaave summarized his conclusions regarding the nature of fire itself. The particles of fire are corporeal. They are the smallest of all bodies yet known, they are the most solid of all bodies. The particles are perfectly smooth, even, and polished on their surfaces. They are never absolutely at rest.[74]

Boerhaave devoted most of the section on fire in his Elementa chemiae to the description of a vast array of heat phenomena without offering much theoretical explanation. He described in detail the production of heat by means of lenses and mirrors, and in this discussion he hinted at the identity of light and elementary heat.[75] He devoted considerable space to describe the production of heat by mixing different substances. He offered no explanation of this heat except to attribute it to some sort of reaction between the substances mixed. In the lengthy section the production of heat by friction and percussion, he attributed the heat to an increased motion of the fire particles contained within the substance.

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[72] Ibid., pp. 285-286.

[73] Ibid., p. 368; cf. Douglas McKie, "Béraut's Theory of Calcination (1747)," Annals of Science, I (1936), 269-293.

[74] Shaw Translation (1753), I, 359-364.

[75] Ibid., pp. 362-364.

In all of Boerhaave's discussion the emphasis is upon agitation, oscillation, or vibration. Indeed, practically all the observable heat phenomena are due to motion, motion in which the role of the fire element seems to receive little emphasis. The universe is a plenum of fire which imparts movement to corporeal substances if there happen to be any present. The character of the fire contained within an object is no different from the fire contained in a vacuum. Fire does not belong to the category of things which may become a constituent part of a substance, although he did state it may adhere for a time to heated objects and expand around them "after the manner of an atmospere [sic]. . . ."[76]

In 1742, 's Gravesande published the third edition of his Mathematical Elements of Natural Philosophy, ten years after the appearance of Boerhaave's ideas concerning the nature and action of fire. In his preface, 's Gravesande specifically acknowledged Boerhaave's treatment of fire;[77] but he by no means agreed with all of the latter's views.

's Gravesande's treatment of the subject in this later edition was considerably longer and more detailed than his earlier discourses. In his earlier editions, for example, he had made no reference to the nature of the particles of fire themselves; in the third edition he made his stand explicit: "The intimate Nature of Fire is unknown; but wherever

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[76] Ibid., p. 286.

[77] Willem Jacob van 's Gravesande, Mathematical Elements of Natural Philosophy, Confirm'd by Experiments, or an Introduction to Sir Isaac Newton's Philosophy, trans. J. T. Desaguliers (2 vols.; 6th ed.; London, 1747), I, xxx. This is a translation of the third Latin edition of 1742. Cf. Willem Jacob van 's Gravesande, "Du Feu," Elémens de physique démontrez mathématiquement et confirmez par des expériences, ou introduction à la philosophie newtonienne, ouvrage traduit du Latin, trans. Elie de Joncourt (2 vols.; Leide, 1746), II, 75-114.

we find Heat and Light, we say that there is what we call Fire."[78] He called heat and light "Tokens of the Presence of Fire."[79] Here he seems opposed to Boerhaave, who had expounded upon the nature of the fire particles and had eliminated both heat and light as valid indicators of the presence of this elementary substance.[80] Yet 's Gravesande noted farther on that expansion "forms a new Token of the Presence of Fire, which is more certain than those mention'd before [heat and light]. . . ."[81] He restated his idea that heat and light are different modifications of fire and his idea that fire can unite to, adhere to, and can be attracted by the particles of other substances.[82]

In addition to accepting some of Boerhaave's views on expansion, 's Gravesande added other ideas which he included for the first time in this 1742 edition. Fire itself, he said, has no sensible weight. Hence the increase in weight of some substances exposed to fire is due to "subtile Parts, distinct from Fire, which penetrate Bodies by the Action of Fire. . . ."[83] 's Gravesande described the communication of heat, without change of state or decomposition, as "the weaker Motion of Fire."[84] The "more violent Motion of Fire" is that which causes fusion and vaporization.[85] His explanation of fusion and vaporization is unchanged from his earlier edition, although he added that the boiling temperature

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[78] Natural Philosophy (6th ed.), II, 63. [79] Ibid.

[80] Cf. Boerhaave's views, p. 17, above.

[81] Natural Philosophy (6th ed.), II, 67.

[82] Ibid., pp. 63-66, 86. [83] Ibid., p. 64.

[84] Ibid., p. 82. [85] Ibid., p. 85.

depends upon the degree of compression of the liquid.[86]

His discussion of heat communication is more detailed. Substances expand when heated; and fire matter tends to equilibrium, that is, fire matter moves until adjacent objects possess equal degrees of heat as determined by a thermometer.[87] Different substances are not heated with equal ease because heat depends upon agitation of the parts of substances, and the parts of different substances differ as to their density and mutual cohesion. For this reason "unequal Actions of Fire are required to the Communication of equal Degrees of Heat: And the Heat is not proportional to the Quantity of Fire."[88] 's Gravesande explicitly differentiated between the quantity and the degree of heat:

> If a Person puts both his Hands, when they are equally hot, one upon Wood, and the other upon Marble, both equal in Bulk, and equally hot, but the Heat of which is sensibly less than that of the Hands; the Hand, which lies upon the Marble, will lose more Heat, and communicate a less Degree of Heat to the Marble, than the Degree which the Wood has acquir'd from the Hand laid upon it, which does not lose so much Heat. These things are so sensible, as to require no other Measures.[89]

Lémery, 's Gravesande, and Boerhaave emphasized that motion is a primary attribute of fire matter and also the essential effect which this matter has on other substances. All agreed on the close association and similarity between light and elementary fire. Homberg and Lémery stated they are the same; 's Gravesande said heat and light are the effects of the same fire; Boerhaave was less definite, but he hinted at

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[86] Ibid., p. 86; cf. Boerhaave's views, pp. 22-23, above.

[87] Ibid. In the earlier edition, 's Gravesande wrote that thermometers are useful but that the relation between degrees of heat and degrees of expansion of the thermometer fluid is unknown; Natural Philosophy (2d ed.), II, 19.

[88] Natural Philosophy (6th ed.), II, 83. [89] Ibid., p. 84.

the identity of fire and light. Lémery, 's Gravesande, and Boerhaave agreed that fire particles easily penetrate all objects, that solidity is the natural state of substances, and that fluids are such only by virtue of the movement imparted to their particles by fire.

The three believed that the primary effect of fire is due to its movement. 's Gravesande and Boerhaave both cited friction and percussion phenomena to demonstrate the role of motion or vibration in producing heat; both were explicit in stating that the heat of a body is not proportional to the quantity of fire contained in it but is due to a combination of quantity and degree of movement of the fire particles. Boerhaave followed 's Gravesande not only in this but also in explaining the operation of many natural phenomena in terms of the constant reaction between the particles of corporeal substances and the particles of fire. The former possess a cohesive force which tends to draw them together while the fire particles are opposed to this cohesion and tend to separate the parts of the former.

Homberg and Lémery agreed that fire matter has weight. 's Gravesande, however, agreed with Boerhaave that elementary fire has no weight and that the greater weight of calces is due to the introduction into the substance of some other matter.

The main difference between Boerhaave and his predecessors is in the role of fire in chemical phenomena. Both Lémery and 's Gravesande treated fire more as a possible constituent of substances than Boerhaave permitted himself to do. Lémery thought fire could be imprisoned within a substance and regain its movement when released. It seems only a short step from this to consider fire as being combined with the particles

of the substance. 's Gravesande went further in this direction by asserting that fire can firmly cohere to the particles of substances, and he added that fire is attracted to bodies at certain distances. It is by means of this cohesion and attraction that the particles of a body are separated from each other and thus set on fire. Boerhaave, following 's Gravesande, stated that fire could adhere for a time to the particles of a substance to explain the time required for a body to cool. But this is all that Boerhaave would admit. For him, combustion is a reaction between the particles of fire and the pabulum, two substances which have to be held together by air pressure in order to react. The question of attraction or adhesion is not involved.

Boerhaave's long and detailed discussion of fire was acknowledged by Petrus van Musschenbroek (1692-1761), a pupil of both Boerhaave and 's Gravesande.

> The famous Boerhaave has treated so completely concerning fire, that we have little else to do but to repeat the same things after him, to which little can be added.[90]

Musschenbroek's beliefs regarding the nature of heat place him in the same tradition as Lémery, 's Gravesande and Boerhaave. "What is Heat in bodies?" It is

> A certain quantity of fire in motion in the interstices of the parts, and concealed in the pores of the particles. And therefore bodies are so much the hotter, as they contain more fire in motion.[91]

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[90]Petrus van Musschenbroek, The Elements of Natural Philosophy, Chiefly Intended for the Use of Students in Universities, trans. John Colson (2 vol.; London, 1744), II, 1.

[91]Ibid., p. 46.

He described fusion as a separation of the parts of substances by the action of fire. In this process, fire overcomes the cohesive force among the parts of substances "so that they are generally dissolved from mutual contact, and swim about in the fire," for if the particles touch, they will cohere.[92] Musschenbroek followed 's Gravesande in believing that light and heat are only different modifications of fire, light resulting when fire moves in straight lines and heat when the motion is disorderly.[93] He agreed with Homberg and Lémery in attributing gravity to the fire element.[94] This is demonstrated by the increase of the weight of substances when calcined.[95] The reason that a heated iron weighs the same as a cold one is that the expansion of the heated iron gives it an increased buoyancy in air. This counteracts the increase in weight due to the fire particles.[96]

Musschenbroek regarded fire as a substance possessing motion, solidity, and gravity. Its particles are extremely subtle and must be "smooth and slippery" in order to penetrate all other substances. Although fire is endowed with mobility, this motion can be reduced or stopped, as evidenced by the absorption of fire in metallic calces.[97]

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[92] Ibid., p. 4.

[93] Ibid., p. 57; cf. 's Gravesande, Natural Philosophy (2d ed.), I, 13-14.

[94] Musschenbroek, II, 19; cf. Lémery, pp. 401-404, 405.

[95] Musschenbroek, II, 15, 19.

[96] Ibid., pp. 15-16. This seems to be a reference to Boerhaave; see Dallowe Translation (1735), I, 154; see p. 23-24, above.

[97] Musschenbroek, II, 19-20.

He later described the state of fire in calces as being imprisoned within the pores of the calx.[98]

The Abbé Jean Antoine Nollet (1700-1770) followed Boerhaave in believing heat to be the effect of fire matter in motion; but he opened his discussion of fire with the pessimistic note that nothing definite had been proven about the nature of this substance:

> Après une étude de deux ou trois mille ans, après les méditations des Descartes, des Newton, des Malbranche, après les observations & les expériences des Boyle, des Boerhaave, des Reaumur, des Lémery, &c. nous en sommes encore à sçavoir definitivement si le feu est une matière simple, inaltérable, destinée à produire par sa présence ou par son action, la chaleur, l'embrasement, la dissolution des corps; ou bien si son essence consiste dans le mouvement seul, ou dans la fermentation des parties qu'on nomme inflammables, & qui entrent comme principes, en plus ou moins grande quantité dans la composition des mixtes.[99]

Nollet said that the opinion that fire consists in movement alone no longer has any supporters. The idea which attributes the internal movement of the particles of substances to the existence of a peculiar fire matter combines the two opposing views; and this is the view which Nollet accepted.[100] He agreed with the majority of physicists

> qu'il y a dans la Nature un fluide propre à cet effect, créé tel dès le commencement, & qui n'a besoin que d'être excité pour agir: que ce soit l'éther, que ce soit le premier ou le second élément de Descartes, c'est ce que je n'examine point ici; le nom n'y fait rien. ...[101]

It makes no difference what this substance is called, and the same matter

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[98] Petrus van Musschenbroek, Cours de physique expérimentale et mathématique, trans. Sigaud de la Fond (3 vols.; Paris, 1769), II, 377. See Lémery's views, pp. 10-11, above.

[99] Jean Antoine Nollet, Leçons de physique expérimentale (3d ed.; 6 vols.; Paris, 1753-1764), IV, 154. In the various editions of this work examined, from this 1753-1764 edition to a "Nouvelle" edition of 1784, the section on fire is unchanged.

[100] Ibid., pp. 154-155. [101] Ibid., p. 155.

causes both burning and vision: "le feu & la lumiere considérés dans leur principe, sont une seule & même substance différemment modifiée."[102]

In Nollet's view, fire cannot be due to movement alone, because all natural movement dies away and finally ceases entirely when distributed to a larger quantity of matter. This is not the case for fire. Indeed, fire may decrease when distributed but it never disappears, and in some cases it actually increases as can be seen when a spark becomes a flame.[103] Thus, fire is true matter. It has extension, solidity, mobility, and fluidity. Its particles are extremely small and they exist everywhere. Fire has weight, although Nollet cited Boerhaave as showing the contrary.[104] The fire matter can actually be seen, or at least its presence is visible in the different refractions which light undergoes when it passes through water being heated over a fire.[105]

Nollet noted that he was following Leonard Euler (1707-1783) when he said that fire acts in two different ways in substances.[106] Sometimes fire only causes a motion of the particles of the substance. This movement "on nomme Chaleur par rapport à nos sens."[107] At other

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[102] Ibid. [103] Ibid., p. 158. [104] Ibid., pp. 168-178.

[105] Jean Antoine Nollet, "Recherches sur les causes du bouillonnement des liquides," Mémoires de l'Académie Royale des Sciences, 1748 (1752), p. 67.

[106] Euler submitted a paper on the nature and propagation of fire for the prize offered by the French Academy of Sciences in 1738. Papers were also submitted by Gabrielle Emilie du Chatelet-Lomont (1706-1749) and François Marie Arouet de Voltaire (1694-1778). For a brief resume of the various views, see the editor's comments in François Marie Arouet de Voltaire, Oeuvres complètes de Voltaire (Nouvelle ed.; 52 vols.; Paris, 1877-1885), XXII, [279]-281. Voltaire's paper is reprinted in ibid., pp. 281-325.

[107] Nollet, Leçons de physique, IV, 190.

times, fire acts to separate and dissipate the molecules of substances, as is seen in combustion.[108]

Fire also may be contained within objects in two different states. It may be completely imprisoned within the substance. Fire is imprisoned when the parts of substances come together to form a small mass. Thus contained, the fire is under more or less tension depending upon its degree of compression.[109] Although Nollet is not explicit, he seems to have believed that it is the fire in this state which, when released, causes the actual separation and dissipation of the parts of substances during combustion. In the second state, fire matter fills the pores within an object. These pores are interconnected and may have access to the surface.[110] Nollet seems to imply that it is while in this latter state that fire acts to move the parts of substances to cause heat.

Lémery's influence is seen where Nollet described the states of imprisonment of fire within a substance. The small masses, which Nollet described as containing the completely imprisoned fire, are something like molecules composed of separate particles. A sensible substance is composed of an accumulation of these molecules; and the fire which causes heat resides in pore spaces existing among these molecules, not inside them. The fire which causes flame is contained within the molecules themselves.

Toward the end of his discussion, Nollet stated that fire is present and always in action in all substances whether inflammable or

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[108] Ibid., p. 191.

[109] Ibid., pp. 201, 204-205.

[110] Ibid., p. 201.

not. He asked the question what kind of motion fire possesses, is it circular or vibrational? He did not know.[111] However, a contemporary of Nollet is and Secretary of the Royal Academy of Sciences, Jean Jacques Dortous de Mairan (1678-1771), thought fire matter consists "de petite tourbillons d'un fluide encore plus subtil qui tourne autour de leur centre ou de leur axe avec une paridité indéfinie."[112]

De Mairan was in the fire-in-motion tradition and expressly accepted Boerhaave's definition as the oasis for his own work:

> Et la matière du feu élémentaire de Boerhaave, de quoi seroit-elle composée, si ce n'est de semblables tourbillons ou globules élastiques? Cet illustre Médecin a montré par mille expériences & par autant de judicieuses réflexions dont sa Chymie est remplie, que la matière de feu étoit répandue dans tous les corps, tant fluides que solides, où elle n'avoit besoin que de certaines circonstances pour se manifester à nos sens; qu'elle étoit toüjours plus ou moins en mouvement, que son caractère distinctif, & auquel se réduisent tous les autres, étoit le ressort, l'expansion & la propriété de raréfier & de dilater tous les corps. Aussi ne trouverois-je nul inconvénient à la prendre pour la matière subtile que j'ai adoptée dans ma Dissertation sur la Glace, elle en a toutes les propriétés, & elle en remplit parfaitement les fonctions.[113]

Boerhaave's fire matter surrounds the particles of substances; and therefore, the state, or cohesion, or durability of a substance depends upon the agitation and elasticity among the particles of fire.[114] For De Mairan, cold is not a negative being; it is only a lesser heat, or a lesser movement of the subtle matter which constitutes fire.[115]

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[111] Ibid., pp. 206-207.

[112] Jean Jacques Dortous de Mairan, Dissertation sur la glace, ou explication physique de la formation de la glace, & de ses divers phénomènes (Paris, 1749), p. 19. For de Mairan's Cartesian views, see Brunet, Newton en France, pp. 115-121, 165-176.

[113] Ibid., p. xxvii.

[114] Ibid., pp. 20-21.

[115] Ibid., p. 31.

Cooling involves both decreasing the elasticity of fire or its degree of motion. He implied, however, that freezing is due primarily to a decrease of movement.[116]

The concept which explained heat phenomena as due to fire matter in motion was the dominant theory during the first half of the eighteenth century. During the middle of the century, however, it began to be influenced by the phlogiston concept of the German chemist, Georg Ernst Stahl (1660-1734), and a new theory of heat came into being.

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[116] Ibid., pp. 36-37, 42-43.

CHAPTER II

FIRE, HEAT, AND IDEAS OF PHLOGISTON

The theory of fire-matter-in-motion underwent an important change during the mid-eighteenth century. In this change, fire matter became an elemental, chemical constituent of substances, able to unite with other principles. At the same time, it retained its former role as an agent in chemical and physical processes. Thus two fires came into existence, fixed fire and free fire; and that which is fixed, united to other principles as a constituent of substances was called phlogiston.

Early expressions of this change in heat theory are found in the Diderot Encyclopédie.[1] Although the Abbé Nollet had mentioned that fire within substances can exist in two states, Gabriel François Venel (1723-1775), professor of chemistry in Montpellier, defined these states as combined and free. Fire that enters into composition with substances is called phlogiston.[2] The other state of fire is the "principe de la chaleur."[3]

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[1] Encyclopédie, ou dictionnaire raisonné des sciences, des arts et des métiers, par une société de gens de lettres, ed. Denis Diderot and Jean Lerond d'Alembert (17 vols.; Paris, 1751-1765); hereafter cited as Encyclopédie. Cf. Gérard Vassails, "L'Encyclopédie et la physique," Revue d'histoire des sciences, IV (1951), 305, 307-309.

[2] Gabriel François Venel, "Feu, (Chimie)," Encyclopédie, VI (1756), 609.

[3] Ibid.

Another writer for the Encyclopédie, Jean Lerond d'Alembert (1717-1783), explained Boerhaave's views in some detail and cited Lémery and 's Gravesande as agreeing with him.[4] D'Alembert dismissed the idea that heat is due to vibrations alone by stating that "Toute cette doctrine est bien vague."[5] Although agreeing with Boerhaave on the general nature of fire, d'Alembert disagreed with him in certain particulars. Most important, he felt that fire has weight. This has been shown by Musschenbroek; and although the increase may be due to the introduction of some other substance, as Boerhaave had claimed, it has never been demonstrated.[6]

D'Alembert also disagreed with Boerhaave's ideas concerning the relation between the expansion of objects and their weight or the degree of cohesion of their particles. If there be a relationship, it is unknown. Boerhaave had implied and 's Gravesande and Lémery had stated that fire and light are the same thing; but d'Alembert said that these two things are different and that Musschenbroek was wrong in saying that they are the same.[7] In other cases, d'Alembert agreed with Boerhaave's explanation. For example, frictional production of heat, he said, is caused "par le mouvement que ce frotement excite dans les parties du feu qu'ils [substances] contiennent. ..."[8]

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[4]Jean Lerond d'Alembert, "Chaleur," Encyclopédie, III (1753), 23.

[5]Ibid., p. 25.

[6]Jean Lerond d'Alembert, "Feu, (Physiq.)," Encyclopédie, VI (1756), 600-601.

[7]Ibid., p. 599.

[8]Ibid., p. 601.

The chemical effects of fire were treated more thoroughly by Paul Henri Thiry, baron d'Holbach (1723-1789). In arguing against the views of the phlogistonist Georg Ernst Stahl (1660-1734) that heat is a movement pure and simple, d'Holbach distinguished "le feu élémentaire," which he described as fire "qui n'est point combiné aux corps," from the fire which is combined.[9] Combined fire is known as phlogiston, and it can become elementary fire when it is set free or disengaged from the substance with which it is combined.

Elementary fire resides within the pores of objects. When a substance is rubbed, the free fire is agitated by vibrations and it communicates its movement to the particles of the substance. The movement of free, elementary fire may also communicate its motion to the fire combined within the object and so bring about combustion. The movement which elementary fire imparts to the particles of substances diminishes the cohesion of these particles and thus causes fusion.[10]

The contributors to the Encyclopédie agreed that heat phenomena are to be explained in terms of the matter of fire in motion. Baron d'Holbach and Venel were acquainted with the work of Stahl.[11] Both of these writers distinguished between combined fire and free, elementary fire, and they attributed most heat phenomena to the movement of the latter. D'Alembert, on the other hand, apparently did not agree with the

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[9]Paul Henri Thiry, baron d'Holbach, "Fusion," Encyclopédie, VII (1757), 400.

[10]Ibid., pp. 398, 400.

[11]Gabriel François Venel, "Calcination," Encyclopédie, II, (1751), 542-545. See p. 36 and n. 2, above.

phlogiston concept.[12] His belief that fire has weight and his citation of the increased weight of calces as proof of this show that he was in the tradition of Lémery and Musschenbroek and considered combustion and calcination as reverse processes.

These data indicate that the concept of combined fire was due to the influence of the phlogiston theory, that some chemists equated phlogiston with fire matter, the same fire matter responsible for other heat phenomena. However, this concept was not that which Stahl propounded. Stahl considered phlogiston, the principle of inflammability, to be an earthy principle which may be activated by heat. Heat, is only an agent or instrument used by chemists; and heat is caused by the motion of the particles of which objects are composed.[13] The concept of phlogiston as being fire matter fixed within substances is a modification of Stahl's ideas by his French disciple, Guillaume François Rouelle (1703-1770).[14] Rouelle taught at the Jardin du Roi from 1742 to 1768 and acquired a reputation as one of the foremost teachers of chemistry in France.[15]

Fire has been accepted as a material, elemental substance by a Stahlian chemist as early as 1737,[16] but it was Rouelle who associated

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[12]See Maurice Daumas, "La chimie dans l'Encyclopédie et dans l'Encyclopédie méthodique," Revue d'histoire des sciences, IV (1951), 337-338.

[13]See pp. 74-75, below, and Hélène Metzger, Newton, Stahl, Boerhaave et la doctrine chimique (Paris, 1930), pp. 159-188.

[14]Rhoda Rappaport, "Rouelle and Stahl: The Phlogistic Revolution in France," Chymia, VII (1961), 73-102.

[15]Rhoda Rappaport, "G. -F. Rouelle, an Eighteenth-Century Chemist and Teacher," Chymia, VI (1960), 68-101; cf. Henry Guerlac, "Some French Antecedents of the Chemical Revolution," Chymia, V (1959), 74-76, 101-102, 105-106.

[16]Jean Baptiste Senac (1693-1770) in his Nouveau cours de

phlogiston with Boerhaave's fire matter in addition to accepting this fire matter as the cause of heat phenomena.[17] Rouelle's views were generally accepted as being Stahl's. One historian of science claims that because of Stahl's verbiage and obtuse style, few read him; and Rouelle's teaching skill coupled with his claim he was only presenting Stahl's views resulted in Rouelle's modified Stahlian theory being accepted as that of Stahl himself.[18]

The sudden popularity of the phlogiston theory in France corresponds to Rouelle's influence as a teacher, and Rouelle's views replaced Boerhaave's during the 1750's and 1760's. Venel implied that Rouelle's ideas were not yet generally accepted in 1756 when he said that "Le chimiste, du moins le chimiste Stahlien, considere le feu sous deux aspects bien différens."[19] The anonymous author of a history of the progress of the sciences which was published in 1760, discussed both the older heat theory and Rouelle's modification of it.[20] In the section

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chymie, suivant les principes de Newton et de Sthall (2 vols.; 2d ed.; Paris, 1737), I, 19-22, 27, cited and discussed in Rappaport, Chymia, VII (1961), 86-89.

[17]Rappaport, Chymia, VII (1961), 76-77, 85-86. Fire and phlogiston were also associated by Johann Heinrich Pott (1692-1777) in his Versuch Chymisch-physicalisher Betrachtungen über die Eigenschaften und Würckungen des Lichts und Feuers (Potsdam, 1746), p. 68, quoted in James R. Partington and Douglas McKie, "Historical Studies on the Phlogiston Theory: I. The Levity of Phlogiston," Annals of Science, II (1937), note, p. 372. Pott, however, seems to have given fire matter the properties of Stahl's phlogiston, rather than the converse as Rouelle did.

[18]Rappaport, Chymia, VII (1961), 94-95.

[19]Gabriel François Venel, "Feu (Chimie)," Encyclopédie, VI (1756), 609.

[20]Histoire de l'Académie Royale des Sciences, centième ou dernier volume de la première centurie contenant un abregé historique

on physics, fire is described as a very subtle and agitated fluid which can be imprisoned within substances as evidenced by the increased weight of calcined metals.[21] In the section on chemistry, however, fire is described as entering the composition of substances in the form of phlogiston, and metals are compounds of phlogiston and calx.[22]

Rouelle's views appear as a modification or an addition to current ideas on the nature of heat as exemplified in Boerhaave's writings. He published virtually nothing concerning his theory of phlogiston, but his teachings spread through the work of his pupuls, for example, Venel, and especially Pierre Joseph Macquer (1718-1784), who later (1771) became professor of chemistry in the Jardin du Roi.[23] Macquer gave further explanation and emphasis to the distinction between free and combined fire. He listed fire along with air, water, and earth as meriting the designation "de principes ou d'élémens" because they are "inaltérables," and cannot be decomposed.[24]

He said that many names have been used to designate the element of fire: "la matiere du soleil, ou de la lumiere, le phlogistique, le feu, le souffre principe, la matiere inflammable."[25] However, the

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de chaque science, avec une liste générale des mémoires de mathématique & de physique jusqu'à l'année 1751 inclusivement (Amsterdam, 1760).

[21] Ibid., pp. 9-12.

[22] Ibid., pp. 161-162, 164. The author said that he took his discussion of chemistry from Pierre Joseph Macquer (1718-1784); ibid., p. 161.

[23] Pierre Joseph Macquer, Elémens de chymie-théorique (Nouvelle ed.; Paris, 1753).

[24] Ibid., p. 2.

[25] Ibid., pp. 11-12.

important thing is not the name but the necessity to distinguish between the two different states in which fire is found.

The first of the two states of fire is fire as a principle in combination within other substances. The second is fire which is free, uncombined, and in its natural state. Macquer said that in this second state, the names "de Feu, de matiere du soleil, de la lumiere & de la chaleur" are equally applicable. Fire is composed of infinitely small particles; and in its natural state, its free state, the particles of fire are agitated by a very rapid and continual movement. Fire is a fluid in its essence and the cause of all fluidity. Indeed the greatest change that fire can produce is to fuse and solidify substances. Without fire, air itself would be solid.[26] Macquer concluded that the characteristics of fire indicate that "il nous est impossible de le retenir & de le fixer dans aucun corps." But we know that fire can be fixed, although by what mechanism he could not say.[27]

Fire which is fixed as a principle or constituent in the composition of substances is called phlogiston. Fixed fire, or phlogiston, differs in several ways from fire in its natural state.[28] First, fixed fire communicates neither heat nor light to the substance with which it unites. Second, it does not change the state of solids or fluids, although it may increase the tendency of solids to fuse. Third, it can be transported from one substance in which it is fixed to another substance and become fixed in the latter without becoming free.[29]

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[26] Ibid., pp. 12-13.

[27] Ibid., p. 15.

[28] Ibid., p. 16.

[29] Ibid.

Macquer hinted that the ability of phlogiston to become fixed within substances indicates a difference between it and fire in its natural state, although he did not speculate upon what this difference might be.[30]

In 1766 Macquer published the first edition of his chemical dictionary. He opened the article on fire by defining the two states in which fire can exist in substances:[31]

> Les Chymistes considerent le Feu, ainsi que les autres élémens, sous deux aspects fort différens: savoir, comme entrant réellement, en qualité de principe ou de partie constituante, dans la composition d'une infinité de corps; & comme étant libre, pur, ne faisant partie d'aucun composé, mais ayant une action très marquée, & très forte sur tous les corps de la nature, & singulierement influant comme un agent très puissant dans toutes les opérations de la Chymie.[32]

He discussed, "Feu combinèe" under the article "Phlogistique." In the article "Feu," he treated "le Feu pur, libre, & non combiné."

Free fire consists of an assemblage of simple, homogeneous, absolutely inalterable particles, infinitely small, and without sensible coherence. Movement is an essential characteristic of these fire particles, and the movement is continual, very rapid, and in all directions. Fire is a fluid "par essence," and it is the only body which is fluid by itself; it is the cause of fluidity in all other substances. Without

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[30] Ibid., pp. 16-17.

[31] [Pierre Joseph Macquer], Dictionnaire de chymie contenant la théorie & la pratique de cette science, son application à la physique, à l'histoire naturelle, à la médecine, & à l'économie animale, avec l'explication détaillée de la vertu & de la manière d'agir des médicamens chymiques, et les principes fondamentaux des arts, manufactures, & métiers dépendans de la chymie (2 vols.; Paris, 1766).

[32] Ibid., I, 498.

fire all matter would be "une seule masse immense, homogene, & d'une dureté absolue."[33]

Following Boerhaave, Macquer asked what is the sure test for the presence of fire. He rejected light because heat and light are not always together, and he concluded that heat (chaleur) is the single, absolutely certain indicator of the presence of fire matter. He stated that some persons think that light and heat are identical; but he did not commit himself on the question of the relationship of the two.[34] He described the fusion of a substance as due to fire interposed among the particles of the substance, disuniting these particles and destroying their adherence to each other.[35]

The only difference between free fire and phlogiston is that combined fire is "privé de son activité" by its union with another substance.[36] Fire does not lose all its movement, however, when it combines; for the ductility of metals, formed from the union of phlogiston and calx, is due to the movement of the combined fire particles.[37] During combustion, phlogiston or combined fire becomes free fire.[38] Macquer's statement that there is no fundamental difference between pure, free fire and phlogiston, except that the latter is fixed within substances, is a change from his Elémens of 1753 where he had implied a difference between them to account for the ability of fire to become fixed.[39]

In his explanations of heat phenomena, Macquer restricted his use of combined fire, or phlogiston, to the explanation of the chemical

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[33] Ibid. [34] Ibid., p. 500. [35] Ibid., p. 594.

[36] Ibid., II, 203. [37] Ibid., p. 216. [38] Ibid., I, 500.

[39] See p. 43, above.

production of heat, particularly heat produced during combustion. He indicated no knowledge of the concept of latent heat, and he explained few heat phenomena except in the most general sense. He offered little that was original, although what he said was perhaps more clearly stated than his predecessors.[40]

Antoine Baumé (1728-1804) was a pharmacist and the lecture demonstrator with whom Macquer had at one time collaborated in giving a private chemistry course. In his chemistry text of 1774, Baumé listed earth, fire, water, and air as elements.[41] Of these, only fire and earth can combine immediately, and this combination is known as phlogiston.[42] Pure fire, however, is without adherence to or combination with other substances. It is essentially fluid and the principle of fluidity in other substances. Its particles are always in movement:[43]

> Les parties du feu ont nécessairement une très grande vîtesse, puiqu'elles font mouvoir les parties des corps qu'elles pénetrant, avec une très grande rapidité, & qu'elles les tiennent dans un mouvement continuel, en entrant & en sortant alternativement.[44]

Of the various signs which indicate the presence of fire, Baumé agreed with Boerhaave that expansion is the only certain one.[45] Fire separates the particles of substances, and expansion is the first stage of disunion. Disunion proceeds until fusion when the parts are completely

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[40] In the second, 1778 edition of his dictionary, Macquer completely reversed himself on the nature of heat. In that edition, he stated that heat and light are entirely different. He redefined phlogiston as the matter of light, and he stated that heat is only a vibration. See pp. 84-88, below.

[41] Antoine Baumé, Chymie expérimentale et raisonnée (4 vols.; Paris, 1774), I, 39.

[42] Ibid., p. 46.

[43] Ibid., pp. 47-48.

[44] Ibid., p. 61.

[45] Ibid., p. 51.

separated.[46] Fire has weight, but its weight is revealed only when it becomes combined. Pure fire is not combined, "mais seulement interposé entre les parties de la matiere."[47]

In the union of fire and earth which forms phlogiston, the fire becomes completely inactive;[48] it is at perfect rest and without fluidity. Fire and earth can combine in an infinite number of proportions.[49] If phlogiston contains more earth, it is more fixed; if it contains more fire, it is more volatile.[50] During some decompositions, Baumé stated, phlogiston itself may be released.[51] In combustion, however, phlogiston itself, decomposes and pure fire is set free.[52]

Although Baumé considered both calcination and combustion to involve a loss of phlogiston, he thought that pure fire must unite with metals when calcined. A greater weight of pure fire enters and unites with the metal than the weight of the phlogiston lost. However, the combination resulting from the union of pure fire with metals during calcination cannot be in the form of phlogiston; indeed, said Baumé, it is difficult to know just what form this combination takes.[53]

Georges Louis Leclerc, comte de Buffon (1707-1788) also believed that heat effects are to be attributed to fire in motion. But on the nature of fire matter itself and the relationship between heat and light, Buffon differed considerably from his contemporaries. Heat plays an

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[46] Ibid., pp. 54-55.
[47] Ibid., p. 54.
[48] Ibid., pp. 49, 146.
[49] Ibid., pp. 50, 149.
[50] Ibid., p. 156.
[51] Ibid., p. 149.
[52] Ibid., p. 156.
[53] Ibid., pp. 59-60.

essential role in his system:

> Les puissances de la Nature, autant qu'elles nous sont connues, peuvent se réduire à deux forces primitives, celle qui cause la pesanteur, & celle qui produit la chaleur.[54]

The essence of heat is a repulsive force, opposed to the force of attraction; but this repulsion itself can be reduced to attraction because of the elasticity of the molecules which compose ordinary matter. "J'avoue," he said, "qu'il faut supposer dans chaque molécule de matiere, dans chaque atome quelconque, un ressort parfait, pour concevoir clairement comment s'opère ce changement de l'attraction en répulsion. ..."[55] As a demonstration of the perfect elasticity of the atoms of matter, he cited the phenomenon of the reflection of light. Not only do the particles of light have perfect elasticity, but light has the greatest expansive force of all substances. The expansive force or repulsion is due to this perfect elasticity.

> La force expansive pourroit donc bien n'être dans la réel que la réaction de la force attractive ... & lorsque ces molécules [of matter] sont absolument libres de toute cohérence, & qu'elles n'obéissent qu'au seul mouvement produit par leur attraction, cette vîtesse acquise est immense dans le point du contact. La chaleur, la lumier, le feu, qui sont les grands effets de la force expansive, seront produits toutes les fois qu'artificiellement ou naturellement les corps seront divisés en parties très petites, & qu'ils se rencontreront dans des directions opposées. ..."[56]

The only difference between the atoms of heat, light, or fire and the atoms of other substances is the coherence among the atoms themselves:

> De-là on doit conclure que toute matiere peut devenir lumiere, chaleur, feu; qu'il suffit que les molécules d'une substance

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[54]Georges Louis Leclerc, comte de Buffon, Histoire naturelle, générale et particuliere (13 vols.; Deux-Ponts, 1785-1786), IV, [5].

[55]Ibid., p. 12. [56]Ibid., pp. 13-14.

> quelconque se trouvent dans un état de liberté, c'est-à-dire, dans un état de division assez grande & de séparation, telle qu'elles puissent obéir sans obstacle à toute la force qui les attire les unes vers les autres. ... Ainsi la lumiere, la chaleur & le feu, ne sont pas des matieres particulieres, des matieres différentes de toute autre matiere; ce n'est toujours que la même matiere qui n'a subi d'autre altération, d'autre modification, qu'une grande division de parties, & une direction de mouvement en sens contraire par l'effet de choc & de la réaction.[57]

The basic material identity between heat, light, fire, and other matter is true only in the general sense. In practice they produce different effects, and they they can be differentiated from each other. The cause of the differences is the degree of coherence and size of the respective particles.[58]

Apparently following Boerhaave, Buffon stated that although fire is often luminous, it is sometimes without light, although it is never without heat. Similarly, heat often occurs without light and light occurs without heat. From the manner in which heat and light appear, it may be concluded that heat matter is very similar to light, but that there is a difference between them. Light, is usually in space whereas heat is usually confined to solid matter. Heat penetrates all bodies, whereas light can penetrate only transparent ones.[59] From this, Buffon concluded that heat

> ... semble donc agir d'une maniere bien plus général & plus palpable que n'agit la lumiere; & quoique les molécules de la chaleur soient excessivement petites, puisqu'elles pénètrent les corps les plus compactes, il me semble réanmoins que l'on peut démontrer qu'elles sont bien plus grosses que celles de la lumiere; car on fait de la chaleur avec la lumiere, en la réunissant en grande quantité; d'ailleurs la chaleur agissant sur le sens du toucher, il est necessaire que son action soit proportionnée à la grossiéreté de ce sens. ...[60]

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[57] Ibid., pp. 15-16.

[58] Ibid., p. 23.

[59] Ibid., pp. 24-27.

[60] Ibid., p. 27.

Internal movement is essential for the production of heat; and attrition seems to be the principle of all heat because "tout frottement, c'est-à-dire, tout mouvement en sens contraire entre des matieres solides, produit de la chaleur."[61] The reason that this heating is not produced in fluids is because the particles of the fluid do not touch enough to be rubbed against each other.

Buffon stated that fire is an element.[62] It has weight.[63] It is composed of the two principles heat and light united to each other.[64] By this, Buffon seems to have meant that "fire" is the general term applying to all the particles of a heat-light spectrum. This spectrum consists of particles which differ only with respect to their speed and size, heat particles being larger and moving more slowly than those of light. These two principles, heat and light, are reciprocally convertible into each other, although Buffon is not clear just how this is brought about. For example, he said that "en augmentant la masse de la chaleur obscure [without light], on peut produire de la lumiere, de la même maniere qu'en augmentant la masse de la lumiere on produit de la chaleur. ..."[65]

Particles of fire, when in the form of light, can unite with other substances. This is usually not the case with heat particles, although some heat matter may become fixed in some instances if it is kept within a substance for a long time.[66] The reason heat usually does not

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[61] Ibid., p. 28.

[62] Ibid., p. 50; cf. VIII, 5-6.

[63] Ibid., VI, 43-44, 64.

[64] Ibid., VIII, 6, 11.

[65] Ibid., VII, 95.

[66] Ibid., VI, 37, 82.

become fixed is that it "semble empêcher au contraire l'union de toutes les parties de la matiere, & n'agir que pour les tenir séparées."[67]

Buffon distinguished between two kinds of heat, luminous and "obscure," which differ with respect to the presence of light and also the speed with which each kind of heat produces its effects.[68] For example, calcination by means of obscure heat takes longer than when luminous heat is used. The difference between these two heats is the speed and size of the particles, although Buffon did not explain this in detail.[69]

Buffon accepted the phlogistic concept that combustion and calcination are analogous processes, but he thought that fire enters and becomes fixed in both reactions. He explained the decreased weight of substances upon combustion as caused by the loss of volatiles which are carried away by the fire united with them. The increase of weight of calces is due to the fixation of fire, light and air within the substance calcined.[70]

Buffon believed that heat is due to fire matter in motion, although he did not emphasize the role of motion as much as some of his predecessors had. He hinted that both the degree of motion of the fire particles and their quantity had an influence on the effects produced by fire, but he did not detail his statement. Although he was not the first

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[67] Ibid., p. 37.

[68] Ibid., pp. 38; VII, 78, 86.

[69] Ibid., VII, 87. For a brief discussion of Buffon's ideas on radiant heat see E. S. Cornell, "Early Studies in Radiant Heat," Annals of Science, I (1936), 219.

[70] Buffon, Histoire naturelle, VI, 43-44.

who thought heat and light were the same things or only different effects or modifications of the fire element, Buffon seems to have been one of the first to have put forth the idea of a heat-light spectrum in explaining the relationships between these two substances and their reciprocal transmutation. In many respects, Buffon's theory seems to be a restatement of Cartesian ideas concerning matter, ideas in which the fundamental differences between different kinds of substances are explained by the varying sizes of constituent particles which have a common material composition.

The theory of fire-matter-in-motion as propounded by Boerhaave and his contemporaries and as modified by the phlogistonists in their distinction between free and combined fire appears in works by lesser known writers, especially in the more popular dictionaries and textbooks, many of which went through numerous editions. Some of the theoretical explanations are virtually unchanged over a period of up to twenty years in some cases.[71] Many authors, either ignorant of or ignoring more original contemporary work, continued to expound uncritically the older theories. This is especially common in dictionaries and some textbooks which traditionally tend to be somewhat behind the times.

An example is the dictionary written in 1761 by Aimé Henri Paulian (1722-1800), a Jesuit and teacher of physics at Avignon.[72] Paulian distinguished between fire "en élément" and fire "en mixte."[73]

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[71]For example, see Jean Antoine Nollet's Leçons de physique expérimentale, n. 98, p. 31, above.

[72]Aimé Henri Paulian, Dictionnaire de physique, dédié à monseigneur le duc de Berry (3 vols.; Avignon, 1761).

[73]Ibid., II, 106.

Fire is the true cause of heat, but to cause heat, it must be in movement: "Des particles de feu agitées d'un mouvement très-violent en tout sens, sont la vraie cause de la chaleur."[74] Paulian thought that there is no difference between fire matter and the "matiére électrique."[75]

The eighth edition of Paulian's dictionary, published in 1781, contains few changes from the 1761 edition. He restated his idea that the cause of heat is fire-in-motion,[76] that fire is the same as the electrical matter,[77] and that the only difference between elemental fire and fire "en mixte" is that the latter is elemental fire joined to inflammables.[78] Light is only fire moving in right lines whereas heat is fire moving "en tout sens."[79] In describing the heat-producing movement, Paulian followed de Mairan and attributed it to a peculiar motion of the fire matter which is caused by "un nombre innombrable de mouvemens en tourbillon, dont chacun se fait autour d'un centre particulier."[80]

Another example is the work of Joseph Aignan Sigaud-Lafond (1730-1810). Sigaud held various academic posts as a teacher of physics and chemistry. He taught in the Collège Royale, in Bourges, and in the Ecole Centrale. Antoine François de Fourcroy (1755-1809) was one of his pupils. In 1767, Sigaud described fire as a fluid, universally expanded throughout

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[74]Ibid., I, 362. [75]Ibid., II, 106.

[76]Aimé Henri Paulian, Dictionnaire de physique dédié au Roi, huitième édition, revue, corrigée & enrichie de découvertes faites dans cette science depuis l'année 1773 (8th ed., revised; 4 vols.; Nimes, 1781), II, 6-7.

[77]Ibid., p. 427. [78]Ibid.

[79]Ibid., pp. 427, 429; cf. 's Gravesande's views, p. 14, above.

[80]Paulian, Dictionnaire de physique, II, 427; see p. 34, above.

nature, filling all space.[81] Heat and light are only "deux modes différens d'une même substance. ..." Light is fire moving in right lines, and heat is "l'agitation de ce même fluide qui se meut en tous sens."[82] The exact nature of the fire element is not known, but it possesses, a priori, all the properties common to matter, and this includes weight.[83]

Sigaud said that fire tends to separate the parts of substances. Vaporization is the complete separation of parts by the activity of fire.[84] In explaining the constancy of temperature during changes of state, Sigaud remarked that the reason that a greater degree of heat is not acquired is "parce que la matiere ignée qui les pénètre alors, ne peut plus être rétenue dans leur masse, & qu'elle passe librement au-dehors."[85] He cited the method of mixtures described by Georg Wilhelm Richmann (1711-1753) and used with water only.[86]

Fire can enter into combination in all "mixtes," and in this form it is called phlogiston.[87] Although Sigaud was thus familiar with the term phlogiston, his explanations of calcination and combustion are in the pre-phlogiston tradition. He thought that fire is absorbed during

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[81]Joseph Aignan Sigaud-Lafond, Leçons de physique expérimentale (2 vols.; Paris, 1767), II, 175-176.

[82]Ibid., p. 176; cf. Paulian's views, above.

[83]Sigaud-Lafond, Leçons de physique, II, 177-178, 180.

[84]Ibid., pp. 195, 202.

[85]Ibid., p. 211; cf. Boerhaave's explanation, p. 23, above.

[86]Sigaud-Lafond, Leçons de physique, II, 188-190. For a discussion of Richmann's technique, see Douglas McKie and Niels H. de V. Heathcote, The Discovery of Specific and Latent Heats (London, 1935), pp. 64-74.

[87]Sigaud-Lafond, Leçons de physique, II, 176.

calcination as shown by the increased weight of metals when calcined.[88] In combustion, fire needs an aliment, which he said is oil, and requires some kind of obstacle to oppose its tendency to dissipate. Air pressure provides the obstacle, as evidenced by the cessation of burning in the absence of air; the increased vehemence of flames in cold air is due to the increased air density and thus increased pressure.[89]

In his dictionary of 1781-1782, Sigaud indicated a better understanding of the phlogiston theory, but his explanations of heat phenomena which do not involve phlogiston are little changed.[90] He remarked upon the difficulty of investigating fire: "S'il est un être en Physique dont la nature soit difficile à saisir & échappe à toute la sagacité de Physicien, c'est sans contredit le feu."[91]

Sigaud believed that there exists in nature a single, unique fire element which is susceptible of a multitude of various combinations, most of which have not yet been determined. In general, two different states of fire can be distinguished. The first is the state of combination as a constituent principle of a substance; in the second, fire is free, separated from all combination.[92] When in the combined state, fire is called "le principe inflammable ou le phlogistique." In the free state it is called "le feu, ou la matière-ignée."[93] When free, fire is

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[88] Ibid., pp. 183-187.

[89] Ibid., pp. 248-251; cf. Boerhaave's theory of combustion, p. 22, above, also Lémery's and Musschenbroek's ideas on calcination, pp. 11, 30, above.

[90] Joseph Aignan Sigaud-Lafond, Dictionnaire de physique [et supplément] (5 vols.; Paris, 1781-1782).

[91] Ibid., II, 228. [92] Ibid., p. 229. [93] Ibid., pp. 229-230.

a fluid, very subtle, endowed with an extremely rapid motion which enables it to penetrate the most compact substances.[94] Heat is produced by the action of fire,[95] and it is fire which expands substances. The relationship between expansion and density of the substance or the adhesion among its particles is not known.[96] "La matière ingée" tends to distribute itself uniformly and become equalized in all substances.[97]

During combustion, Sigaud said, phlogiston becomes free, mobile fire. However, fire in combination can pass from one particular combination into another without becoming free.[98] He again referred to Richmann's method of mixtures,[99] and he admitted that he was unable to explain the cooling caused by evaporation.[100]

Sigaud acknowledged his debt to Macquer and indeed most of what is contained in Sigaud's dictionary can also be found in Macquer's. In several instances Sigaud stated what he believed the case to be, and then cited Macquer, sometimes by name and sometimes not, as believing the contrary. In none of these instances did he attempt to refute what Macquer had said.

The Abbé François Para du Phanjas (1724-1797), a Jesuit who taught in Marseilles, Grenoble, and Besançon, like Sigaud, was pessimistic about the state of knowledge of the nature of fire:[101]

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[94] Ibid., p. 230. [95] Ibid., I, 578. [96] Ibid., II, 232.

[97] Ibid., I, 581. [98] Ibid., III, 566-567.

[99] Ibid., II, 236-238; see n. 85, p. 53, above.

[100] Sigaud-Lafond, Dictionnaire de physique, II, 241-243.

[101] François Para du Panjas, Théorie des êtres sensibles, ou cours complet de physique spéculative, expérimentale, systématique, et géometrique,

> Après toutes les profondes méditations des Descartes, des Newtons, des Leibnitz, des Euler; après toutes les savantes & subtiles expériences des Boërhave [sic], des Boyle, des Réaumur, des Stahl, des Muschenbroëk, des Macquer, des de Buffon, & de tant d'autres célebres Naturalistes; le Monde philosophe est resté incertain & partagé sur la nature de Feu.[102]

Para described three theories of the nature of fire. In the first, fire is an element apart, inalterable, and always in action and motion. It is the unique principle of fluidity and the cause of heat. Para said that this is the theory of Buffon and Boerhaave. The second theory considers fire as a fortuitous grouping of substances to which movement alone gives action. In other words, fire consists in different motions of the molecules of the object itself. In the third theory, fire is treated as a matter apart, intermediate between matter and spirit.[103] Para concluded that "parmi ces trois Opinions, la premiere est plus que vraisemblable: la second est certainement fausse: la troisieme est évidemment inepte & absurde."[104]

In arguing against the motion theory, Para stated that it is a general law that movement imparted to one body decreases and finally becomes insensible when it is distributed to larger quantities of matter. The movement of fire matter, on the other hand, "ne suit pas cette Loi générale."[105]

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mise à la portée de tout le monde, avec une table alphabétique des matières qui en fait un vrai dictionnaire de physique, nouvelle édition, rectifiée, perfectionnée, assortie aux modernes découvertes, & augmentée d'un cinquième volume (5 vols.; Nouvelle ed., enlarged; Paris, 1788); cited hereafter as Cours de physique.

[102] Ibid., III, 377.

[103] Ibid., pp. 377-378.

[104] Ibid., p. 378.

[105] Ibid., p. 379.

In explaining the most probable theory of fire, he said that the fire element should be considered as existing in two different states: first as a "Substance simple & primitive," as "la Feu élémentaire, l'une des quatre Substances primitives qui entrent dans la composition des Corps"; second as a "Substance combinée" with other substances, as "le Phlogistique, ou la partie inflammable des Corps combustibles."[106] It is simple, elementary fire which insinuates itself into the most dense substances, separating their parts and putting them in the fluid state. Indeed, all substances whether fluid or liquid would become solid without the presence of elementary fire.[107]

Para agreed with Sigaud that "le Feu & la Lumiere ne sont qu'un seul & même Elément."[108] The degree of sensible heat is due to the density of the fire or light matter contained within the pores of substances, and not necessarily due to the absolute quantity of fire present.[109] Frictional production of heat is caused by increasing the natural motion of the fire particles contained within an object.[110] The reason for the continual movement of the fire particles is that "l'Auteur de la Nature" wished it so.[111]

> Le Phlogistique ... est une combinaison intime du Feu élémentaire ou du Fluide igné & lumineux, avec une infinité de substances différentes, dans lesquelles le Feu élémentaire prend un état de Fixité, qui lui fait perdre ses deux propriétés caractéristiques; celle d'éclairer, & celle de brûler.[112]

In this union, the affinity between fire and the substance overcomes the

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[106] Ibid., p. 377. [107] Ibid., p. 381. [108] Ibid.

[109] Ibid., pp. 383, 386-387. [110] Ibid., p. 397.

[111] Ibid., p. 405. [112] Ibid., p. 384.

natural tendency of fire to separate and move, and a balance exists between these two tendencies. However, in certain instances fixed fire may be released suddenly, for example, by the application of a single spark to tinder. What happens in this case, said Para, is the spark upsets the balance and increases the expansive tendency of fire over the affinity of the fire for the substance. This inbalance begins at one place within the substance, and by a chain-reaction, the fixed fire is excited and set free from the rest of the substance.[113] Combustion itself is a vibrational movement of all the disunited parts of the combustible, a vibration which accompanies the release of fire and one which requires air to maintain.[114]

Late eighteenth-century discussions of the fire-in-motion hypothesis are not confined to dictionaries and textbooks. Even in journals, which one would expect to reflect more originality, the old views on heat continued to be repeated. For example, the authors who discussed the nature of heat in the articles published up to 1780 in the Observations sur la physique advocated the fire-in-motion theory almost to the complete exclusion of any other view.

Josias Adam Braun (1712-1768), member of the St. Petersburg Academy of Science, explained heat as due to "parties ignées en mouvement,"[115] as did Franz Carl Achard (1753-1821), director of the physics

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[113] Ibid., pp. 391-393.

[114] Ibid., II, 473-475; cf. François Para du Panjas, Théorie des nouvelles découvertes en genre de physique et de chimie pour servir de supplément à la théorie des êtres sensibles, ou au cours complet & au corus élémentaire de physique de m. l'Abbé Para (Paris, 1786), pp. 536-545.

[115] Josias Adam Braun, "Expériences et phénomènes singuliers sur la communication de la chaleur," Observations sur la physique, I (1773), 7.

section of the Berlin Academy of Science.[116] In an unsigned book review in the same journal, the reviewer equated fire with ether "mis en mouvement."[117] A cavalry officer at Orléans, de Servières, said that freezing is caused by the decreased motion of parts of the liquid due to evaporation of most igneous particles coupled with "la diminution de mouvement dans celles [igneous particles] qui restent."[118] Nicholas Philippe Ledru (1731-1807), a French teacher of natural history, described the world as a plenum of igneous fluid, a fluid which is the principle of all movement.[119] Madame de V*** described expansion as the beginning of disunion of the particles of substances caused by the agitation of fire matter which she equated to light.[120]

Most of these writers in the Observations sur la physique followed Macquer s idea that fire is an element and that phlogiston is fire fixed within substances. However, Bernard Germain Etienne de la

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[116]Franz Carl Achard, "Dissertation sur la cause de l'élévation des vapeurs," Observations sur la physique, XV (1780), 469.

[117]"Vues générales sur la physique, traduites de l'Allemand, & imprimées à Erfurd en 1773, de l'union, ou force conjonctive des corps," Observations sur la physique, II (1773), 185, note.

[118]De Servières, "Essai d'explication d'un phénomène assez singulier produit par la fonte de la glace," Observations sur la physique, VI (1775), 183.

[119]Comus [Nicholas Philippe Ledru], "Dissertation sur le mouvement et les élémens de la matière," Observations sur la physique, VI (1775), 421.

[120]Madame de V***, "Lettre de madame de V***, à m. Senebier, bibliothécaire de la République de Genève, sur les différences qu'il établit entre la lumière & le phlogistique," Observations sur la physique, X (1777), 211, note.

Ville sur Illon, comte de Lacépède (1756-1825), professor of natural history at the Jardin du Roi, followed Buffon in believing that there is only basic kind of matter and that the fire element consists of particles of ordinary matter which have the least mutual cohesion.[121] Jean Senebier (1742-1809), a Genevan primarily noted as a plant physiologist, agreed rather with Baumé that phlogiston is fire united to earth.[122] Senebier attributed to phlogiston most of the properties traditionally associated with fire itself.[123] Phlogiston is a volatile constituent of substances. It has no relation to heat except that heat or fire is the agent which imparts activity to phlogiston.[124] Phlogiston is the immediate cause of fusion, evaporation, combustion, and calcination.[125]

Proponents of the fire-in-motion theory did not disappear after 1780. But after that date, the influence of the new pneumatic chemistry,

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[121]Bernard Germain Etienne de la Ville sur Illon, comte de Lacépède, "Mémoire sur les élémens & les affinités," Observations sur la physique, XII (1778), 141-143.

[122]Jean Senebier, "Mémoire sur la phlogistique considéré comme la cause du développement de la vie & de la destruction de tous les êtres dans les trois règnes," Observations sur la physique, VIII (1776), 26; cf. Baumé's views, p. 45, above.

[123]Cf. Pott's views, n. 16, p. 40, above.

[124]Jean Senebier, "Second mémoire sur le phlogistique considéré comme la cause du développement de la vie & de la destruction de tous les êtres dans les trois règnes," Observations sur la physique, IX (1777), 98-99, 102.

[125]Jean Senebier, "Troisième mémoire sur le phlogistique considéré comme la cause du développement de la vie & de la destruction de tous les êtres dans les trois régnes," Observations sur la physique, IX (1777), 368-374; cf. fourth memoir, vol. XI (1778), 330-332; Jean Senebier, "Second lettre à madame de V***, ou mémoire sur la nature de la lumière & de ses effets sur la décoloration des surfaces colorées exposée à son action, & sur l'étiolement des plantes," Observations sur la physique, XIV (1779), 366-368.

especially the ideas of Antoine Laurent Lavoisier (1743-1794), so altered explanations of heat phenomena as to set the later ideas apart, even though some of them contain motion as an inherent characteristic of fire matter. For example, Jean Claude de Lamétherie (1743-1817)[126] and Jean André Deluc (1727-1817)[127] believed in fire matter in motion, and they maintained this idea practically to the end of the eighteenth century. But in their writings, so much space is devoted to controversy over various assumptions of the new chemistry that the idea of motion is given little emphasis; and they accepted enough of the new theory that in many of their explanations, the motion of fire is no longer an essential characteristic.

One of the few persons in the latter eighteenth century for whom the inherent motion of fire matter forms an essential part of his theory was the Genevan, Pierre Prevost (1751-1839). Prevost was interested in radiant heat phenomena and developed his theory of exchanges to explain the apparent radiation of cold.[128] This theory assumes a continual emission of fire particles from all substances at all temperatures. Prevost said that a heated substance continues to receive rays of fire particles even from substances colder than itself, and temperature change is

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[126]See pp. 220-230, below, in Chapter VII.

[127]See especially Jean André Deluc, "Seconde lettre de m. de Luc à m. de la Métherie sur la chaleur, la liquéfaction, et l'évaporation," Observations sur la physique, XXXVI (1790), 196-198.

[128]Pierre Prevost, "Mémoire sur l'équilibre de feu," Observations sur la physique, XXXVIII (1791), 314-323. For a brief discussion of Prevost's theory, see E. S. Cornell, "Early Studies in Radiant Heat," Annals of Science, I (1936), 224-225.

determined by the difference between radiation received and radiation emitted.[129]

Prevost felt that, if his theory were true, it must follow that fire is a discrete fluid and its parts are continually agitated.[130] Fire owes its elasticity and its expansive force to the motion of its particles,[131] a motion so rapid that free fire seems to have all the properties of light. And just as radiation of light from one source does not affect the radiation from another source, so the radiation of fire from one substance cannot influence the radiation from another. Furthermore, the accumulation of fire in a substance cannot hinder the further accumulation of more fire. Fire, he said,

> est si subtil, ses particules ont un diamètre si petit relativement à leurs distances, que leur accumulation, au point où elle a lieu dans les phénomènes observés, n'apporte aucun obstacle au progrès de cette accumulation; jamais le feu introduit dans un corps ne ferme le passage au nouveau feu qui cherche à s'y introduire.[132]

Prevost admitted that his idea of the nature of fire did not conform to those physical theories which held that fire can act upon itself or that two neighboring portions of fire mutually restrain each other when their temperatures are the same.[133] The idea of "tension" or of elasticity of fire matter or of immobile equilibrium cannot explain the phenomenon.[134]

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[129]Prevost, Observations sur la physique, XXXVIII (1791), 316-318.

[130]Ibid., p. 321. [131]Ibid., pp. 315-316.

[132]Pierre Prevost, Recherches physico-méchaniques sur la chaleur (Genève, 1792), p. 19.

[133]Prevost, Observations sur la physique, XXXVIII (1791), 316.

[134]Ibid., p. 320. Prevost's ideas on the nature of fire matter

Most of those who believed in the theory of fire-matter-in-motion were more interested in the chemical production of heat than in expansion or changes of state. All clearly differentiated between fire acting as an agent or instrument and fire acting as a constituent element, compounded within substances. Change of state was explained by all of them in terms of fire acting as a mechanical agent. None of these men showed any knowledge of Joseph Black's ideas, or seemed to have been much interested in the kinds of phenomena with which Black dealt. With respect to chemical heat, none show much if any influence from the new school of pneumatic chemistry as it affected heat theory. For them, the most general assumptions found in the phlogiston theory were all that they needed to give a satisfactory explanation of heat phenomena.

There is very little change in the statement of the fire-in-motion theory after the mid-eighteenth century when ideas of phlogiston came to influence it. Thus there is basically little change in Para's discussion, for example, from that found in the Encyclopédie published thirty years earlier, in those articles in which feu élémentaire is distinguished from feu combinée. And except for this important distinction, the theoretical explanations of Para are virtually unchanged from those of Boerhaave or 's Gravesande.

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are the same as Deluc's (ibid., p. 315; cf. Recherches, p. 11). They considered fire to consist of light united to some unknown, ponderable base. Cf. Jean André Deluc, "Sixième lettre de m. de Luc à m. de la Métherie sur les rapports qui règnent entre la lumière & le feu," Observations sur la physique, XXXVII (1790), 56-58.

CHAPTER III

THE MOTION OF ORDINARY MATTER AS THE CAUSE OF HEAT

The theory of fire-matter-in-motion, although dominant during the first three quarters of the eighteenth century, was not the only theory of heat discussed during this period. A rival school of thought existed which considered heat to be due simply to motion, and expressions of this idea appeared from time to time throughout the century.

Eighteenth century ideas which regarded the cause of heat as due to the internal motion of the particles of ordinary matter are the intellectual descendants of a strong seventeenth century tradition, a tradition to which Francis Bacon (1561-1626) and Robert Boyle (1627-1691) belonged.[1] This tradition considered the vibrations of the particles of matter as an inherent characteristic which could be modified by external influences, depending upon particular circumstances. This

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[1]See Muriel A. Bentham, "Some Seventeenth Century Views concerning the Nature of Heat and Cold," Annals of Science, II (1937), 443-450, for a discussion of the views of Boyle and Edme-Mariotte (ca. 1620-1684). Maurice Daumas cites Descartes views as lending support to the theory of vibration; Lavoisier, théoricien et expérimentateur (Paris, 1955), p. 161; see p. 7, above. For the views of Bacon, see James R. Partington, A History of Chemistry (3 vols.; London, 1961-1964), II, 396-397; for those of Boyle, ibid., p. 506; Robert Hooke (1635-1703), ibid., p. 552. Boyle apparently changed his mind, see ibid., p. 530.

theory utilized an all-pervasive aether to transmit vibrations from one particle or group of particles to another.[2]

An early eighteenth century description of this view of heat was stated by John Harris (1667-1719), secretary and vice-president of the Royal Society, in his Lexicon technicum of 1704.

> Heat, one of the four Primary Qualities, and seems to consist only, or at least chiefly, in the local Motion of the small Parts of a Body Mechanically modified by certain Conditions, of which the Principal is the vehement and various Agitations of those small Insensible Parts.[3]

There are three conditions necessary to produce heat:

> 1. That the small Parts be vehemently and rapidly agitated, or moved in a much greater degree than is necessary to produce the Quality we call Fluidity.
> 2. That the Determinations of the Insensible Corpuscles thus vehemently agitated, be also very various; some moving up, some down, some to the Right Hand, others to the Left, &c. . . .
> 3. 'Tis requisite also to the Production of Heat, That the thus variously and vehemently agitated Particles, be also so small, as generally speaking, to be singly insensible. For unless they are exceedingly fine and subtil, they cannot penetrate readily into the Pores of Contiguous Bodies, and so warm or burn them.[4]

A similar note is found in the writings of Stephen Hales (1677-1761), a minister and Fellow of the Royal Society. Hales's discussion is more complex than Harris's due to Hales's attempt to explain the nature of fire and flame, in which there appears to be a de novo creation of heat. He began by arguing against the idea that fire is a distinct

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[2]Isaac Newton, Opticks, or a Treatise of the Reflections, Refractions, Inflections, and Colours of Light (2d ed., enlarged; London, 1718), pp. 323-324, 343, 352.

[3]John Harris, "Heat," Lexicon technicum, or an Universal English Dictionary of Arts and Sciences, Explaining Not Only the Terms of Art but the Arts Themselves (London, 1704), p. [Ooo3 verso].

[4]Ibid. Except for capitalization and punctuation, both of these quotations appear unchanged in the 4th edition (London, 1725), p. Yy[1 verso].

element and that combustion is the release of this element by the matter being burned:

> If fire was a particular distinct kind of body inherent in sulphur, as Mr. Homberg, Mr. Lemery, and some others imagin [sic] then such sulphureous bodies, when ignited, should rarify and dilate all the circumambient air; whereas it is found by many of the preceding Experiments, that acid sulphureous fuel constantly attracts and condenses a considerable part of the circumambient elastick air. An argument, that there is no fire endued with peculiar properties inherent in sulphur; and also that the heat of fire consists principally in the brisk vibrating action and reaction, between the elastick repelling air, and the strongly attracting acid sulphur. . . .[5]

Hales quoted a passage from Newton's Optics in which Newton discussed the existence of an "etherial medium" which serves to transmit vibrations from hot to cold substances. This aether, according to Newton, must be more rare and subtil, and exceedingly more elastic and active than air.[6] The intensity of the etherial vibration contributes to the degree and duration of the heat in substances. It is also by these aetheral vibrations that light communicates heat. Hales stated that in the case of fire, the elastic force of aether is itself sufficient to give an intense degree of heat, especially when this force is augmented by the action and reaction of the particles of air and fuel which together produce flame.[7]

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[5]Stephen Hales, Vegetable Staticks, or an Account of Some Statical Experiments on the Sap in Vegetables, Being an Essay towards a Natural History of Vegetation, Also a Specimen of an Attempt to Analyse the Air by a Great Variety of Chymio-Statical Experiments Which Were Read at Several Meetings before the Royal Society (London, 1727), p. 283.

[6]Newton, Opticks, pp. 323-324, 325-327.

[7]Ibid., pp. 284-285. Hales belief in the vibrational theory of heat is further indicated in his explanation of animal heat. See Everett Mendelsohn, Heat and Life: The Development of the Theory of Animal Heat (Cambridge, Mass., 1964), pp. 75-76, 78-79.

Particles of air and fuel, however, were not restricted to explaining the production of flame:

> From this manifest attraction, action and reaction, that there is between the acid, sulphureous and elastick aereal particles, we may not unreasonably conclude, that what we call the fire particles in Lime, and several other bodies, which have undergone the fire, are the sulphureous and elastick particles of the fire fixt in the Lime; which particles, while the Lime was hot, were in a very active, attracting and repelling state; and being, as the Lime cooled, detained in the solid body of the Lime, at the several attracting and repelling distances, they then happened to be at, they must necessarily continue in that fixt state, notwithstanding the ethereal medium, which is supposed freely to pervade all bodies, be continually solliciting them to action: But when the solid substances of the Lime is dissolved, by the affusion of some liquid, being thereby emancipated, they are again at liberty to be influenced and agitated by each other's attraction and repulsion, upon which a violent ebullition ensues, from the action and re-action of these particles. . . .[8]

The phenomenon of the production of heat by dissolving lime in water provides an example of the dilemma of those who believed heat to be vibration when they tried to explain the production of heat in chemical reactions. The vibratory theory readily explains the heating of a cold substance by a warmer one. Vibrations of the heated substance are transmitted to the colder one by the all-pervasive, elastic aether. The theory also explains heating due to light. The impact of particles of light upon a solid substance sets up vibrations in either the particles of the substance itself or in the particles of aether contained in the pores of the substance. In the latter case, the aether particles within the pores transmit their vibrations to the particles of the substance itself. In either instance, the particles of the substance are set to vibrating, and it warms.

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[8]Hales, Vegetable Staticks, 285-286. The sulphureous substance to which Hales referred is a general term for the fuel or pabulum of combustion.

However, some chemical reactions were another matter. In the example which Hales gave, two substances at the same temperature, quicklime and water, produce a substantial quantity of heat when mixed together. Where do the vibrations come from? To explain this sudden appearance of heat, Hales followed Newton and elaborated the basic idea of vibrations by assuming that fire is caused by a reaction between air and a gaseous fuel. In this reaction, the particles of air and fuel vibrate violently. These movements cause vibrations in the elastic aether, vibrations which are perceived as heat.

Hales explained that these reacting substances, air and fuel, may become imprisoned within an object exposed to fire, presumably within the pores of the object, only to be released and to resume their action when the walls of their prison are broken. In this case, and in similar cases where heat is produced by chemical means, the basic cause of heat is no longer rapid movement of the particles of matter per se. The cause of heat is indeed motion, but now it is motion of the peculiar substance, or in this case substances, of flame, which may be imprisoned and thus hidden within the pores of matter.[9]

As Hales believed that heat is merely a vibration, it manifestly can have no weight. However, fire is vibration of two ponderable matters, air and fuel; and hence, whenever these matters are collected together or fixed within a substance, the weight of the substance should be increased. This, said Hales, is demonstrated by experiment:

> And that the sulphureous and aereal particles of the fire are lodged in many of those bodies which it acts upon, and thereby

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[9]See Louis Lémery's ideas on the subject of imprisonment, pp. 11-12, above.

> considerably augments their weight, is very evident in Minium or Red Lead, which is observed to increase in weight about 1/20 part in undergoing the action of the fire.[10]

John Theophilus Desaguliers (1683-1744), a professor at Oxford and Fellow of the Royal Society, argued against the existence of a special fire element:

> The Consideration of Fire and Heat is very difficult: we know yet but very little of their Nature; and I think that those Philosophers, who assert the Being of an elementary Fire, (or that Fire is contain'd in all Bodies) assume a little too much. Whoever reads with Attention Dr. Hale's Vegetable Staticks, will soon be of a different Opinion.[11]

As an addition to this statement, Desaguliers quoted almost all of Hales's discussion on heat.[12]

In describing a then prevalent view explaining the ascent of water into the air in the form of vapor, Desaguliers said that particles of fire, separated from sunbeams, adhere to the particles of water, forming molecules which are lighter than air. These molecules then rise until their specific gravity is equal to that of the surrounding air.

> Now this is liable to several Objections. First, It is built upon a Supposition that Fire is a particular Substance, or distinct Element, which has never yet been prov'd by convincing Experiments and sufficient Observations. . . .[13]

In his Vegetable Staticks, Hales had shown that the idea of the existence

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[10]Hales, Vegetable Staticks, p. 286.

[11]John Theophilus Desaguliers, A Course of Experimental Philosophy (3d ed., corrected; 2 vols.; London, 1763). II, 296.

[12]Ibid., pp. 367-370; cf. Hales, Vegetable Staticks, pp. 281-286; see pp. 65-67, above.

[13]John Theophilus Desaguliers, "An Attempt to Solve the Phaenomenon of the Rise of Vapours, Formation of Clouds, and Descent of Rain," Philosophical Transactions of the Royal Society of London, XXXVI (1729), 7.

of a fire element is ill-founded. Besides, said Desaguliers,

> . . . if Particles of Fire were joined with those of Water to raise them up, those igneous Particles must be at least 1000 Times greater in Bulk than the watery ones; so that a Person, who at the Top of a Hill, has his Hands and Face in a Cloud, must feel a very sensible Warmth, by touching a much greater Surface of Fire than Water in the Cloud . . . whereas the contrary is proved by our Senses.[14]

Desaguliers claimed that heat separates the particles of matter from contact with each other; and even though only gases are compressible, the particles of all matter are separated from each other depending upon their degree of heat. The incompressibility of a liquid is due "to the centrifugal Force of its Parts, and not its want of Vacuity. . . ."[15] Heat separates the particles of water until molecules of vapor are formed. The degree of expansion of the vapor is proportional to its degree of heat, but he hesitated to admit that this expansion is caused "by an Increase of repellent Force in each watry Particle. . . ."[16] In his Course of Experimental Philosophy, however, Desaguliers equated the centrifugal force to a repulsion caused by heat.[17]

A more popular and less technical note was written by Benjamin Martin (1704-1782), mathematician, instrument maker and traveling lecturer. In his Philosophical Grammar of 1738, the mysteries of natural philosophy are explained by means of a dialogue:[18]

> A. Please now to let me know, Sir, what your Sentiments are of Heat and Cold in Bodies, and wherein those Qualities do consist?

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[14] Ibid., p. 9. [15] Ibid., p. 14. [16] Ibid., p. 18.

[17] Desaguliers, Course of Experimental Philosophy, II, 338-339, 342, 345.

[18] Benjamin Martin, The Philosophical Grammar, Being a View of the Present State of Experimented Physiology or Natural Philosophy, in Four Parts (2d ed., corrected; London, 1738).

> B. Heat is a Sensation excited in the Mind by a great Agitation of the Particles of the hot Body, which exerteth its Action or Influence on us; so that Heat in us is only the Idea thereof; and in the hot Body, Activity or Motion, and Nothing else. . . .[19]
>
> A. Then, if I take you right, Sir, the Reason or Difference of Heat and Cold, for Instance, in Water, lieth in this: That in the first Case, the Particles are by the Fire put into a greater Motion and Agitation than is in the Hand that feeleth it; and in the latter Case, the Motion of the aqueous Particles is in a less Degree than of those in the Hand; and thus we find it to be either Hot or Cold.
>
> B. Yes, that is the true Nature of the Case, according to modern Philosophy and manifold Experiments.[20]

Martin held fast to this view of the nature of heat. He did not see fit to change a single word of the above quotation in the later editions of this work published in 1755 and 1762. He expressed a similar view in his Bibliotheca technologica:

> HEAT and COLD are the most general and obvious Qualities in Bodies. The former consists in a great Agitation, and violent intestine Motion of the Particles of hot Bodies, which acting on us, excites that Idea in our Minds. On the contrary, Cold proceeds from the Inactivity and motionless State of the Particles of cold Bodies.[21]

Martin's ideas on heat received a picturesque expression in the dialogue between Euphrosyne and Cleonicus who discuss philosophy for young gentlemen and ladies. Cleonicus speaks first:

> Cleon. As I shall shew hereafter, that all Heat consists in the great Velocity or swift Motion of the Parts of Matter, . . . those Particles by their Action always produce the Sensation of Warmth or Heat, and being plentifully imbibed by all Kinds of Bodies, these active Particles are constantly employed to separate the Parts of Bodies, and by this Means to produce the natural Exhalations or Steams from every heated Liquor. . . .

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[19]Cf. 's Gravesande's statement quoted above, p. 14.

[20]Martin, Philosophical Grammar, pp. 114-115.

[21]Benjamin Martin, Bibliotheca technologica, or a Philological Library of Literary Arts and Sciences (London, 1737), pp. 410-411. This statement appears verbatim in the second edition of 1740, p. 324.

> Euphros. Then what you now say, I presume, is the Reason why . . . in a very cold Winter's Day, our very Breath becomes visible to the Eye, as it then wants a sufficient Degree of Heat to rarify the Particles. . . .
>
> Cleon. You understand this matter very well; and in the same Manner you are to imagine, that solid Bodies will have their superficial Parts separated by the Action of Heat, and these Particles so separated will be affected with a repulsive Force. . . . We find by Experience, that all Bodies lose their Parts in Proportion as they are more actuated by the Power or Particles of Heat; and when the Degree of Heat is very intense, there are but few Bodies, whose Parts are so fixed, or cohere so firmly, as not to be separated by their Action. . . .[22]

Here Martin restated his proposition that heat is due to the "Motion of the Parts of Matter." This is the same in all his works. In this last quotation, however, is the suggestion of a certain ambivalence regarding the nature of heat itself. In the first speech of Cleonicus, Martin stated his idea that heat consists of motion of the parts of matter; but further on he seems to have differentiated between these moving parts of matter and the parts of other matter. The moving parts may be "imbibed by all Kinds of Bodies" and may "separate the Parts of Bodies." Further, in the second speech of Cleonicus, Martin stated that the parts of bodies are "actuated by the Power or Particles of Heat [italics mine]." It can be assumed from this discussion that heat is due to the motion of some special matter, matter which separates the parts of bodies. He described flame as a fluid composed of small, luminous, active particles, which are identical to particles of light;[23] but it is not clear that

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[22]Benjamin Martin, The Young Gentleman and Lady's Philosophy, in a Continued Survey of the Works of Nature and Art, by Way of a Dialogue (3 vols.; London, 1759-1782), I, 263-264. As was the case with the Bibliotheca, this quotation appears verbatim in the second edition (1772-1782), I, 257-258.

[23]Martin, Philosophical Grammar, pp. 115-116.

the particles of flame are the same as the "active particles" which cause heat.

A similar discussion is contained in Harris's Lexicon. Like Martin, Harris stated that heat is due to the motion of the parts of a body. However, under the third condition necessary to produce heat, he said that these moving parts must be very small in order that they can penetrate easily into the pores of other substances.[24] Harris also mentioned that the intensity of heat and light depends upon the density of the "Particles of Fire which occasion it. . . ."[25] By "Particles of Fire," he apparently meant the material which comprises flame.

In 1765, Hugh Hamilton (1729-1805), professor of natural philosophy at Trinity College, Dublin, gave an answer to the question of why air is needed to support burning.[26] If fire were only vibrations of the vapor given off by the burning body, as Newton said it is, then the presence or absence of air should have no effect upon the burning process. But air is needed to support fire. Hamilton explained that the role of air is to carry away the minute particles which are given off when an object burns "which otherwise would rest upon its [the object's] surface, and thereby clog and stop the subtile vibrations of the burning matter, in which the nature of fire partly consists."[27] Thus the air

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[24]See p. 65, above.

[25]Harris Lexicon technicum (1704), p. [Ooo3 verso].

[26]Hugh Hamilton, "A Dissertation on the Nature of Evaporation and Several Phaenomena of Air, Water, and Boiling Liquors," Philosophical Transactions of the Royal Society of London, LV (1765), 146-181.

[27]Ibid., p. 174.

"keeps those particles that have just taken fire quite free from any thing that can impede or clog their vibratory motion."[28] In addition, the air may serve another function. By its own motion, the air "may promote these subtile vibrations in the burning matter, by which the fire is propagated through its parts."[29]

Georg Ernst Stahl (1660-1734), a founder of the phlogiston theory, considered fire or heat to be an instrument or agent used in chemical manipulations, and not an element or a constituent of substances. He described phlogiston as "the true matter of fire, the real principle of its motion in all combustions. . . ."[30] But phlogiston does not possess self-motion; it is put into motion by the motion of heat:

> It is important to observe that this firey matter [phlogiston] left to itself, . . . is not found attenuated or volatile; but once it has been attenuated and volatilized by the motion of fire, and by contact with the open air, then it has a subtlety and a dilatation. . . .[31]

Stahl regarded motion as the fundamental cause of heat. In a passage quoted by Baron d'Holbach in the Encyclopédie, Stahl said that students of nature should reflect profoundly upon movement; they should learn what effects movement can have on substances in general and on

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[28] Ibid. [29] Ibid.

[30] Georg Ernst Stahl, Traité du soufre, ou remarques sur la dispute qui s'est élevée entre les chymistes au sujet du soufre, tant commun, combustible, ou volatil, que fixe, &c, traduit de l'Allemand de Stahl, [trans. Baron d'Holbach] (Paris, 1766), p. 56, translated in Rhoda Rappaport, "Rouelle and Stahl: The Phlogistic Revolution in France," Chymia, VII (1961), 85. Cf. Hélène Metzger, Newton, Stahl, Boerhaave, et la doctrine chimique (Paris, 1930), pp. 9, 159-188; see also pp. 39-41, above.

[31] Stahl, Traité du soufre, p. 56, translated in Rappaport, Chymia, VII (1961), 85.

each kind of substance in particular.[32] As familiar examples of the effects of motion, he cited fusion and igniton. It is commonly thought,

> que ce sont les molécules ignées qui s'insinuant corporellement à-travers les parties de ces sortes de corps, produisent ce phénomene: mais il est aisé de voir qu'il ne vient que d'un movement purement & simplement imprimé à leurs plus petites molécules. Ce qu'on avance est prouvé par les expériences connues que nous avons citées. . . .[33]

The experiences to which Stahl referred are those of being able to set fire to wood and to heat metals by friction.

One of the few authors of the eighteenth century who attempted to develop a detailed theory of heat based upon motion was the Russian, Mikhail Vasil'evich Lomonosov (1711-1765), a member of the St. Petersburg Academy of Science. Lomonosov stated that it is well known that heat can be produced by movement. As examples, he cited the same phenomena that Stahl had used: wood can be ignited by friction and iron can be made to glow by striking it with a hammer.

> Ex quibus omnibus evidentissime patet, rationem sufficientem caloris in motu esse positam. Quoniam autem motus sine materia fieri non potest, necessum igitur est, ut ratio sufficiens caloris conistat in motu alicujus materiae.[34]

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[32]Georg Ernst Stahl, paragraph 189; quoted and translated by Baron d'Holbach, "Fusion," Encyclopédie, ou dictionnaire raisonné des sciences, des arts, et des métiers, par une société de gens de lettres, VII (1757), 400.

[33]Ibid.

[34]From all of these [phenomena] it is evident that the sufficient cause of heat is to be found in motion. However as motion cannot exist without matter, it is therefore necessary that the sufficient cause of heat consist in the motion of some kind of matter; Mikhail Vasil'evich Lomonosov, "Meditationes de caloris et frigoris causa, auctore Michaele Lomonosow," M. V. Lomonosov, Polnoe sobranie sochinenĭ , ed. S. I. Vavilov, et al. (10 vols.; Moskva, 1950-1957), II, [8]; cited hereafter as Lomonosov, "De caloris." The article originally appeared in the Novi commentarii Academiae Imperialis Petropolitanae, I (1747-1748), 206-229,

Although movement is not visible in most warm substances, its presence can be known by the effects produced. For example, a hot iron is visibly at rest; yet it melts some objects which are placed upon it and transforms others into vapors. Since the iron produces motion in the parts of these objects, its own parts must be moving also. Further, motion cannot be denied just because it is not visible. The wind is invisible; yet we know it is moving because of the effects it produces. Movement in the iron is invisible because its moving parts are so small.[35]

Having established to his own satisfaction that heat consists of matter in motion, Lomonosov asked what is the nature of this matter which moves.

> Materia in corporibus duplex est, cohaerens, . . . atque fluminis instar poros illius interlabens. Quaeritur itaque, quaenam earum in motu constituta calorem gignat. Huic quaestioni ut satisfiat, excutienda sunt palmaria phaenomena, quae circa corpora calida observantur. Ea vero consideranti occurrit: 1) calorem in corporibus eo majorem existere, quo cohaerens eorum materia est densior, et contre, . . . 2) constat corpora densiora sub eodem volumine plus materiae cohaerentis continere, quam interlabentis. Quoniam autem ex legibus mechanicis notum est, quantitatem motus eo majorem esse, quo copiosior est materia mota, et contra. . . . Verum quoniam contra quantitas caloris respondet potius materiae corporum cohaerenti, patet igitur caloris rationem sufficientem contineri in motu corporum intestino meteriae cohaerentis.[36]

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published in 1750. It is translated in the Ostwald series: Mikhail Vasil'evich Lomonosov, "Gedanken über die Ursachen der Wärme und Kälte," Physikalisch-chemische Abhandlungen M. W. Lomonossows, 1741-1752 (Ostwald's Klassiker der exakten Wissenschaften, Nr. 178), trans. with notes by B. N. Menschutkin and Max Speter (Leipzig, 1910), pp. 19-27. The translation is not very good.

[35]Lomonosov, "De caloris," pp. [8], 10.

[36]There are two kinds of matter in bodies, coherent, . . . and interposed, which flows river-like in the pores of the former [coherent matter]. It is asked, therefore, which of these matters, when set into motion, produces heat. To answer this question, the best phenomena

This internal motion can be of three types: progressive (progressivi) where the particles can change places with each other, rotational (gyratorii), or vibratory (tremuli).[37] In deciding between these possibilities, Lomonosov made the following assumptions: first, that the cause of heat cannot be in an internal motion which can be shown to be absent in a warm substance, and second, the cause cannot be in a movement which is present in a substance of less heat but absent in a substance of greater heat.[38] In other words, as solids, liquids and vapors can possess heat, the cause of heat must be restricted to a kind of motion which is common to all three states.

Cohesion among the particles of fluids is very weak, and these particles possess progressive motion. But this is not true for solids. Thus, Lomonosov said, progressive motion is not the cause of heat.[39] Cohesion can exist only when the particles of matter are touching; and the particles cannot touch if they have vibratory motion. As solids possess a strong cohesion even at very high temperatures, vibratory motion cannot be the cause of heat.[40]

> Remotis igitur progressivo et tremulo intentinis motibus, necessario sequitur calorem consistere in motu intestino gyratorio

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which are observed around heated bodies should be examined. By a consideration of these phenomena, it follows: 1) more heat exists in those bodies in which the coherent matter is more dense, and conversely, . . . 2) it follows that bodies of the same volume contain more coherent matter than interposed matter. From the laws of mechanics, it is noted that the quantity of motion is greater in that body in which the moving matter is more abundant, and conversely. . . . Truly, since, on the contrary, the quantity of heat corresponds more to the coherent matter of the body, it follows therefore, that the sufficient cause of heat consists in the intestine motion of this coherent matter (Ibid., pp. 10, 12).

[37] Ibid., p. 14. [38] Ibid.

[39] Ibid., pp. 16, 18, 20. [40] Ibid., p. 20.

materiae cohaerentis, necesse enim est, ut cuidam ex tribus tribuatur.[41]

Rotation can exist without destroying cohesion as is shown by considering two pieces of polished marble. The two stick together because of cohesion; but one piece will slide easily over the other.[42]

According to Lomonosov, the heat of an object depends upon the speed of rotation of its internal particles.[43] The effect of this rotation creates a repulsive force (vis repulsiva) among these particles. This force overcomes cohesion, resulting in melting and vaporization.[44] As the speed of rotation is proportional to the amount of heat present, the least possible degree of heat is when all motion stops.[45]

Lomonosov argued against the existence of a peculiar matter of heat. When considering natural phenomena, he believed that the affect should correspond to the cause. Thus two substances, at the same temperature, should expand equally when the same amount of heat is given to them; but this obviously does not happen. If heat were a matter, the substances should be equally expanded.[46] Further, some chemists think that the increase of weight of objects when calcined proves the existence of a heat matter. Lomonosov argued that a stronger fire will reduce the calces to metal again with a loss of weight; and why should a further increase of

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[41]As progressive and vibratory intestine motion is thus eliminated, it necessarily follows that heat consists in rotational intestine motion of coherent matter, for it is necessary that it [motion] be attributed to one of these three (Ibid., p. 20).

[42]Ibid., pp. 20, 22.

[43]Ibid., pp. 22.

[44]Ibid., pp. 34.

[45]Ibid., pp. 36, 37.

[46]Ibid., pp. 42, 44.

this supposed heat matter decrease the weight of an object after first increasing it.[47] The increased weight of calces, he said, is due fixation of air or of something from the air.[48]

Henry Cavendish (1731-1810), English chemist and natural philosopher, believed in a vibrational theory of heat but offered neither discussion of his reasons for accepting such a view nor any details as to how his view served to explain heat phenomena. In commenting on efforts to determine the temperature at which mercury freezes, Cavendish mentioned that the heat produced by melting snow is equivalent to heating water 150°.[49] Joseph Black, he said, explained this phenomenon in the same way; but instead of saying that heat is "produced," Black said that latent heat is "evolved" or set free. Cavendish claimed that Black's expressions relate to his idea concerning the nature of heat. Black assumed that the heat in substances

> is owing to their containing more or less of a substance called the matter of heat; and as I think sir ISAAC NEWTON'S opinion, that heat consists in the internal motion of the particles of bodies, much the most probable, I chose to use the expression, heat is generated.[50]

In a later paper discussing the composition of water, Cavendish mentioned that James Watt (1736-1819) explained water as consisting of

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[47] Ibid., pp. 44, 46, 48.

[48] Ibid., p. 46; also quoted in Partington, History of Chemistry, III, 203. Philip Pomper, "Lomonosov and the Discovery of the Law of the Conservation of Matter in Chemical Transformations," Ambix, X (1962), 125-126, apparently has misunderstood Lomonosov's statement.

[49] Henry Cavendish, "Observations on Mr. Hutchins's Experiments for Determining the Degree of Cold at Which Quicksilver Freezes." Philosophical Transactions of the Royal Society of London, LXXIII (1783), 303-328.

[50] Ibid., pp. 312-313, note.

dephlogisticated air and phlogiston deprived of part of their latent heat.[51] Cavendish said that if it is assumed that there is such a thing as latent heat, then a similar mode of speaking should be used in explaining all other changes, because almost all chemical combinations involve some change in temperature. Yet chemists do not speak in this manner.

> Now I have chosen to avoid this form of speaking, both because I think it more likely that there is no such thing as elementary heat, and because saying so in this instance, without using similar expressions in speaking of other chemical unions, would be improper, and would lead to false ideas; and it may even . . . cause more trouble and perplexity than it is worth.[52]

The relationship seen by contemporary chemists between the phlogiston theory and ideas concerning the nature of heat depended to a large extent upon their concepts of the nature of phlogiston itself. The idea that phlogiston is the matter of fire fixed within combustible substances goes hand in hand with a material heat theory; or to put it another way, a material theory of heat complements the idea that phlogiston is fixed fire. If on the other hand, phlogiston is considered to be a substance sui generis, distinct from fire, then belief in phlogiston might have little or no relation to ideas concerning the nature of heat. The scientist believing phlogiston to be a substance sui generis might accept either a material or a vibratory theory of heat without creating a conflict or contradiction between ideas explaining the two separate but related groups of phenomena which the phlogiston theory and heat theory were created to explain.[53]

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[51] Henry Cavendish, "Experiments on Air," Philosophical Transactions of the Royal Society of London, LXXIV (1784), 119-153.

[52] Ibid., pp. 140-141.

[53] Isaac Milner (1750-1820), Jacksonian Professor of Natural

Joseph Priestley (1733-1804), that eminent protagonist of the phlogiston theory, was one of those who saw little or no connection between phlogiston and heat; and in the 1775 edition of his Experiments and Observations on Air, he expressed belief in a vibrational theory.[54] Phlogiston is explained by many chemists as the element fire which is fixed in substances and thereby becomes hidden to the senses unless it is released. But Priestley disliked the use of the term "fire." To use the word in this respect, he said, would force him to distinguish between "fire in a state of action, and fire inactive or quiescent."[55] It is much easier to use the word phlogiston and ban "fire" from chemical discussion. Furthermore, because of its common use, the word "fire" always includes heat phenomena; and heat, said Priestley, "has no more proper connexion with phlogiston than it has with water, or any other constituent part of bodies. . . ."[56] For in reality, heat

> is a state into which the parts of bodies are thrown by their action and reaction with respect to one another; and probably (as the English philosophers in general have supposed) the heated state of bodies may consist of a subtile vibratory motion of their parts.[57]

Philosophy at Cambridge, advocated the vibratory theory of heat in his chemistry lectures for 1784-1788. Milner pointed out that this theory of heat was independent of any particular concept of phlogiston, as long as phlogiston was not assumed to be fixed heat matter; L. J. M. Coleby, "Isaac Milner and the Jacksonian Chair of Natural Philosophy," Annals of Science, X (1954), 244-252.

[54]Joseph Priestley, Experiments and Observations on Different Kinds of Air (2d ed., corrected; London, 1775); cf. Joseph Priestley, Expériences et observations sur différentes espèces d'air, trans. Gibelin (5 vols.; Paris, 1777-1780), I, 364-368.

[55]Priestley, Experiments on Air (1775), p. 283.

[56]Ibid., p. 281. [57]Ibid.

Heat motion has no relation to the phlogiston principle itself, but only to the process whereby this principle may be released from substances in which it is fixed. In these processes, the production of heat is due to "the action and reaction, which necessarily attends the separation of the constituent principles, exciting probably a vibratory motion in them."[58] This relation between heat and phlogiston may be reversed in the sense that instead of heat being produced by the release of phlogiston from substances, phlogiston may be released by the application of heat. Thus heat vibrations may cause the release of phlogiston in one case, or be caused by the release of phlogiston in another.

Priestley's explanation of the differences between combustibles and non-combustibles illustrates further the relationship between heat movement and the principles of inflammability. The essential difference between inflammable and non-inflammable substances is the firmness with which the phlogiston is combined in them. In inflammable substances,

> the heat, or the vibration occasioned by the emission of their own phlogiston, may be sufficient to occasion the emission of more, till the whole be exhausted; that is, till the body be reduced to ashes.

In non-inflammables, on the other hand, "the heat [vibration] occasioned by the emission of their own phlogiston may not be sufficient for this purpose, but an additional heat ab extra may be necessary."[59]

For Priestley, phlogiston is a substance, sui generis; and his overt attempt to dissociate it from "fire" and all the connotations associated with what term indicates that the question of the nature of heat was of limited, secondary importance in his theory. Indeed, it

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[58] Ibid., pp. 260-261. [59] Ibid., p. 281.

seems that he was largely indifferent to the question of the nature of heat; and he was able to incorporate either a material or a vibratory view with equal ease in his system.

His mention of heat is largely confined to the use of heat as an instrument or agent in chemical manipulations, and except for the treatment of heat in the early editions of his Experiments and Observations on Air, Priestley apparently never again gave a detailed discussion of this subject.[60] In some writings, nevertheless, one can infer what his ideas were concerning the nature of heat, and for the most part, he used explanations involving a material theory in his subsequent work.[61]

However, in his Doctrine of Phlogiston Established (1800), his last stand against the oxidation theory, Priestley made a halfhearted, unconvincing attack on the material view of heat so as to cast further doubt upon the new chemistry.[62] As it is in most of his writings, the mention of heat is of distinctly secondary importance. He treated heat primarily as an agent used in chemical manipulations; but in a few instances, there is an implied acceptance of the existence of a material heat substance.[63] At the end of the book, Priestley stated that the chief argument against the existence of phlogiston is its weightlessness.

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[60]The section entitled "Queries, Speculations, and Hints," which contains the discussion of heat in the 1775 edition of his Experiments and Observations on Air, is omitted in the 1790 edition (3 vols.; Birmingham).

[61]See pp. 183-185, below.

[62]Joseph Priestley, The Doctrine of Phlogiston Established and That of the Composition of Water Refuted (Northumberland, 1800).

[63]Ibid., p. 35.

He felt that this argument is a little unfair. None of us, he said, "pretend to have weighed light, or the element of heat," and yet few persons doubt that they are truly substances.[64] Then as a final jab at the new chemistry, Priestley added in a footnote:

> Since this was written it has, I think, been proved by Count Rumford, and Mr. Davy, that heat is not produced by any proper substance, such as is now called calorique, and which is so essential to the new theory.[65]

Although Priestley altered his explanations of heat from the use of a vibrational concept to explanations utilizing a material theory, another phlogistonist switched from a material view to a vibrational one. In the first edition (1766) of his Dictionnaire de chymie, Pierre Joseph Macquer (1718-1784) explained that heat is caused by "le feu pur, libre, & non combiné." Fire is "un assemblage de particules d'une matiere simple, homogene, and absolument inaltérable."[66] As an element, fire may become fixed within bodies, and in this state of combination it is known as "phlogistique."[67] However, in the second edition of this work, published in 1778, Macquer reversed himself and espoused a vibratory theory.[68]

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[64] Ibid., pp. 77-78.

[65] Ibid., p. 78, note. For a brief discussion of the views of Benjamin Thompson, Count Rumford (1753-1814) and Sir Humphry Davy (1778-1829), see pp. 213-215, below.

[66] [Pierre Joseph Macquer], Dictionnaire de chymie, contenant la théorie & la pratique de cette science, son application à la physique, à l'histoire naturelle, à la médecine, & à l'economie animale, avec l'explication détaillée de la vertu & de la maniere d'agir des médicamens chymiques, et les principes fondamentaux des arts, manufactures, & métiers dépendans de la chymie (2 vols.; Paris, 1766), I, 498.

[67] Ibid.; see pp. 43-45, above.

[68] Pierre Joseph Macquer, Dictionnaire de chimie, contenant la

In the second edition, the article "Feu" begins the same as in the 1766 edition. Fire can exist in two states, free and combined. Free fire is a fluid body whose particles are very subtle, infinitely small, without sensible coherence and in continual, very rapid movement.[69] The most obvious effects of fire are those of heat and light, and it is by means of these that most judge the presence or absence of fire. However, for both of these effects to be valid indicators of the presence of the element fire, in every instance in which light and heat appear, one should be able to trace their origin to the presence of the fire element. If, on the other hand, heat and light are shown to proceed from different causes, then one or both of these effects are invalid as indicators of the fire element.[70] Thus, Macquer said, knowledge of the relation between heat and light is prerequisite to ascertaining of the nature of fire itself. In the argument which followed, the question of the nature of fire was ignored, and the important problem for Macquer became the nature of heat and light, the supposed fire indicators.

It must be decided first whether heat and light are the effects of two different substances or the effects of the same substance, perhaps differently modified. There are strong arguments, Macquer said, for and against both views. Light causes heat, and heat causes light. This might lead one to assume that both are merely modifications of the same substance. On the other hand, heat and light are not proportionable.

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théorie et la pratique de cette science, son application à la physique, à l'histoire naturelle, à la médecine, et aux arts dépendans de la chimie (2d ed., enlarged; 2 vols.; Paris, 1778).

[69] Ibid., I, 481. [70] Ibid., p. 482.

In some instances we get much heat with a complete absence of light, for example, in boiling water; and in other instances we get much light with an absence of heat, for example, in moonlight. This might lead one to assume that heat and light are different substances entirely.[71]

He was following Boerhaave; and up to this point, Macquer had added little to what he had said in his first edition. But from this point on, he focused his attention on the differences between the two effects of light and heat, and he concluded that heat and light are not the effects of two different substances, that light is a material being, and that heat has no materiality at all.

Macquer believed that heat and light act in entirely different ways. No substance is impenetrable to heat, but this is not true for light; and two principles which act so differently with respect to other substances are necessarily different. This relationship between heat and light and other substances may be explained as due to heat and light being different modifications of the same substance. However, if we assume this, we would be forced to admit that all substances are mere modifications of some other. Macquer admitted that we cannot nor will ever be able to prove this assumption false. But we must deal not with what may be but with what is; and we should regard as existing only what is proved to exist.[72]

It cannot be doubted that light is a substance distinct from all others. Without it we could not see; and its finite velocity proves it to be a substance. Macquer listed the properties of light peculiar to itself which show it has material existence. Light can move with

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[71] Ibid.

[72] Ibid., pp. 483-484.

finite speed, change direction, be dispersed and reassembled, and last and probably most important, it can enter substances and become a constituent of them.[73]

With respect to heat, it is another matter. It is not easy, said Macquer, to decide if heat be a particular substance like light or a modification to which all kinds of matter are susceptible without distinction. To help decide this question, we should examine the principal phenomena of heat. First is the sensation; second is the change in volume produced by heat; third, heat penetrates all kinds of matter, which is not true of light; heat tends to equilibrium in all substances whatsoever, which is not true of light; the rate of conduction of heat is uniform and unchangeable; and heat decreases the specific gravity of substances without changing their absolute weight. Last and most important, heating and cooling of substances produce no permanent change in them; that is, heat does not combine with them. Thus the same quantity of heat must be put into a substance to raise its temperature a given number of degrees after having been heated and then cooled as before it was heated and cooled.[74]

From these facts, said Macquer, one cannot fail to conclude that

> la chaleur est quelque chose de totalement différent de la lumière, & qu'elle n'est pas même une substance matérielle distinguée, comme la lumière, par des propriétés qui lui soient particulières.[75]

If heat were an imponderable matter, it would be impossible to think of

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[73] Ibid., pp. 483-484. [74] Ibid., pp. 484-486.

[75] Ibid., p. 486.

its particles, however small, as never meeting an obstacle or a deviation by the particles of other substances. This consideration alone, he said,

> me paroît démontrer que la chaleur n'est point une substance; que ce n'est au contraire qu'un état particulier, une manière-d'être, dont toute substance matérielle est susceptible, sans cesser cependant en aucune façon d'être ce qu'elle est; & si l'on peut se livrer à quelques conjectures sur un objet si caché, voice quelles seroient mes idées, auxquellas je n'attache aucune prétention, pas même celle de la nouveauté, & que je suis tout prêt d'abandonner, pour en adopter de plus satisfaisantes sur les phénomènes du feu, dès qu'elles parviendront à ma connoissance.[76]

Comte de Buffon agreed that heat is not a distinct substance. But whereas Buffon believed that any matter could become heat, Macquer denied heat was a substance at all. If heat then is only a manner of being which all substances are susceptible, in what does its essence lie? No physicist doubts, said Macquer, that even in the most dense objects, pores or voids exist and therefore that the elementary molecules of all substances have space to move. Furthermore, these molecules cannot fail to move every time they receive some shock or impulse which is greater than the force of attraction or cohesion which fixes these molecules in their respective positions.[77] The force of friction and percussion, which is proportional to the force of the impulse, tends to derange the particles of objects, while an opposite force of cohesion or attraction tends to return them to their former position. Thus

> il en résulte nécessairement un mouvement intestin d'oscillations ou de vibrations dans toutes les petites parties du corps frotté ou frappé; & ce mouvement est d'autant plus fort, que ces oscillations sont plus rapides. Or, il paroît que ce mouvement intestin suffit pour faire naître dans les corps quelconques l'état que nous nommons chaleur. . . .[78]

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[76] Ibid. [77] Ibid., pp. 486-487. [78] Ibid., p. 487.

Macquer then discussed the phenomena which confirm his thesis that heat is the intestine motion of the particles of common matter. If heat is proportional to movement, then heat should be proportional to the force and speed of movement; and experience, he said, confirms this most positively The dilation of substances is proportional to the intensity of heat. This necessarily follows if heat is movement, for the parts of matter cannot move without altering their positions relative to altering their positions relative to each other. The absolute weight of substances does not increase when heated. As heat is merely movement, the weight should not increase. Heat is not reflected because it is not a material substance as light is.[79] Heat tends to equilibrium and tends to be communicated equally to surrounding substances; this follows the general law of communication of movement. Heat cannot be fixed in substances, for only matter can be fixed. Light striking substances heats them and the heating is proportional to the intensity of light. Macquer explained that light is matter, and thus light particles, moving with great speed, produce movement in the parts of other matter by their impulse.[80]

To explain the glowing of substances heated to a high degree, Macquer assumed a plenum of light particles. These particles are visible only when projected directly from the object to the eye. Vibrating particles of a heated substance, if the vibrations are violent enough, strike these inactive light particles and propel them in all directions.[81] Thus "feu libre ou feu en action," by which Macquer apparently meant

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[79] Macquer did not discuss radiant heat phenomena.

[80] Ibid., pp. 487-488. [81] Ibid., pp. 488-489.

flame, is only the result of movement, partly the movement of light and partly the vibratory movement of the particles of the substance.[82]

In this second edition of his Dictionnaire, Macquer defined phlogiston as the matter of light, "la seule substance matérielle de feu," which is fixed in other substances.[83] His explanation of the evolution of heat during combustion is very much like Priestley's. The release of phlogiston causes a vibratory motion among the particles of the burning substance.[84] Air is an intermediary agent which acts with heat vibration to bring about the separation of the phlogiston from the other constituents of the combustible object.[86]

In explaining the difference between combustibles and non-combustibles, Macquer said that the former have no need of an external heat to cause a continued release of phlogiston. That is, the heat vibration caused by the release of phlogiston is sufficient to cause the release of more phlogiston until the combustible is consumed. Non-combutibles require a continued application of an external heat.[86]

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[82] Ibid., p. 490.

[83] Ibid., p. 261; cf. II, 198. Hélèn Metzger has stated that confidence in Newton's ideas on the materiality of light was almost absolute in the eighteenth century. As combustion was thought to be a process of decomposition in which light appears, it seems natural that some persons would equate light with phlogiston; "Newton: La théorie de l'émission de la lumière et la doctrine chimique au XVIIIème siècle," Archeion, XI (1929), [13]-25; cf. Metzger, Newton, Stahl, Boerhaave, pp. 9, 68-82.

[84] Cf. Priestley, Experiments on Air (1775), pp. 260-261; see pp. 82, above.

[85] Macquer, Dictionnaire (1778), I, 295.

[86] Ibid., pp. 490-491; cf. Priestley's views, p. 82, above.

Macquer cited Buffon in referring the effects of fire to the speed, volume, and mass of the particles involved.[87] The role of air in combustion is not to increase the speed of movement but to increase the quantity of matter which is in motion. Communication of heat depends upon the quantity or volume of the moving matter compared to that of the matter to be moved. Thus the law of the communication of heat is exactly the same, Macquer said, as that of the communication of movement.[88]

In explaining changes of state, Macquer made no mention of Joseph Black and apparently was not familiar with the concepts of specific and latent heats. Changes of state are due to the separation of the particles of substances. This separation disunites the particles so they have no coherence among themselves. The degree of disunion determines the resultant state of the substance.[89] Macquer's explanation of state change in this 1778 edition of his Dictionnaire is essentially the same as in the 1766 edition. He even used the term feu to indicate the heat which causes these changes. The only difference is that in the later edition, feu was defined previously as a vibratory motion. Macquer's primary concern was the explanation of chemical heat phenomena, principally that of combustion. And his theory regarding heat is well adapted to this purpose, although it is incomplete regarding explanation of physical as opposed to chemical phenomena.

Macquer had considerable influence upon his pupil, Antoine François de Fourcroy (1755-1809), professor of chemistry at the Jardin

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[87]Macquer, Dictionnaire (1778), I, 494-495.

[88]Ibid., pp. 496-498. [89]Ibid., p. 492.

du Roi; and the discussion of heat in the latter's Leçons élémentaires de chimie of 1782 appears to have been taken largely from Macquer's Dictionnaire of 1778.[90]

Everyone, said Fourcroy, regards fire as being filled with light and heat. Physicists (physiciens) define it as a very mobile, active, penetrating fluid composed of hard, tenuous particles in a continuous motion which always tends to increase. However, up to now no one has ever been able to isolate this fluid; and thus to ascertain its properties, we must study the effects it produces.[91] Along with Boerhaave, Fourcroy recognized three main effects of fire: heat, light, and rarefaction. Light, is a substance with demonstrated existence. It is elastic; its particles are extremely hard; it has weight as proved by diffraction phenomena; and it seems to obey the laws of affinity in combining with other substances. Macquer, he said, equates it with Stahl's phlogiston.[92]

With respect to heat, on the other hand, there is no such agreement on its nature. Fourcroy cited the Swedish chemist, Torbern Bergman (1735-1784) as believing heat to be a particular substance, and he cited Macquer as thinking it only a modification to which all substances are susceptible. To decide between these two views, Fourcroy followed Macquer and examined the principal heat effects. Heat penetrates all substances without exception. It is not reflected since a

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[90]Antoine François de Fourcroy, Leçons élémentaires d'histoire naturelle et de chimie, dans lesquelles on s'est propose, 1°, de donner un ensemble méthodique des connoissances chimiques acquises jusqu'à ce jour, 2°, d'offrir un tableau comparé de la doctrine de Stahl & de celle de quelques modernes, pour servir de résumé à un cours complet sur ces deux sciences (2 vols.; Paris, 1782).

[91]Ibid., I, 41. [92]Ibid., pp. 41-43.

substance becomes soft when heated. Softening indicates that heat has been absorbed. Heat tends to equilibrium; it has no weight. It cannot be fixed in any substance; and it reacts exactly the same with all substances.[93]

> Toutes ces propriétés ne démontrent pas la présence d'un corps, & nous pensons d'après cela que la chaleur n'est qu'une modification semblable au mouvement.[94]

Fourcroy continued by saying that Macquer thinks the motion theory is established by the following considerations: movement always produces heat, for example, when a stone strikes a piece of iron; heat is always the cause of movement; and substances which are the easiest to move are those heated most quickly [?]. Fourcroy added that the idea of motion easily explains why substances heated a long time become luminous (the movement impels light particles), why some heated substances are without light (the movement is too small to impel the light), why some substances are luminous without heat (due to the peculiar shape of the molecules of the substance), and why light itself can excite heat (the impulse of light particles causes the molecules of the body to move).[95]

Boerhaave's third effect of fire is the dilation of bodies. At first sight, said Fourcroy, this seems to be due to the introduction of some foreign substance into the small cavities of the body which acts like small wedges, separating the molecules. However, as the object dilated by heat does not increase its absolute weight, Fourcroy concluded that dilation consists only in a simple separation of the molecules.

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[93] Ibid., pp. 43-44. [94] Ibid., p. 44. [95] Ibid., pp. 44-45.

This causes an increase in pore space and results in more void and less solid matter being contained in a given volume.[96]

Fourcroy's reliance upon Macquer is clear both from the sequence of presentation and the arguments he used, especially his statements that heat cannot be reflected and that heat never becomes fixed in substances. Both Macquer and Fourcroy were primarily interested in chemical phenomena and both gave short shrift to change of state. Both ignored radiant heat phenomena and appeared ignorant of the ideas of Black.

Throughout his discussion and comparison of the phlogiston theory and the "chimie pneumatique," Fourcroy repeatedly claimed to take neither side and to be playing the role of mere recorder of other's views: "je prends le simple parti d'Historien."[97] However, there is little doubt that he favored the new chemistry.[98] But Fourcroy's belittling of phlogiston had no effect on his views of the nature of heat, although he rejected the vibration theory later when he became more strongly partisan in favor of the oxidation theory.[99]

Advocates of the vibratory theory, however, did not vanish with Fourcroy's conversion to the heat theory associated with the new chemistry. The concept of vibrations was offered in opposition to the new caloric theory as it had been offered against the idea of fire-matter-

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[96] Ibid., p. 46.

[97] Ibid., p. xxiii; cf. ibid., p. 22.

[98] See especially ibid., pp. 53-56. James R. Partington claims Fourcroy adopted a modified oxidation theory as early as 1777; "Berthollet and the Antiphlogistic Theory," Chymia, V (1959), 134-135.

[99] See pp. 163-176, below.

in-motion.[100] For example, Stephen Dickson, an Irish physician and professor at Trinity College, Dublin, objected to the view of the French chemists that the cause of heat is a material substance. This idea

> has not been established by satisfactory proof. It has been controverted by natural philosophers of the first rank, particularly by the philosopher of the highest authority in physics [Macquer?]; and I am satisfied that it is not, as some imagine, essentially necessary to the construction of an intelligible and consistent theory of chemistry.[101]

A similar objection was offered by the chemist James Keir (1735-1820). As early as 1777, in his translation of Macquer's dictionary, Keir had indicated a belief in the idea that heat is due to the vibrations of the particles of matter.[102] In 1789 he was still carrying the banner for Macquer, including his ideas on heat. In the preface to his own chemical dictionary, in which he described Macquer's work as having perhaps "contributed more to the diffusion of chemical knowledge than any other book. . . ,"[103] Keir examined claims that the new chemistry is founded without preconceived hypothesis.[104] This claim is utterly

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[100]For a discussion of the caloric theory of heat, see Chapter IV, below.

[101]Stephen Dickson, An Essay on Chemical Nomenclature (London, 1796), p. 68.

[102][Pierre Joseph Macquer], A Dictionary of Chemistry Containing the Theory and Practice of That Science, Its Application to Natural Philosophy, Natural History, Medicine, and Animal Economy, with Full Explanations of the Qualities and Modes of Action of Chemical Remedies and the Fundamental Principles of the Arts, Trades, and Manufactures Dependent on Chemistry, Translated from the French with Notes, Additions, and Plates, the Second Edition, to Which Is Added as an Appendix, a Treatise on the Various Kinds of Permanently Elastic Fluids or Gases, [trans. James Keir] (2d ed., enlarged; 3 vols.; London, 1777), III, Appendix, p. 102.

[103]J[ames] K[eir], The First Part of a Dictionary of Chemistry, &c (Birmingham, 1789), p. [i].

[104]Ibid., pp. vii-viii.

false. What is more hypothetical, he asked, than the assumption that airs and gases are composed of some unknown base united to the matter of heat?

> What can be more hypothetical than the existence of this matter of heat, of a substance of which Mr. Lavoisier has candidly acknowledged, after the most scrupulous investigation, that he can discover no sensible weight. Nevertheless, although this common attraction or gravitation, the most general of all properties of matter, and by which the quantity of all other matter has been always ascertained, cannot be traced; yet this matter [heat] is supposed, according to this system, not only to exist, but to possess the peculiar attractions called chemical affinities.[105]

Keir admitted that many heat phenomena associated with chemical reactions can be explained by assuming a material heat substance. But he continued to maintain that the existence of this heat matter is only an assumption and an ill-grounded one at that.[106]

In discussing the supposed composition of inflammable gas, Keir again attacked the idea of a material heat. Not only has the existence of heat matter not been demonstrated but its existence has not even been made probable. Lavoisier himself has shown that heat has no weight;[107]

> But gravitation is the most general property of matter, and that by which we measure its quantity. Before we can admit a being void of gravitation as material, and capable of chemical combination, we must relinquish every philosophical and every popular idea of matter, and soar into the region of hypothesis without resting one foot on the solid earth. Yet this fanciful being makes a distinguished figure in the system of those philosophers who reject hypothesis.[108]

In his critique of Keir's dictionary, Claude Louis Berthollet (1748-1822), supporter of the oxidation theory and later professor at the Ecole Polytechnique, claimed that Keir most often cited caloric (the

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[105] Ibid., pp. viii-vx. [106] Ibid., p. 110.

[107] Ibid., pp. 207-208. [108] Ibid., p. 208.

matter of heat in the new theory) to prove that the antiphlogistonists only multiply their assumptions.[109] Berthollet's argument in support of the new chemistry was to deny that belief in caloric as a material substance is part of the oxidation theory. He quoted Lavoisier to the effect that he treats caloric as an elastic fluid only because of the usefulness of this manner of speaking.

> Après avoir considéré la chaleur comme la produit d'une substance particulière ou comme l'effet du mouvement, nous ne déciderons point, disent les auteurs [Lavoisier and Laplace], entre les deux hypothèses précédentes.[110]

Fourcroy, he said, says the same thing in his Elemens of 1789.[111] The concept of the matter of heat is not, Berthollet repeated, part of the antiphlogistic theory.[112]

During the eighteenth century, acceptance of the motion, or vibrational, theory of heat appears to have been due primarily to the influence of Newton who was himself following an older tradition. Compared to the numbers of philosophers who maintained the existence of elemental fire, adherents to the motion theory were in a distinct minority. Members of this minority group theory were mostly Englishmen. Peter Shaw (1694-1763), translator, physician, and Fellow of the Royal Society, remarked in 1741 in his translation of Boerhaave's chemistry,

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[109] Claude Louis Berthollet, "Observations sur le nouveau dictionnaire de chimie de m. Keir," Annales de chimie, X (1791), 144.

[110] Ibid., p. 145. Berthollet here is referring to an article by Lavoisier and Laplace which appeared in the memoirs of the French Academy of Sciences for 1780. For a discussion of this article, see pp. 113-119, below.

[111] See pp. 164-166, below.

[112] Berthollet, Annales de chimie, X (1791), 144-145.

> The doctrine of fire here laid hown [sic] by our author [Boerhaave], will appear new and extraordinary; at least among us, who have used to consider fire in the light it is set by Lord Bacon, Mr. Boyle, and Sir I. Newton.[113]

But even in England the influence of the fire-in-motion theory was almost irresistible. Virtually all the English encyclopedias and dictionaries published after 1730 explain heat and fire in terms of a material theory.[114] Although the Harris Lexicon in 1704 had referred the intensity of heat to the density of fire particles, Harris apparently meant the density of particles of flame rather than elementary fire.[115] The article on heat in which this statement occurs is unchanged through the fifth edition of 1736.[116] In a second volume, first published in 1710 as a supplement to the first, Harris added a very short article on fire in which he alluded to a Cartesian theory.[117] This article was not

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[113]Herman Boerhaave, A New Method of Chemistry, Including the History, Theory, and Practice of the Art, Translated from the Original Latin of Dr. Boerhaave's Elementa chemiae, as Published by Himself, to Which Are Added Notes and an Appendix, Shewing the Necessity and Utility of Enlarging the Bounds of Chemistry, with Sculptures, trans. Peter Shaw (3d ed., corrected; 2 vols.; London, 1753), I, 206. Partington describes this edition as an unchanged reprint of the 1741, 2d ed. (History of Chemistry, II, 744).

[114]See a short discussion in Arthur Hughes, "Science in English Encyclopaedias, 1704-1875: II. Theories of the Elementary Composition of Matter," Annals of Science, VIII (1952), 347-350.

[115]Harris, Lexicon technicum (1704), p. [Ooo3 verso]; see p. 73, above.

[116]John Harris, "Heat," Lexicon technicum, or an Universal English Dictionary of Arts and Sciences, Explaining Not Only the Terms of Art, but the Arts Themselves (5th ed., enlarged; 2 vols.; London, 1736), I, 3Zz[1 recto]-[3Zz2 verso].

[117]John Harris, "Fire," Lexicon technicum, or an Universal English Dictionary of Arts and Sciences Explaining Not Only the Terms of Art, but The Arts Themselves, Volume II (London, 1710), p. [Cccl verso].

changed until the 1736 edition and then the fire-in-motion theory was accepted completely.[118]

Nathan Bailey (d. 1742), in his Dictionarium Britannicum published in 1730, explained fire as earthy particles moved by the matter of the first element,[119] and heat as agitation of the parts of a substance and the fire contained in it.[120] The first edition (1728) of the Cyclopaedia of Ephraim Chambers (ca. 1680-1740) contains a lengthy discussion of the fire-in-motion theory.[121] The article on heat is very similar to Shaw's notes to his translation of Boerhaave, and although the article is favorable to Boerhaave's views, the question of the nature

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[118]Harris, Lexicon technicum (1736), I, [3Y1 verso]-[3Y2 recto].

[119]This is apparently the Cartesian "first element." See p. 7 and n. 2, p. 7, above.

[120]Nathan Bailey, George Gordon, and Philip Miller, Dictionarium Britannicum, or a More Compleat Universal Etymological English Dictionary than Any Extant, Containing Not Only the Words and Their Explication, but Their Etymologies from the Ancient British, Teutonick, Low and High Dutch, Saxon, Danish, Norman, and Modern French, Italian, Spanish, Latin, Greek, Hebrew, Chaldee, &c., Each in Its Proper Character, Also Explaining Hard and Technical Words, or Terms of Art, in All the Arts, Sciences, and Mysteries Following Together with Accents Directing to Their Proper Pronuntiation, Shewing Both the Orthography and Orthoepia of the English Tongue (London, 1730), pp. Iiii, [4M2 verso].

[121]Ephraim Chambers, Cyclopaedia, or an Universal Dictionary of Arts and Sciences, Containing the Definitions of the Terms, and Accounts of the Things Signify'd Thereby in the Several Arts, Both Liberal and Mechanical, and the Several Sciences, Human and Divine, the Figures, Kinds, Properties, Productions, Preparations, and Uses of Things Natural and Artificial, the Rise, Progress, and State of Things Ecclesiastical, Civil, Military, and Commercial, with the Several Systems, Sects, Opinions &c. among Philosophers, Divines, Mathematicians, Physicians, Antiquaries, Criticks, &c., the Whole Intended as a Course of Antient and Modern Learning, Compiled from the Best Authors, Dictionaries, Journals, Memoirs, Transactions, Emphemerides, &c., in Several Languages (2 vols.; London, 1728).

of heat is not explicitly decided.[122] In the article on fire, however, Chambers gave the nod to Boerhaave: "That Author [Boerhaave] has indeed done Wonders: The Sum of his Doctrine we shall here subjoin."[123] The fire-in-motion theory was expounded in A New and Complete Dictionary of Arts and Sciences, 1754-1755,[124] by Temple Henry Croker (1730?-1790?) in his dictionary published in 1764-1766,[125] and also by John Barrow (fl. 1735) in his New and Universal Dictionary of 1764.[126] Barrow's

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[122] Ibid., I, [*Kkk2 recto]-[*Ll12 verso]. For a résumé of Shaw's notes, see note 43, p. 17, above. According to F. W. Gibbs, "Peter Shaw and the Revival of Chemistry," Annals of Science, VII (1951), 231, Shaw's notes to his translation of Boerhaave were taken largely from an earlier (1727) translation based upon an unauthorized text. Shaw and Chambers collaborated in preparing this earlier translation (ibid., pp. 215-216). This explains the similarity between Chamber's articles and Shaw's notes and also Chambers's citation of Boerhaave's work in the 1728 edition of the Cyclopaedia, four years before the printing of the Elementa chemiae in 1732.

[123] Chambers, Cyclopaedia (1728), I, [*I2 recto]. The articles on heat and fire appear slightly changed in the second edition (1738), and the wording in the second edition is repeated verbatim in editions through the 7th, 1751-1752.

[124] A New and Complete Dictionary of Arts and Sciences Comprehending All the Branches of Useful Knowledge with Accurate Descriptions as Well of the Various Machines, Instruments, Tools, Figures, and Schemes Necessary for Illustrating Them, as of the Classes, Kinds, Preparations, and Uses of Natural Productions, whether Animals, Vegetables, Minerals, Fossils, or Fluids, Together with the Kingdoms, Provinces, Cities, Towns, and Other Remarkable Places Throughout the World, Illustrated with Above Three Hundred Copper-Plates, Curiously Engraved by Mr. Jefferys, Geographer and Engraver to His Royal Highness the Prince of Wales, the Whole Extracted from the Best Authors in All Languages (4 vols. in 8; London), II, 2123-2136; II, Part 2, 1754-1759.

[125] Temple Henry Croker, et al., The Complete Dictionary of Arts and Sciences in Which the Whole Circle of Human Learning Is Explained and the Difficulties Attending the Acquisition of Every Art whether Liberal or Mechanical Are Removed in the Most Easy and Familiar Manner (3 vols.; London), II (1765), [Bb2 recto]-Cc[1 recto], [Llll verso]-[Ll12 recto]. Croker copied most of what he said from Chamber's Cyclopaedia and the New and Complete Dictionary.

[126] [John Barrow], "Fire," A New and Universal Dictionary of

on fire ends with the note referring the reader to the first volume of Boerhaave's chemistry, "where we presume they will meet with entire satisfaction."[127]

A consideration of the content of these dictionaries, which commonly tend to reflect conservative, orthodox opinions, suggests that those Englishmen who advanced the motion theory after about 1740 are not representative of a strong, virile, theoretical scientific tradition. They appear more as exceptions who expounded an older, generally abandoned point of view and seem ignorant of the existence of any competing ideas.

Although proponents of the motion theory maintained heat to be the motion of the parts of ordinary matter, in almost every case, where they attempted to explain the production of heat by chemical means, some material agent had to be utilized. In other words, something else had to be invoked to explain the apparently spontaneous production of movement, whether it is the air and sulphureous acid of Hales and Desaguliers or the phlogiston of Stahl, Macquer and Priestley. Lomonosov, practically the only one besides Macquer who attempted a detailed theory based upon the motion hypothesis, omitted the explanation of chemical heat from his system.

Explanations of changes of state in terms of the motion concept are very similar to those in terms of the idea of fire-matter-in-motion.

Arts and Sciences, Containing Not Only an Explanation of the Various Terms Made Use of in the Following Arts and Sciences, but Also Whatever Else is Requisite to Render Those Branches of Literature Themselves Easy and Familiar to the Meanest Capacities (2d ed.; London, 1764), [5H2 recto]-[5H2 verso].

[127] Ibid., p. [5H2 verso].

In both theories, these changes are explained as caused by a simple, progressive separation of the particles of which ordinary substances are composed. In both, heat acts as a mechanical agent to oppose the mutual cohesion among these ultimate particles. The only difference between the two concepts is in the nature of the cause of the separation. For one theory, it is a combination of matter and motion; for the other, it is motion alone.

CHAPTER IV

LAVOISIER AND THE CALORIC THEORY OF HEAT

The inclusion of movement as an essential feature of the fire-in-motion theory gave that theory some latitude in the types of explanations that could be applied to phenomena. In this theory, heat is a function of both the quantity of fire matter present and degree of movement or agitation of the particles of fire and the particles of ordinary matter. It was thus possible in some instances to ascribe temperature changes to changes in the degree of movement instead of having to resort to an actual transfer of fire matter. This feature was particularly suited to the explanation of the mechanical, that is, frictional, percussional, or compressional, production of heat. However, emphasis upon the movement or agitation of fire matter disappeared during the last quarter of the eighteenth century.[1]

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[1]The changing viewpoint in the material theory of heat is reflected in theories of animal heat. Disappearance during the last quarter of the century of the inherent motion of fire matter in general heat theory is paralleled in biological theory by an increasing emphasis upon explanations involving respiration and analogous theories of combustion, with a concomitant deprecation of explanations of animal heat involving friction and agitation. See Everett Mendelsohn, Heat and Life: The Development of the Theory of Animal Heat (Cambridge, Mass., 1964), pp. 105-139. G. J. Goodfield claims that mechanical explanations of animal heat died out around 1750; The Growth of Scientific Physiology: Physiological Method and the Mechanist-Vitalist Controversy, Illustrated by the Problems of Respiration and Animal Heat (London, 1960), p. 29.

Reasons for the declining use of movement in the material heat theory are not clear. It seems that arguments offered against the theory of heat as vibration of the parts of ordinary matter would have been equally applicable in objecting to the motion of fire matter. But arguments against the vibratory motion of fire are virtually nonexistent. In the second edition of the Britannica, the author of the article "Fire" argued against Newton's vibratory theory of heat on the grounds that momentum always decreases when transferred from one substance to another.[2] The loss in momentum is due to the resistance of particles to motion; the loss does not depend upon the size of the particles; and the small particles of fire are no exception.[3]

Jean Baptiste Pierre Antoine de Monet de Lamarck (1744-1829) specifically denied any particular movement as an inherent characteristic of fire matter.[4] The idea of perpetual movement, he said, is contrary to the essential qualities of matter in general. Fire, being a form of

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[2]"Fire," Encyclopaedia Britannica (2d ed., enlarged; 10 vols.; Edinburgh, 1778-1783), IV (1779), 3003. The articles on heat and fire in this edition were probably written by James Tytler (1747?-1805), a literary hack and scientific dabbler; see Arthur Hughes, "Science in English Encyclopaedias, 1704-1875: II. Theories of the Elementary Composition of Matter," Annals of Science, VII (1952), 351-356.

[3]Ibid.

[4]Jean Baptiste Pierre Antoine de Monet de Lamarck, Recherches sur les causes des principaux faits physiques, et particulièrement sur celles de la combustion, de l'élévation de l'eau dans l'état de vapeurs de la chaleur produite par le frottement des corps solides entre eux, de la chaleur qui se rend sensible dans les décompositions subites, dans les effervescences et dans le corps de beaucoup d'animaux pendant la durée de leur view, de la causticité, de la saveur et de l'odeur de certains composés, de la couleur des corps, de l'origine des composés et de tous les minéraux, enfin de l'entretien de la view des êtres organiques, de leur accroissement, de leur état de viguer, de leur dépérissement, et de leur mort, avec une planche (2 vols.; Paris, An II [1794]), I, 51.

matter, should not possess a property which is not common to all matter.[5]

Most writers, however, simply ignored the question; and in the material heat theory prominent during the last two decades of the century, the motion feature is absent. This may have been because heat theory became involved in the atmosphere of conflict over the theory of phlogiston, which resulted in more interest and emphasis being placed upon the chemical rather than the mechanical production of heat. But whatever the reason for the absence, the omission of motion necessitated somewhat more complicated and sometimes strained explanations of mechanical heat production. This weakness in the material heat theory occurred precisely in that area in which the motion feature was so admirably suited, that is, the frictional production of heat. It was this weakness which Benjamin Thompson, Count Rumford (1753-1814), exploited in his unsuccessful attempt to revive the vibratory theory of heat in 1798.[6]

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[5] Ibid., pp. 66-67. Lamarck's arguments are similar to those of others who maintained heat matter must possess weight, despite the inability to demonstrate this weight. Weight, they said, is an inherent characteristic of all matter, and heat, being matter, must possess it; see the views of Jeremias Benjamin Richter (1762-1807), discussed in James R. Partington and Douglas McKie, "Historical Studies on the Phlogiston Theory: IV. Last Phases of the Theory," Annals of Science, IV (1939), 131, and James R. Partington, A History of Chemistry (3 vols.; London, 1961-1964), III, 631. Even arguments in favor of crediting phlogiston with specific lightness did not deny that phlogiston, being matter, must be subject to the laws of gravity; see Louis Bernard Guyton de Morveau, Défense de la volatilité du phlogistique, ou lettre de l'auteur des digressions académiques, &c (Dijon, 1773), cited in James R. Partington and Douglas McKie, "Historical Studies on the Phlogiston Theory: I. The Levity of Phlogiston," Annals of Science, II (1937), 397. See also the views of Armand Séguin (ca. 1765-1835), pp. 146-147, 159, below, and those of James Hutton (1726-1797), p. 235, below.

[6] Benjamin Thompson, Count Rumford, "An Inquiry Concerning the Source of the Heat Which Is Excited by Friction," Philosophical Transactions of the Royal Society of London, LXXXVIII (1798), 80-102.

The heat theory which emerged during the last quarter of the century is very similar to the fire-in-motion hypothesis. The primary difference between them is that the later theory does not ascribe any motion to the fire matter itself. The absence of motion necessitated changes in explanations of some heat phenomena, especially in explanations which the fire-in-motion theory attributed heat change to change in the degree of motion or agitation of the particles of fire matter.

One of the earliest exponents of this new theory of heat was Antoine Laurent Lavoisier (1743-1794).[7] He discussed heat theory in two papers printed in the memoirs of the French Academy of Sciences for 1777. At the beginning of the first paper, he stated clearly and concisely his general assumptions regarding fire matter.

> Je supposerai dans ce Mémoire, & dans ceux qui le suivront, que la Planète que nous habitons est environnée de toutes parts d'un fluide très-subtile, qui pénètre, à ce qu'il paroît sans exception, tous les corps qui la composent; que ce fluide, que j'appellerai fluide igné, matière du feu, de la chaleur & de la lumière, tend à se mettre en équilibre dans tous les corps, mais qu'il ne les pénètre pas tous avec une égale facilité; enfin, que ce fluide existe tantôt dans un état de liberté, tantôt sous forme fixe, & combiné avec les corps.[8]

In explaining the difference between free fire and combined fire, Lavoisier drew an anology to combinations which are formed with water. In these combinations, water plays two different roles. One part

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[7]Antoine Laurent Lavoisier, "De la combinaison de la matière du feu avec les fluides évaporables, et de la formation des fluides élastiques aëriformes," Mémoires de l'Académie Royale des Sciences, 1777 (1780), pp. 420-432. For a very brief summary of Lavoisier's heat theory and a comparison with earlier views see Maurice Daumas, Lavoisier, théoricien et expérimentateur (Paris, 1955), pp. 160-165, 167. Cf. speculations on meaning of caloric for Lavoisier in Charles C. Gillispie, The Edge of Objectivity: An Essay in the History of Scientific Ideas (Princeton, 1960), pp. 235-241.

[8]Lavoisier, Mémoires 1777 (1780), p. 420.

of the water is absorbed in the combination; another part holds the parts resulting from the combination separated, that is, it holds them in solution. The "fluide igné" does the same thing. Combined fire does not register on a thermometer; and what is called the intensity of fire matter is only a measure of the quantity of free, uncombined fire.[9]

Lavoisier explained that when substances are mixed or are combined, there are three possible results regarding fire matter. If the quantity of fire matter in the new combination is the same as the quantity contained within the substances before the combination, then there is no change in the state of fire. If, on the other hand, less fire is used in the new combination, then some of the fire becomes free when the combination takes place, and heat (chaleur) is produced. If more fire is used in the new combination than is contained in the constituents before combining, then fire is absorbed and passes from the free state into the combined state. In this last case, there is a decrease of free fire in the surrounding substances and cooling results.[10]

Lavoisier continued his argument by saying that if he could demonstrate that there is cooling every time a vapor is formed, then, based on the explanation of temperature changes during mixing and combinations, he could show "que les vapeurs sont un résultat de la combinaison de la matière de feu avec le fluide réduit en vapeurs."[11] The

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[9] Ibid., p. 421. [10] Ibid., pp. 422-423.

[11] Ibid., p. 424. Lavoisier's explanation of evaporative cooling, the states of fire matter and release or absorption of fire during combinations had been formulated as early as 1772-1773, as evidenced by a manuscript published by René Fric, "Contribution à l'étude de l'évolution des idées de Lavoisier sur la nature de l'air et sur la calcination

previous researches of Georg Wilhelm Richman, Jean Jacques Dortous de Mairan, William Cullen (1710-1790), and Antoine Baumé have shown that evaporation causes cooling.[12] Thus, "les vapeurs & en général, les substances aëriformes, sont un composé d'un fluide quelconque, dissout & combiné avec la matière de feu."[13]

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des métaux," Archives internationales d'histoire des sciences, XII (1959), [137]-168. In this manuscript, Lavoisier said (p. 142) that evaporative cooling "nest autre chose qu'une combinaison dune matierre quelconque avec la matierre du feu." He also said (pp. 142-143) that the two states of fire are "Comme combinée avec les autres elemens" and "comme un fluide Stagnant qui penetre les porres de tous les Corps. ..." In another section (p. 145), Lavoisier added that fire enters the composition of all substances, and if the quantity contained in the combination is less than that contained in the substances before combination, then fire would be released. This manuscript is reproduced in Henry Guerlac, Lavoisier, the Crucial Year: The Background and Origin of His First Experiments on Combustion in 1772 (Ithaca, N. Y., 1961), pp. 218-222.

[12]Lavoisier, Mémoires, 1777 (1780), pp. 424-425.

[13]Ibid., pp. 425. In a similar statement made in 1774, Lavoisier said that "tout fluide élastique résulte de la combinaison d'un corps quelconque, solide ou fluide, avec un principe inflammable, ou peut-être même avec la matière du feu pur, et que c'est de cette combinaison que dépend l'état d'élasticité ..."; Antoine Laurent Lavoisier, "Opuscules physiques et chimiques," Oeuvres de Lavoisier, publiées par les soins de son excellence le ministre de l'instruction publique et des cultes (6 vols.; Paris, 1862-1893), I, 612. This statement also appears in the second edition of the Opuscules [Paris, An IX (1801)], pp. 288-289. Lavoisier was familiar with some of Joseph Black's work on latent heat; Antoine Laurent Lavoisier, "Expérience sur le passage de l'eau en glace, communiquée à l'Académie des Sciences," Introduction aux observations sur la physique, II (1772), 510-511. For details regarding Lavoisier's knowledge of Black, see Guerlac, Lavoisier, pp. 92-94. In 1786, Sir James Hall cited Lavoisier as saying that the idea of latent heat "had occurred to him [Lavoisier] without any knowledge of Black tho' he believes Black hit upon it long before him . . ."; quoted in V. A. Eyles, "The Evolution of a Chemist: Sir James Hall, Bt., F.R.S., P.R.S.E., of Dunglass, Haddingtonshire, (1761-1832), and His Relations with Joseph Black, Antoine Lavoisier, and other Scientists of the Period," Annals of Science, XIX (1963), 167.

Lavoisier's experiments with vacuum pumps, with the help of Pierre Simon, marquis de Laplace (1749-1827) had shown that evaporation is increased when the air pressure is reduced. From this, Lavoisier deduced that the weight of the atmosphere offers a resistance which has to be overcome in order to bring about evaporation. Thus the amount of fire required to cause evaporation depends to some extent upon the opposition to expansion caused by air pressure.[14]

In the second paper, Lavoisier extended his general assumptions regarding fire matter in the mixing and combining of substances to the processes of combustion and calcination.[15] In all cases of combustion, fire matter is released. Citing Macquer as his source, Lavoisier said that calcination is only slow combustion and thus fire matter is also released during that process. He agreed with Benjamin Franklin (1706-1790) and with Boerhaave that fire matter is a very subtle, rare, elastic fluid, found everywhere, and when free, tends to equilibrium.[16]

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[14]Lavoisier, Mémoires, 1777 (1780), p. 425.

[15]Antoine Laurent Lavoisier, "Mémoire sur la combustion en général," Mémoires de l'Académie Royale des Sciences, 1777 (1780), pp. 592-600.

[16]Franklin referred to fire in several places in his writings. He said that fire is a substance diffused more or less in all bodies; Benjamin Franklin, Experiments and Observations on Electricity Made at Philadelphia in America ([4th ed.]; London, 1769), pp. 50-51. In 1757, he explained that fire can permeate all substances and it tends to equilibrium. The particles of objects can attract fire, which may be consolidated within them. Later, fire may recover its fluid state as occurs in burning and fermentation; ibid., pp. 343-349; cf. Benjamin Franklin, "Première lettre de m. Franklin au docteur Lining, sur le rafraîchissement produit par l'évaporation des liquers," Observations sur la physique, II (1773), 276-281. Heat caused by electricity is due to the electricity exciting the fire matter contained within an object; Observations on Electricity, pp. 51, 412-413. Franklin's discussions can be found also

Fire matter is the dissolvent of numerous substances, and it may be combine with some of them. When fire combines with objects, they acquire new properties. All elastic fluids, he said, are the result of the combination of fire matter with some substance. Dephlogisticated air, for example, is "une combinaison ingée" in which the matter of fire or light forms the dissolvent and another substance forms the base. If the base of dephlogisticated air unites with another substance for which it has a greater affinity than it does for fire matter, then the dissolvent, fire matter is set free. This is what happens during combustion and calcination.[17] There is little fire contained in combustibles or for that matter in all solids. What little fire matter there is in solids is probably only free fire which is present due to the property of fire matter to tend to equilibrium.[18]

Almost all substances can exist in the three states of solid, liquid, and gaseous. These states "ne dépendent que de la quantité plus ou moins grande de matière du feu dont ces corps sont pénétrés & avec laquelle ils sont combinés."[19]

Benjamin Franklin, Oeuvres de m. Franklin, trans. Barbeu Doubourg from the 4th English ed. (2 vols.; Paris, 1773), I, 48-49, 227-228; II, 183-190; and in Benjamin Franklin, Benjamin Franklin's Experiments: A New Edition of Franklin's Experiments and Observations on Electricity, ed. I. Bernard Cohen (Cambridge, Mass., 1941), pp. 210-211, 340-345, 371-372. As short as it is, Franklin's most detailed discussion of the nature of heat is in a letter to David Rittenhouse (1732-1796) entitled "New and Curious Theory of Light and Heat [no date]" in Benjamin Franklin, The Complete Works in Philosophy, Politics, and Morals, of the Late Dr. Benjamin Franklin, Now First Collected and Arranged, with Memoirs of His Early Life Written by Himself (2d ed; 3 vols.; London [n. d.]), II, 122-125. This letter does not appear in any of the other works above.

[17]Lavoisier, Mémoires, 1777 (1780), pp. 593-596.

[18]Ibid., p. 596.

[19]Ibid., p. 598.

In a third paper presented at the same time as the first two, but published in the memoirs of 1778, Lavoisier identified the base of dephlogisticated air, to which fire matter is united, as the acidifying principle or oxygen:[20]

> ... le principe acidifiant ou oxygine, combiné avec la matière du feu, de la chaleur & de la lumière, forme l'air le plus pur, celui que M. Priestley a nommé air déphlogistiqué. ...[21]

Lavoisier added that this assumption

> n'est pas rigoureusement démontrée, & peut-être même n'est-elle pas susceptible de l'être; aussi ne l'ai-je donnée que comme une idée que je regarde comme très-probable. ...[22]

In these three articles, Lavoisier stated the chief elements of his heat theory, the essence of which remained unchanged in his subsequent writings. In his Opuscules of 1774 he had equated fire matter with phlogiston or the "principe inflammable."[23] However, the purpose of these articles was to lay a foundation for his oxidation theory, and therefore the material cause of heat is expressed in a different fashion.

In the first article of 1777, Lavoisier used the expression "fluide igné, matière du feu, de la chaleur & de la lumière" to indicate the matter of heat or fire.[24] Up to 1787, the time of publication of the revised nomenclature, he used this phrase or parts of it with seeming

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[20] Antoine Laurent Lavoisier, "Considérations générales sur la nature des acides et sur les principes dont ils sont composés," Mémoires de l'Académie Royale des Sciences, 1778 (1781), pp. 535-547. A notation on the first page of this article reads "Présenté le 5 Septemb. 1777. Lû le 23 Nov. 1779." September 5 is the same date given on the first page of the two previous articles cited; see notes 6 and 14, above.

[21] Ibid., p. 536. [22] Ibid.

[23] Lavoisier, Oeuvre, I, 612.

[24] See p. 106, above.

indifference to indicate the material cause of heat. For example he called the cause of heat the "fluide igné,"[25] or "la matière du feu,"[26] or "la matière de la chaleur,"[27] or "le principe de la chaleur,"[88] or the "matière du feu ou de la lumière,"[29] in addition to other similar phrases. Except for terminology, Lavoisier made little subsequent change in his statements regarding the nature and action of fire matter.

Briefly, Lavoisier's views were these. He thought fire to be a subtle matter which can penetrate all other substances and which tends to equilibrium. Fire matter can exist in two distinct states: free and able to affect a thermometer, or combined and unable to affect a thermometer. He explained temperature changes which occur during mixing or combining of substances in terms of the amount of fire fixed in the mixture or compound compared to the amount of fire fixed in the separate substances before mixing or combining. If more fire is fixed in the compound or mixture than was fixed in the separate substances, then fire is absorbed and the temperature decreases. If, on the other hand, less fire

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[25]Antoine Laurent Lavoisier, "Mémoire sur quelques fluides qu'on peut obtenir dans l'état aériforme, à un degré de chaleur peu supérieur à la température moyenne de la terre," Mémoires de l'Académie Royale des Sciences, 1780 (1784), p. 342.

[26]See p. 108, above.

[27]Antoine Laurent Lavoisier, "Mémoire dans lequel on a pour objet de prouver que l'eau n'est point une substance simple, un élément proprement dit, mais qu'elle est susceptible de dédomposition & de recomposition," Mémoires de l'Académie Royale des Sciences, 1781 (1784), p. 486.

[28]Antoine Laurent Lavoisier, "Considérations générales sur la dissolution des métaux dans les acides," Mémoires de l'Académie Royale des Sciences, 1782 (1785), p. 492.

[29]Lavoisier, Mémoires, 1777 (1780), p. 593.

is fixed in the compound than was fixed in the separate substances, then fire is released and the temperature increases. Thus all temperature change is due to the transformation of free, thermometric fire into fixed fire, or vice versa. From this assumption and the observation that cooling accompanies evaporation, Lavoisier deduced that fire becomes fixed in the formation of vapors. Indeed, he said, all aeriform substances, and especially dephlogisticated air, are the result of the combination or fixation of fire with some fluid or base.

In explaining calcination and combustion, Lavoisier treated fire matter as behaving like any other constituent element. In both of these processes, the base of dephlogisticated air is combined with the object calcined or burned, and the fire matter which does not enter into the new combination is set free.

In discussing changes of state, Lavoisier said that all substances are capable of existing in the three states of solid, fluid, and gaseous. These states depend solely upon the greater of lesser quantity of heat to which the substances are exposed. Because changes of state usually involve changes of volume, external factors which facilitate or inhibit volume change may also affect the quantity of heat necessary to produce changes of state. Specifically, Lavoisier cited air pressure as a factor tending to inhibit volume increase and thus tending to increase the quantity of heat required to vaporize a substance.

In 1783 Lavoisier and Laplace read to the French Academy a lengthy paper devoted exclusively to heat and heat phenomena.[30] In

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[30]Antoine Laurent Lavoisier and Pierre Simon, marquis de Laplace, "Mémoire sur la chaleur," Mémoires de l'Académie Royale des Sciences, 1780 (1784), pp. 355-408. This memoir is dated June 18, 1783. It is not known

discussing the nature of heat, the authors exhibit considerable caution and circumspection. They began with a rather short statement of the view that heat is a material substance:

> Les Physiciens sont partagés sur la nature de la chaleur; plusieurs d'entre'eux la regardent comme un fluide répandu dans toute la Nature, & dont les corps sont plus ou moins pénétrés, à raison de leur température, & de leur disposition particulière à le retenir; il peut se combiner avec eux, & dans cet état il cesse d'agir sur le thermomètre, & de se communiquer d'un corps à l'autre; ce n'est que dans l'état de liberté qui lui permet de se mettre en équilibre dans les corps, qu'il forme ce que nous nommons chaleur libre.[31]

This paragraph is followed by a much longer section in which the theory of vibrations is discussed:

> D'autres Physiciens pensent que la chaleur n'est que le rèsultat des mouvemens insensibles des molécules de la matière. On sait que les corps, même les plus denses, sont remplis d'un grand nombre de pores ou de petits vides, dont le volume peut surpasser considérablement celui de la matière qu'ils renferment: ces espaces vides laissent à leurs parties insensibles, la liberté d'osciller dans tous les sens, & il est naturel de pense que ces parties sont dans une agitation continuelle, qui, si elle augmente jusqu'à un certain point, peut les désunir & décomposer les corps; c'est ce mouvement intestin qui, suivant les Physiciens dont nous parlons, constitue la chaleur.[32]

Laplace and Lavoisier continued to explain the motion theory by stating a general law applicable to all movement, the "Principe de la conservation des forces vives." In the theory of vibrations, "la chaleur est la force vive qui résulte des mouvemens insensibles des molécules

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why it was included in the Mémoires for 1780. Materials contained in Lavoisier's notebooks indicate that work which resulted in this article was not begun until 1782; see Marcelline Pierre Eugène Berthelot, La révolution chimique, Lavoisier, ouvrage suivi de notices et extraits des registres inédits de laboratorie de Lavoisier (Paris, 1890), p. 280; Douglas McKie and Niels H. de V. Heathcote, The Discovery of Specific and Latent Heats (London, 1935), p. 45, n. 3. For the implications of this memoir for theories of animal heat, see Mendelsohn, Heat and Life, pp. 147-151, and Goodfield, Scientific Physiology, pp. 38-45.

[31] Ibid., p. 357. [32] Ibid.

d'un corps; elle est la somme des produits de la masse de chaque molécule, par le carré de sa vîtesse."[33] This force is conserved. Thus the decrease in force vive in a substance of higher temperature will exactly equal the increase in force vive in a substance of lower temperature, if the two substances are placed in contact with each other and allowed to reach a common temperature.[34]

The vibratory theory of heat easily explains why the direct impulse of light rays in inappreciable. Impulse, they said, is the product of mass multiplied by speed, and since the mass of the rays is so small, the product is practically zero. The force vive, or heat, on the other hand, corresponds to the square of the velocity and is thus a much greater magnitude than impulse. This accounts for the great heating effect of solar rays.[35]

After this rather unbalanced treatment of the two theories of the nature of heat, the authors stated that "Nous ne déciderons point entre les deux hypothèses précédentes. ..."[36] Some phenomena are favorable to the theory of vibrations, for example, heat produced by rubbing together two solid substances. Other phenomena, however, are more simply explained in terms of the material theory. "Quoi qu'il en soit, comme on ne peut former que ces deux hypothèses sur la nature de la chaleur; on doit admettre les principes qui leur sont communs. ..."[37]

Lavoisier and Laplace stated two principles which they felt are evident, generally admitted by all physicists, and independent of

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[33] Ibid., pp. 357-358. [34] Ibid., p. 358. [35] Ibid.
[36] Ibid. [37] Ibid., pp. 358-359.

of all hypotheses regarding the nature of heat. The first of these is that "la quantité de chaleur libre reste toujours la même dans le simple mélange des corps."[38] The second principle is, in the most general form, "Toutes les variations de chaleur, soit réelles, soit apparentes, qu'éprouve un système de corps, en changeant d'état, se reproduisent dans un ordre inverse, lorsque le systéme repasse à son premier état."[39]

Except for an occasional lapse, the authors kept to their avowed purpose of describing heat phenomena without explanation in terms of either the vibrational or the material theory of heat. If explanation was provided, it was couched in terms which, in their view, would not be objectionable to proponents of either theory. They defined heat capacities (capacités de chaleur) or specific heats (chaleurs spécifiques) as the quantity of heat necessary to raise the temperature of a given mass of a substance one degree compared to that required for the same mass of water.[40] They discussed the method of mixtures for determining specific heats and concluded that it was too inexact.[41] They then described their own ice-calorimeter and the technique of its use. This is followed by experiments and their results pertaining to specific heats, and the heat evolved from various mixtures, detonations, combustions, and respirations.[42]

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[38] Ibid., p. 359. [39] Ibid., pp. 359-360.

[40] Ibid., p. 361. The use of water as a standard was not original with Lavoisier and Laplace; see pp. 197-198 and n. 58, p. 198, below.

[41] Ibid., pp. 361-364.

[42] Ibid., pp. 364-408, passim. For a brief survey of these experiments, see Abraham Wolf, A History of Science, Technology, and Philosophy in the Eighteenth Century (2d ed., revised; London, 1952), pp. 183-188.

Certain conclusions and generalizations, although not bearing directly upon the question of the nature of heat, tended to clarify discussions of some specific heat phenomena, and they are more detailed than in Lavoisier's earlier articles. The authors gave a clear statement of the concept of latent heat although the term "latent heat" was not used. They explained that in all changes of state caused by the addition of heat, there is always an absorption of fire which does not change the temperature of the system of substances involved. From this statement and the second principle stated above, it follows that the same holds for state changes caused by the removal of heat.[43]

The authors remarked that the more precise knowledge of specific heats of substances had not enabled them to predict the quantity of heat that would be evolved or absorbed in a given combination. In other words, knowing the specific heats of both the reactants and their combinations does not enable the experimenter to predict temperature change resulting from the combinations.[44]

This criticism of the predictive value of specific heats was extended to censoring theories upon which techniques of computing absolute zero were based. Laplace and Lavoisier recognized that the various heat quantities and constants are entirely relative and that even "Le zéro de thermomètre indique conséquemment une chaleur considérable. ..." But they did believe that there does exist, in theory at least, an absolute zero, a temperature at which there is no heat.[45] As a basis for computing absolute zero, it was assumed that the specific heat of a

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[43] Ibid., p. 388. [44] Ibid., p. 387. [45] Ibid., p. 381.

substance represents a certain quantity of heat contained in it, and that specific heat remains constant at all temperatures unless a change of state occurs.

The results of the authors's attempts to compute absolute zero were without value, as the calculated temperature differs over a range of several hundred degrees.[46] Although Lavoisier and Laplace admitted that some of the inconsistencies in the computed values may have been due to imprecise values of specific heats, they were more inclined to credit the inconsistencies to the falsity of the idea that specific heats are constant.[47]

The Englishman, Adair Crawford (1749-1795) was the most notable proponent of the idea of the constancy of specific heats and the use of this as a basis for computing absolute zero. It is probable that the criticisms of Lavoisier and Laplace are directed against Crawford, although his name is not directly connected with this discussion. Although the authors discounted any relationship between specific heat and the absolute quantity of heat in a substance, they remarked that Crawford's high value for the specific heat of pure air, if it were confirmed, would support their assumptions regarding pure air as the source of heat released during combustion and calcination.[48]

Lavoisier and Laplace avoided a specific commitment on the question of the nature of heat; but a belief in a material theory can be inferred from certain expressions used, expressions which have

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[46] Ibid., pp. 382-385. [47] Ibid., pp. 385, 388-389.

[48] Ibid., p. 394. For a discussion of Crawford's views, see pp. 186-196, below.

meaning only if a material heat is assumed. For example, they said that all substances on earth and the earth itself "sont pénétrés d'une grande quantité de chaleur. ..."[49] In discussing changes of state, they said that the coming together of molecules, due to the force of affinity, disengages the heat which tends to separate them.[50] And they described aeriform substances as resulting from "la grande quantité de chaleur qui y est combinée. ..."[51]

Although belief in a material theory implied in some statements was a departure from the avowed intent of Laplace and Lavoisier in their 1780 article, there is no doubt about Lavoisier's propounding a material theory in his article in the Mémoires of 1783.[52] The well known phenomenon that objects expand when heated and contract when cooled offers a clue to the internal structure of substances. It follows from this phenomenon, that the molecules of an object do not touch, that there exists space between them which heat increases and cold diminishes.

> On ne peut guère concevoir ces phénomènes, qu'en admettant l'existence d'un fluide particulier dont l'accumulation est la cause de la chaleur, & dont l'absence est la cause de froid: c'est sans doute ce fluide qui se loge entre les particules des corps, qui les écarte & qui occupe la place qu'elles laissent entre'elles. Je nomme, avec le plus grand nombre des Physiciens, ce fluide quel qu'il soit, fluide igné, matière de la chaleur & du feu.[53]

Lavoisier defended himself against the charge that the existence of this fluid is only an assumption:

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[49] Ibid., p. 381. [50] Ibid., p. 391. [51] Ibid., p. 399.

[52] Antoine Laurent Lavoisier, "Réflexions sur le phlogistique pour servir de développement à la théorie de la combustion & de la calcination publiée en 1777," Mémoires de l'Académie Royale des Sciences, 1783 (1786), pp. 505-538.

[53] Ibid., pp. 523-524.

> Je ne nie pas que l'existence de ce fluide ne soit jusqu'à un certain point hypothetique; mais en supposant que ce soit une hypothèse, qu'elle ne soit pas rigoureusement prouvée, c'est la seule que je serai obligé de former. Les partisans de la doctrine du phlogistique ne sont pas plus avancés que moi sur cet article, & si l'existence de fluide igné est une hypothèse, elle est commune à leur systèm & au mien.[54]

As molecules do not touch, solidity of substances must be due to the force of attraction, an attraction, "quelle qu'en soit la cause, est une loi générale de la Nature à laquelle toute la matière paroît être soumise."[55] Thus all substances are acted upon by two forces, the expansive force of "le fluide igné, la matière du feu qui tend continuellement à en écarter les molécules, & l'attraction qui contre-balance cette force. . . ."[56] The three states of matter, solid, liquid, and gaseous, depend upon the balance between these two opposing forces. If attraction is greater, the substance remains solid; if the two forces are equal, the substance becomes liquid; if the expansive force of heat matter is greater, the substance assumes the aeriform state.[57] It can be inferred from this discussion that Lavoisier considered fire matter as acting as a simple mechanical agent in causing changes of state, although this does not agree with what he said about fire combining with substances.

The "fluide igné, ou principe de la chaleur" can exist in two different states. As "feu combiné" or "chaleur combinée," it is a fixed

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[54] Ibid., p. 524. [55] Ibid. [56] Ibid.

[57] Ibid. This same idea was stated earlier in Antoine Laurent Lavoisier, "Mémoire sur l'affinité du principe oxygine avec les différentes substances auxquelles il est susceptible de s'unir," Mémoires de l'Académie Royale des Sciences, 1782 (1785), p. 531. Cf. Mémoires, 1780 (1784), p. 391.

constituent of a substance. The great elasticity which fire matter possesses is completely overcome when it becomes fixed or combined. The other state of fire matter is that of "chaleur libre." All fire which is not combined is in this free state.[58] Lavoisier explained that change of state is due to the change of heat matter from the free state to the combined state, and vice versa. The quantity of heat involved in this transformation is always constant and determined.[59]

This explanation does not agree with Lavoisier's description of the various states as depending upon the balance between attraction and the repulsive force of heat. Since heat matter loses its elasticity when it combines, as Lavoisier said, and since its power to separate molecules presumably depends upon this elasticity, then when fire combines it can no longer affect the balance of forces which determine the state of the substance.

Although denying a relation between specific heat and the quantity of absolute heat contained in a substance,[60] Lavoisier believed that specific heat is to some extent determined by the distances among the molecules of a substance; that is, specific heat is related to the capacity of the substance to contain heat matter. For a given substance, the molecules in the liquid state should be more separated than in the solid. Thus the liquid should have greater capacity to contain heat matter than the corresponding solid. It should require more heat to raise the temperature of the liquid a given number of degrees than the

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[58] Lavoisier, Mémoires, 1783 (1786), p. 526.

[59] Ibid., p. 527.

[60] See pp. 117-118, above.

solid, because there is greater space among the molecules of the liquid into which the heat fluid can move. From this, one might predict that the specific heat of the liquid state of a substance will be greater than that of the solid, and that the specific heat of the gaseous state will be greater than that of the liquid, simply on the basis that the molecules are more separated in the first state than the second.[61] This reasoning implies that temperature is somehow related to the density or pressure of the fire fluid within the pores of the substance.

Because heat fluid occupies space, a change in pore space will result in heat being given off or absorbed. Lavoisier said that the relation between heat matter and a substance is like the relation between water and a sponge. Press the sponge and water is extruded; expand the sponge and it can contain more water.[62] This relationship enables one to predict in a general way whether heat will be released or not in a given reaction. An aeriform substance which becomes solid in some reaction should have less capacity to contain heat as a solid than it had as a gas, and heat should be released.

In both combustion and calcination the base of vital air unites with some object. In this union, vital air is condensed and releases the heat matter which had been used to keep it in its aeriform state.[63] But what of the union of oxygen with carbon? The product of this combination is a gas, and yet heat is also evolved. Lavoisier said that the volume of the product is less than that of vital air. The heat

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[61] Ibid., pp. 527-528. [62] Ibid., pp. 530-531.

[63] Ibid.

evolved is partly due to this decrease in volume and in part due to the presence of carbon in the combination as the carbon particles occupy space which otherwise would be filled with heat. Because fixed air has less pore space, it should have a lesser heat capacity than vital air and therefore a smaller specific heat, and experiment shows that it does.[64]

The revision of chemical nomenclature, published in 1787, contains only a cursory treatment of heat theory. A material theory of heat was assumed; but the expression of ideas concerning this substance are infrequent and short.[65] The importance of the new nomenclature for heat theory was the proposal of the term calorique for the material cause of heat. Louis Bernard Guyton de Morveau (1737-1816), Dijon layer and chemist who later became professor of chemistry at the Ecole Polytechnique, was the chief architect of the new nomenclature.

In discussing the new nomenclature, the authors described five classes of simple substances, substances which cannot be decomposed.

> La première [class] comprend les principes qui, sans présenter entr'eux une analogie bien marquée, ont néanmoins cela de commun qu'ils semblent se rapprocher davantage de l'état de simplicité, qui les fait résister à l'analyse, & les rend en même-temps si actifs dans les combinaisons.
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[64] Ibid., pp. 531-532. Armand Séguin (ca. 1765-1835) claimed to have convinced Lavoisier that there was no necessary correlation between expansion or inter-molecular distance and heat capacity; "Réponse de m. Séguin, à la lettre de m. de Luc insérée dans le Journal de physique du moins de mars 1790," Observations sur la physique, XXXVI (1790), 420. Some of Lavoisier's later discussions, however, indicate he was not entirely convinced (see p. 132, below).

[65] Louis Bernard Guyton de Morveau, et al., Méthode de nomenclature chimique, proposée par mm. de Morveau, Lavoisier, Bertholet, & de Fourcroy; on y a joint un nouveau systême de caracters chimiques, adaptés à cette nomenclature, par mm. Hassenfratz & Adet (Paris, 1787).

> Les substances de la première classe sont au nombre de cinq; savoir: la lumière, la matière de la chaleur, l'air appellé d'abord déphlogistiqué, puis air vital, le gaz inflammable & l'air phlogistiqué. ...[66]

The authors explained the reason for citing both heat and light as simple substances and the necessity of distinguishing the sensation of heat from the cause of the sensation:

> La lumière & la chaleur paroissent en quelques circonstances produire les mêmes effets; mais nos connoissances n'étant pas assez avancées pour pouvoir affirmer leur identité ou leur différence, nous leur avons conservé à chacune leur dénomination propre; nous avons seulement pensé qu'il falloit distinguer la chaleur, qui s'entend ordinairement d'une sensation, du principe matérial qui en la cause, & nous avons désigné ce dernier par le mot calorique. Ainse nous dirons que le calorique produit la chaleur, que le calorique a passé d'une combinaison dans une autre sans produire une chaleur sensible, &c. Cette expression sera aussi claire & moins embarrassante dans le discours, que celle de matière de la chaleur que la nécessité de se faire entendre avoit introduite depuis quelques années.[67]

This statement concerning heat and light indicates the lack of a consensus at the time regarding the relationship between these two principles. In the theoretical discussions which follow, although these are not extensive, light is rarely mentioned while caloric receives relatively more attention. In a footnote to a discussion of the role of

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[66] Ibid., pp. 28-30.

[67] Ibid., p. 30. The word "calorific" or "calorifique," as an adjective meaning "heating" or "having the ability to heat," had seen wide-spread usage throughout the eighteenth century. Guyton however, had used the word "calorifique" as a noun signifying the matter of heat or of fire; Louis Bernard Guyton de Morveau, "Lettre de m. de Morveau à m. de la Métherie sur une table synoptique des parties constituantes de quelques substances principales, suivant toutes les hypotheses," Observations sur la physique, XXX (1787), 45-46. In the MS preparation of his Traité élémentaire de chimie (1789), written prior to the nomenclature revision, Lavoisier had proposed the terms "thermogène" and "principe échauffant" to designate the matter of heat; Maurice Daumas, "L'élaboration du Traité de chimie de Lavoisier," Archives internationales d'histoire des sciences, III (1950), 580, 584.

caloric in changes of state, Lavoisier remarked that

> Nous ne distinguons point ici le calorique de la lumière, quoique cette distinction fût cependant nécessaire; mais nous avons craint d'interrompre le fil du raisonnement par de trop longues discussions.[68]

Further on, he mentioned that the gaseous state of oxygen is due to its union with both caloric and light.[69]

In this work, explanations of the role of caloric are virtually unchanged from Lavoisier's earlier discussions of the role of fire matter. Lavoisier stated, however, that he did not deny the existence of caloric in solids or in gases other than oxygen gas. In fact, the reason that so much heat is evolved in burning inflammable gas than say in burning phosphorous is that in the former reaction both oxygen and inflammable gas furnish caloric, whereas in the latter, only oxygen gas furnishes heat.[70]

In general, Lavoisier's chemistry textbook restates the various elements of heat theory which had already appeared in one form or another in his previous writings.[71] He stated that the molecules of a substance

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[68]Guyton de Morveau, Méthode de nomenclature chimique, p. 293, note.

[69]Ibid., p. 296. Hélène Metzger claimed that Lavoisier's indifference to the question of the role of light in chemical reactions, in addition to his concept of combustion as a process of combination rather than decomposition, resulted in depriving the material theory of light of much of the support it had formerly received from chemical theory. This left the way open to the possible acceptance of an alternate explanation of the nature of light; "Newton: La théorie de l'émission de la lumière et la doctrine chimique au XVIIIème siècle," Archeion, XI (1929), 24-25; Metzger, Newton, Stahl, Boerhaave, pp. 81-82.

[70]Ibid., pp. 294-297.

[71]Antoine Laurent Lavoisier, Traité élémentaire de chimie, présenté dans un ordre nouveau et d'après les découvertes modernes, avec

are not touching, a conclusion which "est impossible de se refuser."[72] These molecules obey two forces, "la force attractive de leurs molécules & la force répulsive de la chaleur," and the three states of matter depend upon the balance between these forces.[73] Atmospheric pressure is one important external force which can effect the balance between the forces acting among molecules.[74]

It is difficult to think of these phenomena, Lavoisier said, without admitting that they are the effects of a very subtle fluid, eminently elastic, which is called calorique in the new nomenclature.[75] Although he regarded the cause of heat as being a material substance, he admitted that

> rigoureusement parlant, nous ne sommes par même obligés de supposer que le calorique soit une matière réelle: il suffit, ... que ce soit une cause répulsive quelconque qui écarte les molécules de la matière, & on peut ainsi en envisager les effets d'une manière abstraite & mathématique.[76]

Caloric surrounds all parts of a substance and fills the spaces among its molecules.[77] As well as being very subtle, this fluid has great elasticity; its particles have a great tendency to separate from each other.[78] The elasticity of gases is due entirely to the elasticity of caloric.[79]

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figures (2 vols.; Paris, 1789). Lavoisier's discussion of heat remained unchanged in the second edition (2 vols.; Paris, 1793) and in the third edition (2 vols.; Paris, An IX (1801)).

[72] Traité élémenatire (1789), I, 3.

[73] Ibid., pp. 3-4. [74] Ibid., pp. 7-8.

[75] Ibid., pp. 4-5. [76] Ibid., pp. 5-6.

[77] Ibid., p. 18. [78] Ibid., pp. 20, 25. [79] Ibid., p. 24.

Caloric can exist in two distinct states. Le calorique libre is that which is not combined. Although not combined, it is never absolutely free, for it always has some adherence to other substances.[80] Le calorique combiné is caloric which is bound to other matter by forces of affinity or attraction.[81] It thus may become an elemental constituent of a substance, and an object may assume any state "dépendent de la quantité de calorique qui lui est combinée."[82]

Oxygen gas is a compound of oxygen and caloric, and the release of caloric during combustion is due to the greater affinity which the base, oxygen, has for the substance burned than the affinity the base has for caloric. The base unites with the substance, and part but not necessarily all of the caloric is set free. Lavoisier devoted several pages to discussing the relative amounts of caloric which are retained in combination when certain compounds of oxygen are formed.

The burning of one livre of phosphorous releases enough caloric to melt one-hundred livres of ice. The burning of one livre of carbon melts about ninety-six livres of ice, whereas burning one livre of hydrogen will melt over two-hundred-ninety-five livres of ice. The one livre of phosphorous, Lavoisier said, combines with about one and a half livres of oxygen. Therefore in this combination, one livre of oxygen releases enough caloric to melt a little over sixty-six livres of ice. Carbon, on the other hand, combines with over two and a half livres of oxygen.

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[80] Ibid., p. 21. [81] Ibid.

[82] Ibid., p. 17.

Lavoisier assumed that the amount of caloric released by oxygen in combining with phosphorous represents practically all the caloric which is combined in oxygen gas, because the result of the combination is a solid and thus probably has very little caloric left in it. If the quantity of caloric released in the burning of phosphorous represents all the caloric in oxygen gas, then the amount of oxygen which combines with carbon should have released enough caloric to melt over 171 livres of ice, whereas only about 96 livres are melted. Lavoisier said that this means that the oxygen combined in carbonic acid retains in combination enough caloric to melt about 75 livres of ice; part of this caloric is used to maintain the acid in the gaseous state. Hydrogen combines with almost 6 livres of oxygen which should have melted almost 378 livres of ice whereas only about 296 livres are melted. From this relationship, Lavoisier concluded that water at 0°C contains enough caloric to melt almost 12 1/2 livres of ice. He reiterated that the presence of caloric in the compound is due to caloric being retained by oxygen when it unites with various substances. Oxygen retains least when it combines with phosphorous.[83]

In his tables of binary compounds of various simple substances, Lavoisier placed the compound of the substance with caloric first on the list.[84] For example, the compound of oxygen and caloric is "Le gaz oxygène."[85] However, he did not give any tables for the compounds of light and caloric because "nous n'avons point encore des idées suffisamment arrêtées sur ces sortes de combinaisons."[86]

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[83] Ibid., pp. 103-106. [84] Ibid., pp. 203, 216, 220, 222, tables.

[85] Ibid., p. 203; table. [86] Ibid., p. 200.

In a concise statement of the general operation of caloric in nature, Lavoisier said that

> Nous savons, en général, que tous les corps de la nature sont plongés dans le calorique, qu'ils en sont environnés, pénétrés de toutes parts, & qu'il remplit tous les intervalles que laissent entr'elles leur molécules: que dans certains cas le calorique se fixe dans les corps, de manière même à constituer leurs parties solides; mais que le plus souvent il en écarte les molécules, il exerce sur elles une force répulsive, & que c'est de son action ou de son accumulation plus ou moins grande que dépend le passage des corps de l'état solide à l'état liquide, de l'état liquide à aériforme. Enfin nous avons appelé du nom générique de gaz toutes les substances portées à l'état aériforme par une addition suffisante de calorique.[87]

The Traité élémentaire does not contain a systematic treatment of heat theory. Lavoisier's purpose was to show that gases in general, and oxygen gas in particulr, contain a great quantity of caloric in them. He argued for the idea that the so-called permanently elastic fluids are basically no different from elastic fluids which are patently the consequence of a change in state caused by the addition of caloric to some liquid. Gases then are only vapors of a fluid which has a boiling point much lower than any temperature naturally observable or artificially producible. Thus the presence of caloric in gases is due entirely to their gaseous state; and it is thus explicable in terms of the theory of combined caloric, the theory that state change is caused by the combination of caloric with a substance. Lavoisier's discussion of heat theory is confined almost entirely to this argument.[88] The mention of caloric in more general terms seems almost incidental. He made little effort to

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[87] Ibid.

[88] Maurice Daumas remarks that Lavoisier's discussion of caloric is "indispenable pour comprendre sa théorie des gaz ..."; Archives internationales d'histoire des sciences, III (1950), 586.

argue for the idea of caloric combining to bring about changes of state. He stated this as though it were already generally accepted doctrine, and more space is devoted to an explanation of state change in terms of a balance of forces among molecules, an idea which seems to contradict the idea of combination.

Lavoisier's most complete and most detailed discussion of heat theory is in his Mémoires de chimie.[89] This work is purported to be a collection of Lavoisier's memoirs read to the French Academy, intercalated with works on similar subjects by some of his followers.[90] In actuality, the Mémoires de chime contain several articles published there for the first time, and most articles, purportedly reprinted from the Mémoires, were rewritten at least to the extent of changing phraseology to conform to the new nomenclature. Revision in some cases was extensive enough to result in a substantially new treatise.[91] The first volume of this work is devoted entirely to heat phenomena and theory.

Lavoisier's first article is on the nature of "calorique," and it begins verbatim as a passage in the French Academy Mémoires for 1777 in which he discussed the great extent of the caloric fluid in nature.[92]

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[89]Antoine Laurent Lavoisier, Mémoires de chimie (2 vols.; [Paris?, 1805?]). Madame Lavoisier, in the brief introduction, said that work on this was begun in 1792 (I, [iii]). Lavoisier, in one of the memoirs, stated that he was writing in 1793 (I, 122). For a discussion of the facts of publication, see Denis I. Duveen and Herbert S. Klickstein, A Bibliography of the Works of Antoine Laurent Lavoisier, 1743-1794 (London, 1954), pp. 199-201.

[90]Lavoisier, Mémoires de chime, I, [iii].

[91]See Duveen and Klickstein, pp. 204-214, for a short discussion of the content of each article.

[92]Lavoisier, Mémoires de chimie, I [1]; see quotation, page 106, above.

In the Academy Mémoires, Lavoisier stated that he would dispense with proofs of the existence of this fluid because opinion in favor of its existence is so general.[93] Lavoisier replaced this statement in his Mémoires de chimie:

> Je suis loin de la [the existence of fluid caloric] regarder comme démontrée, et peut-être n'est-elle pas susceptible de l'être, dans l'état actuel de nos connoissances; je ne la présente donc, dans ce moment, que comme une hypothèse: mais lorsque j'aurai fait voir, dans la suite des mémoires que je publie, qu'elle est par-tout d'accord avec les phénomènes, que par-tout elle explique d'une manière naturelle et simple le résultat des expériences, cette hypothèse cessera d'en être une, et on pourra la regarder comme une vérité.[94]

This concession made, he proceeded to discuss heat phenomena and theory exclusively in terms of a material caloric. All the theoretical elements expressed in this work can be found in his earlier writings.

Explanations in the first article tend to be physical rather than chemical. In theory, caloric can exist in three states: as completely free caloric without touching or combining with another substance; as "le calorique adhérent" which penetrates substances, separates their molecules, and adheres to the molecules with which it is in contact; and as combined caloric.[95] The existence of caloric in a completely free state is impossible, Lavoisier said, and thus it exists as either combined or more or less adherent. He thought that all gradations between combined and free caloric should exist although it is impossible for caloric to be completely free.[96]

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[93]Lavoisier, Mémoires, 1777 (1780), p. 420.

[94]Lavoisier, Mémoires de chimie, I, 2.

[95]Ibid., p. 13.

[96]Ibid., p. 14.

Expansion is due to the separation of molecules by the accumulation of caloric among them. Other things being equal, molecules closer together will admit less caloric because there is less space and also because when molecules are close together, they exhibit increased attraction and thus offer more resistance to separation. If in a chemical combination the space between molecules changes, caloric is either absorbed or given off, depending upon the relation between the pore space or heat capacity of the constituents compared with the space or capacity of the combination.[97]

Caloric, like water, said Lavoisier, exercises a dissolving force on substances; but the dissolving effects of caloric differ from those of water because caloric is highly compressible, whereas water is not, and caloric can traverse all enclosures, whereas water is confined. Caloric dissolves ether as water dissolves salt; that is, ether molecules are separated from each other because caloric is introduced among them.[98] Lavoisier said that it is difficult to explain these phenomena by postulating a heat fluid without also admitting that the molecules of this fluid "sont douées d'une force répulsive, les unes par rapport aux autres."[99]

Lavoisier explained changes of state in terms of his balance of forces concept while at the same time maintaining that caloric combines with the substance to cause the state change. In this discussion, it is clear that Lavoisier considered combination with caloric and dissolution

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[97] Ibid., pp. 4, 10, 16-17. [98] Ibid., pp. 20-22.

[99] Ibid., p. 25.

by caloric as equivalent statements. Water is "véritablement une combinaison de glace et de calorique." In the margin opposite this statement, he said that water "est une dissolution de glace par le calorique."[100] This explanation applies to the change of all solids into liquids. In all cases, caloric "passe de l'état libre à l'état combine."[101]

Lavoisier said that Adair Crawford explained the absorption of heat during changes of state as being caused by changes in heat capacity.[102] This is very plausible as far as the change of a liquid into a gas. In this case, Lavoisier said, the volume of the gas is greater than that of the liquid, and consequently there is increased pore space among molecules. However, Lavoisier felt that Crawford's view fails to explain the change from a solid to a liquid, for in this case, there is no increase in volume, and in many cases there is a decrease in volume. Thus there must be a change of free caloric into combined caloric, or to say it differently, some caloric must lose its elasticity or its repulsive force.[103]

Having stated that liquefaction is caused by the combination of caloric, he went on to describe all changes of state as a process of dissolution:

> Quoiqu'il [the combination of caloric in the formation of liquids] en soit, je continuerai à regarder la liquéfaction et la vaporisation des corps comme une dissolution par le calorique, dissolution analogue à beaucoup d'égards à celle des sels par l'eau. ...[104]

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[100] Ibid., p. 284. [101] Ibid., p. 286.

[102] For Crawford's views, see pp. 189-191, below.

[103] Ibid., pp. 286-287. [104] Ibid., p. 287.

Then, seemingly contradicting himself, he said that dissolution begins only

> au moment où le corps devient liquide: c'est alors que les molécules attractives des corps solides, se trouvant combinés à une quantité suffisante de molécules répulsives de calorique, tendent à s'écarter les unes des autres, c'est-à-dire à se transformer en un fluide aëriforme; et en effet, un fluide aëriforme n'est autre chose qu'un fluide dont les molécules sont en état de répulsion. ...
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> On conçoit plus facilement dans cette maniére de voir pourquoi il disparait une quantité considérable de calorique au moment où le corps solide devient liquids; c'est-à-dire pourquoi une quantité considérable de calorique perd tout-à-coup son élasticité et sa qualité répulsive: c'est que cette force répulsive est employée à neutraliser la force attractive des molécules de l'eau.[105]

Molecules of liquids, at their melting point, cease to be within the sphere of attraction of their neighbors and they tend to obey a repulsive force due to the presence of caloric.[106] Because no more attraction exists among the molecules, only an infinitesimal increase in the quantity of caloric is necessary to transform the liquid into a gas. A liquid remains in the liquid state only because of the external force of atmospheric pressure, and this pressure is responsible for the thermometric interval between melting and vaporization. Properly speaking, there would be no liquids without atmospheric pressure:

> Il ne faut point perdre de vue que l'état de liquide n'est, en quelque façon, qu'un état précaire qui est soumis à toutes les variations de pesanteur de l'atmosphère, et qui n'existeroit pas sans cette pesanteur.[107]

Vapors and in generall all aeriform substances are the result "de la combinaison de calorique, avec les substances évaporables."[108] In this combination, caloric overcomes the resistance to expansion

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[105] Ibid., p. 288. [106] Ibid., p. 282; cf. pp. 287-288.

[107] Ibid., pp. 296-297. [108] Ibid., p. 313.

caused by atmospheric pressure. In the change from solid to a liquid, however, caloric overcomes the attraction among the molecules of the substance. He considered this combination of caloric with a substance in forming a gas to be the same as a dissolution of the substance by caloric. An elastic fluid is a "composé de calorique combiné avec une substance évaporable, autrement dit, une dissolution d'une substance quelconque par le calorique. ..."[109]

Lavoisier implied a difference between what happens when a solid is transformed into a liquid and when a liquid is transformed into a gas. In the first case, caloric loses its elasticity when combining. However, in the second case, most of this elasticity is patently retained. Indeed, Lavoisier said that caloric is the principle of elasticity; and although he explained both changes from solid to liquid and liquid to gas as due to the combination of caloric, this combination can not be the same process in both instances.

In the case of change from liquid to gas, absorption of caloric without temperature change can be explained as due to a physical rather than a chemical change caused by the increase in volume of the gas over that of the liquid. Lavoisier did imply that Crawford's explanation based upon capacity change may be valid in this case. If caloric does combine in this instance, it is not clear how this combination is substantially different from a simple interjection of free caloric among the molecules of the liquid.

Although Lavoisier described fusion as a dissolution by caloric, similar to the action of water on salt, he also stated that this

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[109] Ibid., p. 322; cf. p. 315.

dissolution begins only when the solid becomes liquid. It is not clear what Lavoisier meant when he equated combination with caloric to dissolution by caloric. It seems unlikely that he meant these two processes to be different explanations of equal validity. It also seems unlikely that he meant combination to be the cause and dissolution the physical description of the effect. Judging from the space devoted to discussion of dissolution, he considered this process to be the more important.[110]

He believed that combined caloric and free caloric describe only the limits of all the possible relations which may exist between caloric and the molecules of other substances, and that there is a complete gradation between these two extremes, differing in the degree of adherence of caloric to the molecules of another substance. This suggests that he did not consider combined caloric to be in a state radically different from caloric which was simply adherent.

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[110] A clue to Lavoisier's ideas on solution and combination of caloric is found in the views of Guyton de Morveau on chemical affinity. Guyton thought that the force of chemical affinity is reducible to the force of gravitation, a force which at small distances is affected by the size and shape of the particles of matter. He thought chemical change could only take place by solution in which the affinity of one constituent of an object is greater for the solvent than for the other constituents; see William A. Smeaton, "Guyton de Morveau and Chemical Affinity," Ambix, XI (1963), [55]-64. Guyton said that fire is the only substance fluid by itself and that other fluids are such only when fire dissolves them; Digressions académiques, ou essais sur quelques sujets de physique, de chymie, & d'histoire naturelle (Dijon, 1762), p. 356, note. He described fusion as a true dissolution by fire and solidification by cooling as a true crystallization; "Observation de la crystallisation du fer [1775]," Mémoires de mathématique et de physique présentés à l'Académie Royale des Sciences par divers savans, & lûs dans ses assemblées, IX (1780), 513. In 1779 he said "Le feu est exactement aux metaux ce que l'eau est aux sels; la fusion est une dissolution; le refroidissement n'est autre chose qu'une évaporation d'une portion de la matière ignée"; "Lettre de m. de Morveau à l'auteur de ce recueil sur les crystallisations métalliques," Observations sur la physique, XIII (1779), 90. Lavoisier was familiar with Guyton's ideas; see Maurice Daumas, "Les conceptions de Lavoisier sur les affinités chimiques et la constitution de la matière," Thales, VI (1949-1950), [69]-80; and Daumas, Lavoisier, pp. 174-176.

Lavoisier's theory of heat differs from earlier material theories in several respects. First, the inherent motion of fire matter, which from the beginning of the eighteenth century had been a hallmark of all material theories of heat, is completely absent in caloric. In Lavoisier's theory, particles of caloric are quiescent except as they are acted upon by the force of their own self-repulsion and the force of attraction for the particles of ordinary matter.

Second, in Lavoisier's system the role of heat matter as an agent or instrument in chemical operations is reduced. This reduction is due to his explanation of changes of state as being caused by caloric becoming combined or released, that is acting as a constituent of substances. Whereas previous material theories had explained these changes as caused by heat matter acting as a simple agent to separate the particles of objects, the caloric theory offered a chemical explanation in which heat matter obeys the forces of chemical affinity. Lavoisier's break with the past, however, was not complete, for he frequently offered the old explanation as well as his new one, and it is often difficult, if not impossible, to decide which of the two he preferred.

In both the older heat theory and the caloric concept, the matter of heat loses its characteristic properties when it combines with other substances; that is, it loses its ability to effect a thermometer and becomes latent. In the old theory, fire matter combines as phlogiston to form combustibles and metals. In the caloric theory, however, heat matter combines only to bring about changes of state. It is in this respect that Lavoisier's ideas concerning heat become fundamental to his oxidation concept. Having found the combination of vital air with

substances to be the single phenomenon common in all cases of combustion and calcination, he eliminated phlogiston from existence. But phlogiston is the matter of fire fixed in substances and hence hidden or latent until it is released during combustion or calcination. With phlogiston gone, whence the heat and flame of combustion? Eliminating fire fixed in the form of phlogiston, Lavoisier created fire fixed in the form of the latent heat of vaporization. The heat and flame of combustion come not from the combustible substance but from oxygen gas, and the release of heat from this gas when its base unites with a substance is in no way different from the release of heat from steam when it condenses. In this sense, caloric is the new phlogiston, and a phlogistic explanation would say that oxygen gas is the single combustible substance in nature.

This is not to say that Lavoisier's ideas on changes of state and on the nature of aeriform substances preceded the development of his ideas concerning combustion and calcination. It is more likely that these concepts developed together, for each is dependent upon the other.

The concept of latent heat is crucial to the oxidation theory, and there is some evidence that Lavoisier himself so considered it.[111] Although he was familiar with the work of Joseph Black, it is probable that he independently arrived at the idea that heat becomes latent in changes of state.[112] Yet in spite of the importance to his chemical theory of these phenomena and their explanation, and in spite of the experimental work he performed in this field, Lavoisier remained relatively

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[111]See n. 49, pp. 230-231, below.

[112]See n. 13, p. 108, above.

uninterested in heat theory in general. To justify the presence of heat matter in oxygen gas so as to account for the heat released during combustion was his chief concern, and considering his work as a whole, his discussion of heat in a more general sense seems incidental.

CHAPTER V

FRENCH PROPONENTS OF THE CALORIC THEORY

Gaspard Monge (1746-1818) is primarily noted as a mathematician and physicist, but his writings did include some works on subjects dealing with chemistry. For example in 1782, he published an article in the memoirs of the French Academy in which he discussed some experiments on igniting inflammable air and dephlogisticated air.[1] In concluding this article, he stated that there are two different views regarding the composition of the two gases involved in the reaction. The first view is that inflammable air and dephlogisticated air are two distinct substances both of which are dissolved in "le fluide du feu." The union of these two substances produces water and results in the release of the solvent, fire, in which the two substances had been dissolved.

The other view is that these two airs are composed of a single base, water, dissolved in different elastic fluids. When the airs unite, the two elastic fluids in which the base was dissolved combine to form the fluid of fire and light, and water is released. Mongue said that the results of the experiment cannot decide between these two views of the composition of the airs and of water. However, the view that the two

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[1]Gaspard Monge, "Mémoire sur la résultat de l'inflammation du gaz inflammable & de l'air déphlogistiqué dans des vaisseaux clos," Mémoires de l'Académie Royale des Sciences, 1783 (1786), pp. 78-88.

gases are indeed separate substances dissolved in fire fluid is supported by the action of plants in decomposing water, absorbing inflammable air, and giving off dephlogisticated air which is united with the heat and light the plants absorb from the sun.[2]

Monge's seeming acceptance of Lavoisier's theory regarding the structure of the two gases and of water is hedged by a concluding criticism. If the two gases are regarded as two distinct substances dissolved in fire fluid, why is more heat needed to start the reaction? Why does an increase of the dissolvent, fire fluid, decrease the adherence of this fluid to the bases of the two gases? Monge said that this "est absolument contraire à ce qu'on observe dans toutes les opérations analogues de la Chimie."[3]

Monge came to accept the new chemistry sometime during 1786 or 1787.[4] He had written the article on calorique which was to have been published in the second volume of the Dictionnaire de physique,[5] but the manuscript of this article was lost. The unknown author of the article "Calorique" in the second volume of the Dictionnaire published in 1816 deplored the loss of Monge's paper and as an apology gave a lengthy quotation from an article Monge published in 1790 in "un journal absolument ignoré, qui avoit pour titre Journal gratuit. ..."[6]

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[2]Ibid., p. 87. [3]Ibid., p. 88.

[4]René Taton, L'oeuvre scientifique de Monge (Bibliothèque de philosophie contemporaine) (Paris, 1951) pp. 335-336.

[5]Gaspard Monge, et al., Dictionnaire de physique (Encyclopédie méthodique) (4 vols.; Paris, 1793-1822).

[6]Ibid., II (1816), p. 170; Gaspard Monge, "Sur la théorie du calorique," Journal gratuit par une société de gens de lettres, X (1790),

In this quotation, Monge exhibits a complete acceptance of Lavoisier's views on the nature and operation of caloric.

> Le calorique est un fluide impénétrable, extrémement élastique, & si rare, que se pesanteur n'est manifestée par aucum phénomène.[7]

He explained heat phenomena entirely in terms of forces: the mutual attraction among the molecules of a substance, attraction between caloric and the molecules of a substance, and external pressure. Caloric is attracted by the molecules of all substances and the force of attraction is proportional to the distance of caloric from the substance and the nature of the substance itself. In its action, caloric conforms to its mass and to the compression it undergoes. The molecules of a substance do not touch and they are separated by layers of caloric. Caloric in these layers is more or less compressed depending upon the tendency of caloric toward the molecules to which it is adherent, the pressure of layers of caloric farther away which are also drawn towards the molecule, the force of attraction of neighboring molecules, and external pressure, if the substance is flexible.[8]

There are two forces favoring the introduction of caloric into a substance. One is the compressive force of caloric outside the substance which acts on the internal caloric. The second is the attraction

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26-32, 41-44, 49-53, 65-67, 81-83, cited in Taton, L'oeuvre de Monge, p. 379. Taton says (p. 325) that this article was also reproduced in Hachette, Programme d'un cours de physique (2d ed.; Paris, 1809), pp. 54-72; see Taton's discussion in L'oeuvre de Monge, pp. 323-325 and René Taton, "A propos de l'oeuvre de Monge en physique," Revue d'histoire des sciences, III (1950), 174-179.

[7]Monge, Dictionnaire de physique, II, 170.

[8]Ibid.

of the caloric for the molecules of the substance. The word "temperature" expresses the first of these forces. Monge explained changes of state as caused by some sort of change in the second force. The absorption of caloric which is caused by the change in attraction of caloric for the molecules of an object does not effect a thermometer and is called "calorique latent."[9]

Monge said that there are also two forces which oppose the introduction of caloric into an object. The first is the mutual adherence of the molecules of the substance. Adherence among molecules is neutralized by latent caloric, and an increase of adherence will cause a contraction among molecules and an extrusion of the interposed caloric. The second force is external pressure, which will affect a substance only if the substance is flexible. As examples of the effects of this pressure, Monge cited friction, the expulsion of caloric when metals are struck by a hammer, and the compression of air. External pressure is the only force which opposes the introduction of caloric into liquids.[10] When this pressure is overcome, "les molécules du liquide, absolument libres, se dissolvent dans le calorique, & constituent un fluide élastique."[11] Indeed, Monge said, we owe the liquid state entirely to atmospheric pressure, "& sans cette pression ils n'auroient d'autre état habituel que celui de solide & de fluide élastique."[12]

Armand Séguin (ca. 1765-1835), a wealthy army contractor who collaborated with Lavoisier, was one of the most prolific French writers on heat theory. One of the most complete early presentations of a

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[9] Ibid., p. 171. [10] Ibid., pp. 171-172. [11] Ibid., p. 172.
[12] Ibid., p. 171.

discussion of heat theory which follows the new nomenclature is contained in two papers that Séguin published in the Annales de chimie in 1789 and 1790. The first paper is the more general. In it Séguin defined various terms used in discussions of heat theory and phenomena, discussed various laboratory techniques, and explained the heat phenomena involved in changes of state and some chemical reactions.[13] The second paper contains a lengthy list of corrections for the first article followed by a more detailed discussion of methods of computing absolute zero, techniques for determining the heat capacity of substances and results of some of these determinations, and a discussion of respiration.[14]

These articles seem to be largely a poorly organized commentary on Adair Crawford's Animal Heat[15] in which Séguin was to a great extent dependent upon Lavoisier's and Laplace's Mémoire of 1783.[16] In most cases, Séguin accepted the theoretical views of Lavoisier.

> Jusqu'A l'époque où l'on a publié la nouvelle nomenclature, le mot chaleur a souvent eu une double signification; il servoit indistinctement alors à désigner la sensation qu'on éprouve, & le

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[13]Armand Séguin, "Observations générales sur le calorique & ses différens effets, & réflexions sur la théorie de mm. Black, Crawfort, Lavoisier, & de Laplace, sur la chaleur animale & sur celle qui se dégage pendant la combustion, avec un résumé de tout ce qui a été fait & écrit jusqu'à ce moment sur ce sujet," Annales de chimie, III (1789), 148-242.

[14]Armand Séguin, "Second mémoire sur le calorique," Annales de chimie, V (1790), 191-271.

[15]Adair Crawford, Experiments and Observations on Animal Heat and the Inflammation of Combustible Bodies, Being an Attempt to Resolve These Phenomena into a General Law of Nature (2d ed., enlarged; London, 1788); see pp. 186-196, below.

[16]Antoine Laurent Lavoisier and Pierre Simon, marquis de Laplace, "Mémoire sur la chaleur," Mémoires de l'Académie Royale des Sciences, 1780 (1784), pp. 355-408. See the discussion of this in Chapter IV, pp. 113-119, above.

> principe inconnu qui le [sic] produit ... : c'est pour séparer la cause d'avec l'effet qu'on a donné le nom de calorique à ce principe inconnu, soit qu'on le considère comme une qualité ou comme une substance, & qu'on a réservé les mots chaleur & froid, pour exprimer les sensations différentes qu'il produit sur nos organes, en vertu de la propriété dont il jouit de se mettre en équilibre dans tous les corps qui sont en contact.[17]

Séquin then defined the various terms used in discussing heat phenomena. The temperature of a substance is the measure of expansion of the liquids used in construction of thermometers.[18] "Calorique spécifique, ou quantité spécifique de calorique" is the total quantity of caloric contained in one substance compared with that contained in another substance of equal weight and temperature.[19]

Séguin said that the different quantities of caloric which different substances contain indicate a difference among the substances in their abilities to collect and retain caloric. He called these abilities the "capacités des corps pour contenir le calorique. ..."[20] This capacity should be considered as a force or property which depends upon two causes: the cause "de l'affinité qu'ont les molécules les unes pour les autres, & de pouvoir qu'a le calorique de les écarter. ..."[21] He defined "Chaleur spécifique" as the quantity of caloric necessary to raise the temperature of a substance a given number of degrees, compared to that required for another substance. Specific heat and capacity represent the same idea because relationships between specific heats are always proportional to the relationships between capacities.[22]

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[17] Séguin, Annales de chimie, III (1789), 148-149.

[18] Ibid., p. 150. [19] Ibid., p. 151. [20] Ibid., pp. 152-153.

[21] Ibid., pp. 154-155. [22] Ibid., p. 153.

Séguin cited Lavoisier as stating that heat capacities (Séguin's specific heats) are affected by the spaces which exist among the molecules of a substance.[23] If this relationship were valid, then capacity would be proportional to the degree of expansion of a substance; and this is not the case as long as there is no change of state. At a given temperature, the "calorique interposé," the intermolecular caloric, is proportional to the space among molecules; but the capacity (specific heat) is not.[24]

"On n'a point encore déterminé d'une manière exacte, la nature du calorique."[25] Séguin said that there were three different views regarding the nature of this substance:

> Quelques personnes pensent que c'est un être simple, dépendant de lui seul, répandu par-tout en grande quantité, & dont quel-ques effets ont de l'analogie avec ceux que produit la lumière, tandis que d'autres en diffèrent essentiellement.
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> D'autres physiciens, mais en bien plus petit nombre, pensent qu'il n'existe point de substance à laquelle on puisse donner le nom de calorique, & que la chaleur n'est que le résultat des mouvemeus [sic] insensibles des molécules de la matière.
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> . . . . . .
>
> Quelques personnes enfin croyent que le calorique n'est point un être simple. Suivant M. de Luc, c'est un composé de lumière, & d'une base qui nous est inconnue dans son état de liberté, ou que du moins nous obtenons peut-être sans nous en douter.[26]

One might object to the last opinion on the grounds that the base of caloric should have weight, and yet none is observed. But no

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[23] Antoine Laurent Lavoisier, "Réflexions sur la phlogistique, pour servir de développement à la théorie de la combustion & de la calcination publiée en 1777," Mémoires de l'Académie Royale des Sciences, 1783 (1786), pp. 527-528; see pp. 121-122, Chapter IV, above.

[24] Séguin, Annales de chimie, III (1789), 154, note.

[25] Ibid., p. 182.

[26] Ibid., pp. 182, 184. For a brief discussion of the theory of Jean André Deluc, see p. 61, and n. 134, pp. 62-63, above.

experiment has truly demonstrated that light and caloric do not have weight. All that these experiments have shown is that the instruments used are not delicate enough to detect this weight. It is very probable that caloric does have some weight because "notre idée se refuse à l'existence d'un corps dont la pesanteur est absolument nulle."[27]

Although the absence of weight is not argument against the idea that caloric is a compound, the base to which caloric is supposed to combine should make itself known by the appearance of some new property when the base is combined with another substance; and this does not occur:

> La base du calorique ne nous étant donc point connue, & aucune des expériences qui ont été faites jusqu'à ce moment, ne peuvant pas même nous la faire soupçonner, nous pouvons regarder l'opinion que le calorique est un composé, comme une véritable supposition: & telle est sa nature qu'elle ne peut être appuyée d'aucume probabilité.[28]

Séguin admitted that there is a very striking analogy among gases, vapors, and caloric which would tend to indicate that caloric is a compound; but facts, not analogies, are needed to support conclusions.[29] There are arguments for and against both the idea that caloric is a simple substance and the idea that it is a compound. The theory that caloric is a compound, however, assumes more unknowns than the theory that it is a simple substance, and therefore the latter idea is preferable.[30]

The three opinions on the nature of heat are only "hypothétiques, puisqu'il est impossible de les démontrer d'une manière rigoureuse, & que jamais peut-être nous n'arriverons à ce dégré de connoissance."[31]

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[27] Ibid., p. 185. [28] Ibid., p. 187. [29] Ibid.

[30] Ibid., pp. 209-211. [31] Ibid., pp. 187-188.

In the present state of knowledge, all that can be done is to say that one theory is better than another. In any case, "Il me semble donc qu'il est essentiel pour l'intérêt de la science, de ne point admettre sur la nature du calorique, aucune opinion exclusive, jusqu'à ce que nos connoissances soient plus étendues. ..."[32]

Séguin did not explicitly espouse a particular theory of heat, but his presentation shows that he was committed to the view that caloric is a simple substance. He ignored the motion theory beyond citing this idea as one of the three existing opinions and including a quotation from the Lavoisier and Laplace memoir which explained this motion theory;[33] his periodic criticisms of the theory of a compound caloric has been mentioned.

He wrote that caloric can exist in three states: as "calorique libre, calorique interposé, & calorique combiné."[34] As the name implies, interposed caloric is that located within the pores of a substance, among the molecules. Caloric in this state is responsible for the temperature and the expansion of substances. This caloric is compressible, it serves to separate the molecules of an object and consequently to overcome the affinities which the molecules have for each other.[35] As long as the quantity of caloric is sufficient to equalize the force of affinity among molecules, the compressive force of caloric and the force of affinity are

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[32] Ibid., pp. 188-189.

[33] Ibid., pp. 182-184; see quotation, p. 146, above; Lavoisier and Laplace, Mémoires, 1780 (1784), pp. 357-358; see Chapter IV, pp. 114-115, above.

[34] Ibid., p. 194.

[35] Ibid., p. 191.

always in equilibrium. If more interposed caloric is added, the balance is re-established by a separation of molecules.[36] It is this property which accounts for the tendency of caloric to equilibrium.[37]

Temperature is a measure of the compression of interposed caloric;[38] and because compression and mutual attraction among molecules are in equilibrium, temperature is also a measure of this mutual attraction.[39] Séguin said that temperatures measured with thermometers represent an unknown fraction of absolute temperature, and consequently to say that the temperature of one substance is double or triple that of another conveys a false idea.[40] For this reason, affinity should be measured in degrees of absolute temperature (température réelle).[41] Because absolute temperature indicates the degree of attraction between molecules, temperature offers a means of predicting the temperature at which a given reaction will take place, or if it will take place at all. If a compound of two substances forms at a given absolute temperature, and if one of the constituents can unite with a third substance at a lower temperature, then one can predict that the original compound will decompose and that one constituent will unite with the third substance.[42]

In discussing changes of state, Séguin said that

> Beaucoup de corps dans la nature peuvent subir trois modifications, la solidité, la liquidité & la fluidité. Ces modifications dépendant du pouvoir qu'a la calorique de vaincre l'attraction qu'ont les molécules des corps les unes pour les autres; mais ce pouvoir est ensuite modéré par la pression plus ou moins forte de l'atmosphère.[43]

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[36] Ibid., p. 192; cf. p. 195. [37] Ibid., p. 195.

[38] Ibid.; cf. p. 201. [39] Ibid., p. 201. [40] Ibid., pp. 164-165.

[41] Ibid., p. 201. [42] Ibid., pp. 201-205. [43] Ibid., p. 160.

This statement seems to indicate that Séguin accepted Lavoisier's explanation of state change in terms of the balance between the forces of attraction among the molecules of a substance and force of caloric tending to separate these molecules. With this concession made to his mentor, Séguin went on to credit state change entirely to the combination of caloric:

> Jusqu'au moment de la liquéfaction, ce n'est donc qu'une simple interposition [of caloric]; mais pendant ce changement c'est une nouvelle combinaison opérée en vertu d'une affinité supérieure. Ces molécules du solide s'unissent avec une certaine quantité de calorique pour former un liquide; ce calorique est absolument nécessaire à la nature de ce nouveau corps. ...[44]

The molecules of a solid not only unite with caloric to form a liquid, but this caloric is "absolument nécessaire à la nature de ce nouveau corps. ...."[45] Liquefaction takes place at the moment when the affinity of the molecules for each other becomes less than the affinity the molecules have for caloric. When the caloric combines, it "perd par cette combinaison toutes ses qualités distinctives,[46] it is "réellement combinée."[47] Séguin added that there are certain facts of combustion which are impossible to explain unless it is assumed that caloric does combine.[48]

Molecules of objects in the liquid state still exercise some attractive force on their neighbors; and additional caloric enters the

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[44] Ibid., p. 193-194. [45] Ibid., p. 194.

[46] Ibid., p. 193. Séguin insisted that the space between the molecules affects only the interposed caloric, implying that combined caloric is unaffected by this space; see his discussion p. 148-149, above.

[47] Séguin, Annales de chimie, III (1789), 195.

[48] Ibid., p. 193.

substance as interposed caloric, the compressive force of which is balanced by attraction among the molecules. Vaporization occurs when the attraction of the molecules for caloric is greater than their attraction for each other. The affinity of molecules for caloric is constant, but their mutual attraction decreases as the substance expands. It is for this reason that external pressure, for example, atmospheric pressure, tends to prevent vaporization by keeping a constant distance among the molecules.[49]

The temperature of a substance is indicative of the attractive force among its molecules;[50] and the temperature of a substance remains constant during a change of state, indicating that the mutual attraction among molecules after state change is the same as before. Because attraction is proportional to the distances among the molecules, the separation "entre les molécules du nouveau composé [the liquid] soit à trés-peu près égal à celui qui existoit entre celles du solide. ..."[51] Remembering that water occupies less space than ice, Séguin remarked that it has never been shown that water really does occupy less space, and the appearance that is does is due to "causes secondaires" which he can ignore.[52]

He applied the same argument to the change from a liquid into a vapor. Because the temperature is constant during this change, the mutual attraction among the molecules of the liquid must be the same as that among the molecules of the vapor. Thus at the instant of change

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[49] Ibid., pp. 194-197.

[50] See p. 149, above.

[51] Ibid., p. 194.

[52] Ibid., p. 198.

the molecules of the liquid and the vapor must be the same distance apart. Séguin explained that for an instant, air pressure keeps the molecules at the same distance before the newly formed vapor can expand against it.[53]

Séguin's explanation of changes of state as being caused by the combination of caloric with the substance involved is completely opposed to the explanation offered by Adair Crawford. According to Crawford's theory, change of state and the concomitant absorption or release of caloric is due to a change in heat capacity. Crawford completely denied that caloric combines during this transformation.[54] Séguin said that if this were the case, caloric would be absorbed only after the change had occurred, and one must look for another cause to bring about the change in capacity in the first place.

Furthermore, if Crawford's theory were true, then the change in heat capacity should account for all the caloric which is released or absorbed. Crawford had assumed that capacity is related to the specific caloric, that a given heat capacity represents a certain quantity of caloric contained in the substance. Séguin said that capacity is not proportional to specific caloric and that this argument is thus invalid.[55] He concluded that Crawford's theory is completely lacking in conclusive proof and "d'ailleurs le phénomène [of state change] s'explique d'une

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[53] Ibid., pp. 196-200.

[54] See pp. 189-191, Chapter VI, below; for Lavoisier's criticisms of Crawford, see p. 133, Chapter IV, above.

[55] Séguin, Annales de chimie, III (1789), 177-179.

manière bien plus simple & bien moins forcée, par l'admission de la combinaison du calorique."[56]

Séguin followed Lavoisier completely in explaining heat phenomena resulting from chemical change. Heat or cold produced during combinations is caused by one or more of the following: change in volume, change in the affinities of the molecules, change in the amount of combined caloric in the new compound compared with that in the constituents, or a combination of these causes. In the present state of knowledge, Séguin thought, it is impossible to state exactly which of these causes are involved in any particular combination.[57]

Séguin called the molecules of a substance to which the caloric is combined the base of caloric. If the molecules of the base have a greater attraction for other molecules than they do for caloric, then the molecules will unite and caloric will be released.[58] The amount of caloric released in a reaction, all other things being equal, depends upon the state of the resultants. That is, if a solid is formed, more caloric is liberated than if a gas is formed. This is because the molecules of a solid, on one hand, are closer together and because much caloric is absorbed, on the other hand, in forming a gas.[59] If the reaction results in combustion, then vital air is involved, and vital air furnishes the light and caloric observed. If there is no combustion,

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[56] Ibid., p. 179; cf. p. 231. [57] Ibid., pp. 206-207.

[58] Ibid., p. 208.

[59] Ibid., pp. 215-216. See the discussion of the heat released during the combustion of carbon in Armand Séguin and Antoine Laurent Lavoisier, "Premier mémoire sur la respiration des animaux," Mémoires de l'Académie Royale des Sciences, 1789 (1793), pp. 566-567.

then all the caloric must come from the other substances. Thus the heating and reddening of iron by hammering and friction must be explained by the molecules of the iron coming closer together and forcing out caloric and light. This applies unless combustion results; then vital air is involved.[60]

With respect to the light released in some reactions, Séguin preferred the explanation that light and caloric are two distinct, simple substances which are not united. Either or both may be contained in another object. Séguin explained phenomena where both heat and light are produced both in terms of caloric and light being united together and in terms of them being two distinct, separate substances. He considered the latter idea to be preferable.[61]

The corrections to this paper, which are contained in Séguin's second article on heat, tend to make his definitions of the terms more precise.[62] The definition of calorique specifique is reworded but substantially unchanged from the first article.[63] Séguin replaced the term "chaleur specifique" with "capacité," to indicate the quantity of heat necessary to increase the temperature of a substance a given number of degrees compared to that required for another substance.[64] In making this change, Séguin was conforming to the definition of capacity as given

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[60]Séguin, Annales de chimie, III (1789), 212.

[61]Ibid., pp. 208-229.

[62]Séguin, Annales de chimie, V (1790), 191-200.

[63]Ibid. cf. Armand Séguin, "Observations générales sur la respiration et sur la chaleur animale, lues à la Société de Médecin, le 22 mai 1790," Observations sur la physique, XXXVII (1790), 471.

by Lavoisier and Laplace.[65] This change necessitated a corresponding change in his definition of "capacité" as this term was used in the first paper; but he only altered the former definition from the ability of a substance to contain caloric to the ability of a substance to admit caloric among its molecules.[66] Thus he used the term heat capacity to indicate two different things. The other changes sharpened the distinction already made between interposed and combined caloric so as to make it perfectly clear that temperature and expansion are caused by the former.[67]

Séguin's discussion of absolute zero[68] is based on that of Lavoisier and Laplace in their memoir of 1783,[69] and that in Crawford's Animal Heat.[70] Séguin's conclusions are the same as those of Lavoisier and Laplace. He defined absolute zero as being the absence of interposed caloric, not a total absence of caloric:

> ... le zéro réel n'annonce donc pas une privation totale de calorique spécifique, mais tout au plus une privation totale de calorique interposé ... car il est possible qu'il en entre une certaine quantité [of caloric] dans la composition de chaque molécule ... : [Le] zéro

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[65] Mémoires, 1780 (1784), p. 361.

[66] Séguin, Annales de chimie, V (1790), 191.

[67] Ibid., pp. 193, 231-232.

[68] Ibid., pp. 231-257. This section on absolute zero was purportedly extracted in Antoine Laurent Lavoisier, Mémoires de chimie (2 vols.; [Paris?, 1805?]), I, 226-245. This extract is much shorter than the original; although the results are substantially the same, most of what remains was rewritten.

[69] Mémoires, 1780 (1784), pp. 381-385, 388-389; see pp. 118-119, Chapter IV, above.

[70] (2d ed, enlarged; 1788), pp. 253-270, 453-456; for Crawford's discussion of absolute zero, see pp. 191-193, below.

réel n'indique que l'état d'un corps qui seroit presque totalement privé de son calorique interposé.[71]

After comparing the results of Lavoisier and Laplace with those of Crawford and noting the wide disagreement among the computed values, Séguin concluded with discussing the possible causes of these variations. The calculations are based on the idea that caloric does not combine with substances, the idea that the heat capacities of substances represent a certain quantity of caloric contained in a substance, and the idea that these capacities are constant at all temperatures as long as there is no change of state. Séguin said that one or all of these suppositions may be wrong.[72]

He had already argued against these three assumptions in his first paper. He had described the idea that caloric combines with substances as being less forced and more simple than Crawford's ideas, and had explained changes of state entirely in these terms; he had also denied that any relation existed between the capacities of substances and the quantity of caloric they contained.[73] He had admitted that Crawford's experiments have demonstrated that the heat capacity of an object is indeed constant between the temperature of freezing water to that of vaporization of water.[74] But does this show that heat capacities are permanent at all temperatures? Séguin had answered that "ce n'est-là qu'une supposition qui, dénuée de preuves, peut n'être point admise par ceux qui se sont un devoir de ne rien déduire au-delà de l'experience."[75]

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[71] Séguin, Annales de chimie, V (1790), 231-232.

[72] Ibid., p. 256.

[73] See pp. 152-153, above.

[74] Séguin, Annales de chimie, III (1789), 163.

[75] Ibid., p. 169.

This consideration "me paroît renverser la théorie du docteur Crawford sur la chaleur."[76]

Séguin never systematically argued against the motion hypothesis. This theory was cited as one of the possible explanations of heat phenomena, but he never went beyond this citation; and he always explained heat phenomena in terms of a material theory.[77] His argument was that the motion theory was one without supporters and thus did not require refutation; besides the material theory is adequate to explain the phenomena. For example, in 1791 Séguin wrote that

> Quoiqu'on ait cru pendant long-tems, que la chaleur étoit le résultat des mouvemens insensibles des molécules de la matière; presque tous les physiciens sont maintenant persuadés, qu'elle est produite par une substance particulière.
>
> Cette dernière opinion étant à peu-près générale, nous l'admettrons d'autant plus volontiers, qu'elle conduit immédiatement à l'explication de presque tous les phénomènes de la nature.[78]

Again in 1792 he restated his argument.[79] Having listed vibratory motion as a possibility, he said

> Comme tous les phénomènes chimiques s'expliquent avec plus de facilité dans cette dernière supposition [that the cause of heat is a particular fluid called caloric], et que d'ailleurs elle a été admise par la plus grande partie des physiciens, je me conformerai

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[76]Séguin, Annales de chimie, V (1790), 256.

[77]See pp. 146, 148, above.

[78]Armand Séguin, "Observations générales sur les sensations, & particulièrement sur celles que nous nommons chaleur & froid, lues à la Societé Royale de Médecine, le 24 décembre 1790," Annales de chimie, VIII (1791), 185.

[79]Armand Séguin, "Quatrième mémoire sur quelques principaux phénomènes chimiques, lu à la société philomatique, le 24 mars 1790," Vol. I, pp. 148-225, in Antoine Laurent Lavoisier, Mémoires de chimie (2 vols.; [Paris?, 1805?]); cited hereafter as Séguin, "Sur quelques phénomènes chimiques," Mémoires de chimie.

à cette opinion, que, de tous temps, j'ai trouvé plus satisfaisante et plus conforme aux observations.[80]

In his Mémoires de chimie, Lavoisier included a paper of Séguin's in which the discussion of heat theory is much better organized than the two articles just described.[81] With a few notable exceptions, Séguin's discussion repeated what he had said previously. He stated the various opinions of the nature of heat, dismissing the idea of the Swedish chemist Karl Wilhelm Scheele (1742-1786) that heat is a compound of phlogiston and vital air on the grounds that the existence of phlogiston is regarded as being hypothetical.[82] He gave similar treatment to Deluc's view that caloric is a compound of light and some unknown base. As experience has shown no indication of the base, "on peut, sans crainte d'être taxé de partialité, ne point admettre la composition de ce fluide [caloric]."[83]

Séguin then addressed himself to the problem of whether the particles of caloric repel themselves, and if they do, how this can be

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[80] Ibid., p. 154.

[81] Ibid., pp. 148-225. A footnote at the beginning of this article (ibid., p. 148) says "Revu et corrigé à la fin de 1792." For a discussion of this work of Lavoisier's, see pp. 129-131, and n. 89, in Chapter IV, above.

[82] Séguin, "Sur quelques phénomènes chimiques," Mémoires de chimie, I, 156. For Scheele's views see Karl Wilhelm Scheele, Chemical Observations and Experiments on Air and Fire, trans. J. R. Forster (London, 1780), especially pp. 32-33. This was first published in 1777. Scheele thought that "fire air" (vital air) and phlogiston can combine in various proportions; the more phlogiston and the less vital air in the compound, the more the compound behaves like light. Light, however, is not pure phlogiston, for if it were, it would combine with the fire air of the atmosphere and cause total darkness (Scheele, Aire and Fire, pp. 87, 97.).

[83] Séguin, "Sur quelques phénomènes chimiques," Mémoires de chimie, I, 157.

made to agree with the attraction which caloric has for molecules of other substances.

> De quelque manière qu'on envisage le calorique, si on le considère comme une substance, il est impossible de ne point admettre dans ses atomes une propriété attractive, et conséquemment une pésanteur quelconque; si les atomes de calorique n'avoient aucune pésanteur, ou, ce qui revient au même, n'attiroient avec une force quelconque les molécules des autres corps, celles-ci, obéissant à leur affinité d'aggrégation, chasseroient promptement, malgré toutes les pressions extérieures, la calorique qui est interposé entre-elles, et alors tous les corps de la nature seroient solides: les atomes de calorique jouissent donc d'une propriété attractive. ...[84]

Having concluded that caloric must have an attraction for the molecules of other substances, he asked how caloric can also have a force of repulsion? How can the same substance, caloric, at one time possess two opposing properties? Besides, heat phenomena can be explained without resorting to repulsion:

> A la rigeur, il me semble que, sans admettre une force répulsive dans les atomes du calorique, on peut expliquer les effets de ce fluide, en supposant une si foible densité et une forme telle dans ses atomes, que leurs points de contact soient infiniment peu nombreux.[85]

Séguin's denial of a repulsive force among the atoms of caloric is contrary to what Lavoisier had said on the subject in the same volume of Mémoires de chimie in which Séguin's article appears.[86]

Séguin's discussion of the relationships between caloric and the molecules of the substance to which the caloric adheres is in much greater detail than in his previous writings. An isolated molecule of a substance, placed in a region containing a certain number of caloric

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[84] Ibid., pp. 158-159, note. [85] Ibid., p. 159, note.

[86] Ibid., p. 25; see pp. 133,134, Chapter IV, above. Cf. Antoine Laurent Lavoisier, Traité élémentaire de chimie, présenté dans un ordre nouveau et d'après les découvertes modernes, avec figures (2 vols.; Paris, 1789), I, 20, 25; see p. 126, Chapter IV, above.

atoms, will attract these atoms of caloric. The caloric will form successive layers around the molecule and these layers will build up until the outermost layer is "jusqu'à l'estrêmité du rayon de se [the molecule's] sphère d'activité, c'est-à-dire, jusqu'à la distance où la molécule n'exercera plus d'action sur les atomes de calorique."[87]

Caloric thus forms an "atmosphère" around the molecule, although the depth of this atmosphere, which corresponds to the radius of the sphere of activity of the molecule, is totally unknown.[88] The caloric atmosphere not only forms around the molecule itself but also around the components of the molecule. For example, caloric added to water not only separates molecules of water from each other, but it also separates the atoms of oxygen from those of hydrogen.[89] The tendency to equilibrium which caloric exhibits is due to the caloric in the outermost layer of this atmosphere being attracted to another molecule more strongly than it is attracted to the molecule of which it forms the outer layer.[90] The innermost layers of caloric surrounding a particular molecule are more adherent than caloric in the outermost layers, for in addition to being attracted toward the molecule, caloric in the inner layers is forced toward the molecule by the pressure exerted by caloric in the outer layers which is also attracted toward the molecule.[91]

Séguin noted that the force of attraction for caloric depends not only upon the distances among the molecules but also upon their shape

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[87]Séguin, "Sur quelques phénomènes chimiques," Mémoires de chimie, I, 160.

[88]Ibid., p. 161; note, p. 160. [89]Ibid., p. 184.

[90]Ibid., pp. 160-161. [91]Ibid., p. 167.

and density. Thus in a heterogeneous substance, the radius of the sphere of activity of each molecule and consequently the atmospheres of caloric will be different for each molecule.[92] Also the atmosphere varies depending upon the location of the molecule within the substance. This is true even for homogeneous substances. For example, molecules in the interior of a substance will have a greater force acting upon them tending to bring them together than molecules at or near the surface of the substance. Thus the atmospheres of caloric surrounding the interior molecules will be much less expanded than the atmospheres of the exterior molecules.[93]

Séguin assumed two forces of attraction: the mutual attraction among the molecules and the attraction between these molecules and caloric. Both of these forces depend upon the distance among the various particles, although the relationship of the forces to the distance is different for the two kinds of attraction. The force of mutual attraction among the molecules is an obstacle to the introduction of caloric into the interior of the substance. In this paper, Séguin explained changes of state, and especially the phenomenon of absorption of caloric without temperature change, entirely in terms of these forces. He occasionally used the term "combinaison" to indicate this process, but his mechanism is no different from that which causes a substance to expand by increasing the layers of caloric surrounding each molecule. This is a complete departure from his earlier views, a departure probably due to the influence of Lavoisier.

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[92] Ibid., note, p. 168. [93] Ibid., p. 166.

"L'absorption de calorique, pendant la fusion et la vaporisation, s'explique d'une manière satisfaisante, par la seule considération de l'affinité."[94] Considering that the atmospheres of caloric surrounding the interior molecules of a substance are compressed because of the mutual attraction of neighboring molecules, and considering that this mutual attraction offers an obstacle to the introduction of additional caloric, it is easy to see how, if this mutual attraction be eliminated, the molecules can move easily with respect to each other and how they can absorb all the caloric which is communicated to them. This, Séguin said, is precisely what takes place during fusion.

The mutual affinity among the molecules is gradually decreased as the substance expands. At the degree of expansion at which the molecules no longer exercise attraction for each other, they no longer present an obstacle to the introduction of caloric. The only obstacle present at this instant is due to atmospheric pressure.[95]

> C'est-là le moment de la liquéfaction, c'est-à-dire, le moment où les molécules, pour completter leurs couches de calorique, s'emparent de tout celui qu'on leur communique, de telle sorte que le mercure de thermomètre, mis en contact, ne pouvant s'approprier aucune portion de ce calorique communiqué, reste, jusqu'à ce que la liquéfaction soit totalement terminée, au même degré de dilatation où il se trouvoit avant le contact.[96]

As the obstacle of mutual attraction among the molecules is no longer present, the atmospheres of caloric will increase until the compressive

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[94] Ibid., p. 177.

[95] Ibid., pp. 178-179. Further on (pp. 181-182), Séguin indicated that the mutual affinity among molecules of a liquid, although very weak, is not totally destroyed by fusion, viz. the sphericity of small drops of water.

[96] Ibid., pp. 178-179.

force of the caloric balances atmospheric pressure. Atmospheric pressure can be overcome only by making the molecules of the liquid specifically lighter than those of the atmosphere. Séguin said that this is done by increasing the effective volume of the liquid molecules by the addition of caloric to them.[97] His attribution of the liquid state to atmospheric pressure is a change from his earlier views, another change probably due to Lavoisier's influence.

In the remaining part of his paper, Séguin stated nothing which is different from his earlier views. He defined the various terms used in discussing and explaining heat phenomena, using for the most part the definitions as corrected in his 1790 article in the Annales de chimie. He discussed the different methods of determining the heat capacity of various substances and the results of these determinations. His explanation of heat produced in various chemical changes involves the relative amounts of caloric contained in the compound vis-à-vis the components. He discussed Crawford's theory of state change as being caused by change in capacity and added in a note that "En admettant toutes ces hypotheses [Crawford's], on simplifieroit la théorie du calorique; mais probablement on s'éloigneroit beaucoup de la vérité."[98]

Another Frenchman who supported the new chemistry and who wrote a great deal concerning heat theory was Antoine François de Fourcroy (1755-1809). In 1782, Fourcroy was following Macquer and had argued for a vibrational theory of heat.[99] Although he advocated this theory at the same time

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[97] Ibid., p. 180.

[98] Ibid., p. 198, note.

[99] See pp. 92-95, Chapter III, above.

he indicated preference for the new pneumatic chemistry, he came to accept the material theory of heat as he became more strongly committed to Lavoisier's oxidation theory.

Fourcroy's discussion of heat in his Elémens d'historie naturelle et de chimie of 1789 shows the same organization as his earlier presentation. He began by stating that there are many substances which are now considered to be elements, and some of the traditional elements are no longer accepted as such. Formerly it was thought that fire was the simplest and most active element, but now, all the properties of this element seem to be pure conjecture.[100] Considering light, however, there are no doubts as to its existence and properties.[101] Heat, on the other hand, is much more difficult to examine. There is the question, Fourcroy said, whether heat should be considered as an element in itself or merely as one effect of fire. He stated the chief properties of heat as being the ability to penetrate all substances, its property to tend to equilibrium, its ability to expand all substances and to cause changes of state. Heat can be communicated in three ways: by contact with a hot substance, by movement (friction), and by the act of combination, for example, when quick-lime is mixed with water.[102]

Fourcroy said that the most exact and most delicate work done to date had shown nothing positive about the nature of heat. Bacon and Macquer thought heat to be a vibration, but other physicists and some

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[100] Antoine François de Fourcroy, Elémens d'historie naturelle et de chimie (3d ed.; 5 vols.; Paris, 1789), I, 101-106; cited hereafter as Elémens de chimie (1789).

[101] Ibid., pp. 107-112. [102] Ibid., pp. 115-117.

modern chemists think it to be a substance. This latter group believes that heat can exist in two states: that of combination and that of freedom. When combined, heat is not sensible; it is in a state of compression; but it may become free. The latter group also explains changes of state by heat substance becoming combined or being set free.[103]

He disagreed with Scheele's and Bergman's idea that heat is compounded from phlogiston and vital air.[104] He also disagreed with those who thought that heat and light have different effects and thus cannot be the same substance.[105] Fourcroy erroneously cited Lavoisier and Laplace as assuming that "la chaleur consiste dans l'existence d'un corps particulier, & dans les oscillations intestines des corps excitées par sa présence."[106]

Returning to the question of the relationship between light and heat, Fourcroy said that these two effects cannot be due to a single substance, for sometimes there is light without heat and sometimes heat without light. Solar rays produce heat "par la percussion des corps sur lesquels ils sont reçus, & par le frottement qu'ils éprouvent de la part de ceux qui s'opposent à leur passage."[107] Light produced by combustion

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[103] Ibid., pp. 118-120.

[104] For Scheele's views, see n. 82, above; for Bergman's acceptance of these ideas, see Torbern Olof Bergman, A Dissertation on Elective Attractions, trans. Translator of Spallanzani's Dissertations [T. Beddoes] (London, 1785), pp. 234-235. This was first published in 1777 and revised in 1783. Bergman opposed the theory of vibrations (ibid., pp. 229-230).

[105] Fourcroy, Elémens de chimie (1789), I, 212.

[106] Ibid., p. 122; for Lavoisier's and Laplace's statement, see quotation, p. 115, above.

[107] Ibid., p. 125.

can come either from the burning substance or from the air; in any case "rien ne démontre que c'est la chaleur qui se change en lumière."[108]

The best observational data and especially those concerning the differences in the heat contained in different substances, the ability of substances to absorb heat, and the elective attractions which heat appears to obey "rendent l'opinion de l'existence de la chaleur comme corps particulier, beaucoup plus forte que jamais."[109] The motion theory "n'existe plus parmi les savans qui cultivent la chimie."[110]

Heat substance is the lightest of all natural substances, and it exists in two different states:

> l'une qui est intimement combinée, & qu'on appelle chaleur latente ou calorique, parce qu'elle n'y est pas sensible; l'autre qui y est simplement disséminée. Celle-ci peut en être chassée par le seule pression ou par des moyens mécaniques; c'est ainsi que lorsqu'on frappe une barre de fer, & qu'on rapproche ses molécules par le choc, la chaleur s'en échappe, comme l'eau sort d'une éponge humide que l'on presse. La chaleur vraiment combinée ne sort des corps que par de nouvelles combinaisons chimiques.[111]

Fourcroy's use of "calorique" in the passage above is the first use of this word in some fifty pages of discussion of heat phenomena. In fact, in this edition he rarely used the word at all; and where it does appear, it is used to indicate heat in the combined state only. He defined caloric as heat in the state of combination "parce qu'en effet quand ce corps [heat matter] est fixé, il n'est plus chaleur, & il ne le devient que lorsqu'il est mis en liberté."[112] In other words, heat can change into caloric and caloric into heat.[113] Fourcroy's only change in the 1791 edition of his Elémens was, in a few passages, to substitute the

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[108] Ibid., p. 126. [109] Ibid., p. 127. [110] Ibid., p. 106.

[111] Ibid., pp. 127-218. [112] Ibid., p. 159. [113] Ibid.

word "calorique" for "chaleur."[114] In one passage in the 1791 edition, Fourcroy used caloric to indicate uncombined heat.[115] This suggests a tendency on Fourcroy's part toward a more general use of this term.

The most striking effect of heat is expansion of substances. Expansion "indique l'intromission d'une substance quelconque dans les petites cavités des corps raréfies; cette substance, qui est la chaleur elle-même, agit comme des coins ou des ressorts qui séparent & éloignent les molécules de ces corps."[116]

Fourcroy said almost nothing about change of state beyond attributing it to combination or release of heat matter.[117] He did state that caloric is combined in elastic fluids[118] and that there is no valid distinction which can be made between fluids which are permanently elastic and those which are not.[119] He described elastic fluids as "une manière d'être des corps, due à la chaleur combinée, ... un composé d'une base plus ou moins solide, & de la matière de la chaleur. ..."[120] Vital air is composed of a fixable base called oxygen which is "tenue en dissolution dans l'état de fluide élastique par le calorique & la lumière."[121]

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[114] Elémens d'histoire naturelle et de chimie (4th ed.; 5 vols.; Paris, 1791), cited hereafter as Elémens de chimie (1791). The pagination in this edition, with minor exceptions, follows that of the 1789 edition. For examples of the change in terminology see the following volumes and pages in both editions: I, 60; I, 128-129; V, 169 (p. 174 in 4th ed.); V, 170 (p. 174 in the 4th ed.).

[115] Elémens de chimie (1791), I, 128-129; cf. Elémens de chimie (1789), I, 128-129.

[116] Elémens de chimie (1789), I, 128-129.

[117] Ibid., pp. 120, 136. [118] Ibid., I, 59-60; V, 169.

[119] Ibid., I, 158. [120] Ibid., p. 157. [121] Ibid., II, 303.

Temperature change during chemical reaction is caused by heat being combined or released.[122] The amounts released depend upon the solidity or the specific heat of the new combination.[123] In chemical reactions, caloric plays the same role as any other constituent element. Since caloric follows the laws of attraction which are peculiar to it,

> il quitte un corps pour s'unir à un autre, ou bien les corps auxquels le calorique est uni, ayant pour d'autres corps une attraction plus forte que celle qu'ils ont pour le calorique, laissent échapper ce principe pour s'unir à ces corps.[124]

Fourcroy did not completely abandon motion as being involved somehow in the heat phenomena. For example, he stated that when a substance is expanded by heat, its molecules undergo "un mouvement intentin. ..."[125] He criticized parts of Lavoisier's theory on the grounds that it does not explain entirely the "movement rapide excité dans l'inflammation, & de tous les changemens qui l'accompagnent."[126] He described the laws of heat communication as being "analogues à celles du mouvement. ..."[127] He stated that heat can excite vibrations and oscillations in molecules of solids, and agitation in molecules of fluids.[128]

Fourcroy had no doubts about the validity of Lavoisier's theory of oxidation. Stahl's ideas are unacceptable, to be sure; but Fourcroy felt that many modern chemists had been overly extravagant in their claims to have destroyed completely all vestiges of the old theory and especially the idea of phlogiston upon which it is based. He said that

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[122] Ibid., I, 66.

[123] Ibid., p. 160; V, 170.

[124] Ibid., V, 136.

[125] Ibid., I, 129.

[126] Ibid., p. 143; cf. V, 171.

[127] Ibid., I, 117.

[128] Ibid., p. 153.

the single phenomenon which is common in all processes of combustion is the release of fire, that is, heat and light.[129] To the followers of Stahl, this heat and light is caused by the release of phlogiston, the matter of fire itself, fixed in the combustible substance. Modern chemistry, on the other hand, has found another phenomenon common to every process of combustion: the fixation of vital or pure air. According to the new school of thought, combustion is synonymous with the process of fixation of pure air; and hence the appearance of heat and light, the characteristic phenomenon of combustion, must be explained by a recourse to the properties of pure air, rather than to some property of combustibles.

Because of this, Fourcroy thought that the foundations of the new theory are based entirely upon the roles of two kinds of substances, caloric and elastic fluids: "... on conçoit que la base de la théorie chimique porte sur les propriétés, l'action de la chaleur, la formation & la fixation des fluides élastiques."[130] The new chemistry thus rests ultimately upon the nature and role of caloric, because caloric is essential to the formation of elastic fluids. Since much caloric is used in the formation of these fluids, and especially vital air, vital air must be the source of the heat and light released during combustion, that is, during the fixation of this air.

Phlogiston is only a term indicating fire matter fixed in combustibles. The term "caloric" also signifies fire matter; but caloric is fire matter fixed in vital air and other elastic fluids, rather than

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[129] Ibid., V, 140-141. [130] Ibid., pp. 134-135.

in combustible substances. Fourcroy said that because both phlogiston and caloric are only different names for the same substance, some modern chemists had acted too rashly in denying the existence of phlogiston.

> Il ne faut cependant entendre ceci [denial of the existence of phlogiston] qu'avec quelques restrictions; malgré les recherches immenses faites depuis quelques années sur les corps combustibles & sur la combustion, on n'a point encore pu renoncer à la matière du feu fixée dans les corps, & on a changé son nom de phlogistique en celui de calorique ou de chaleur combinée; mais ce n'est point à cette matière que l'on attribue la propriété combustible. Sa présence dans les corps inflammables, n'est pas ce qui détermine leur inflammabilité.[131]

The new theory has thus taken phlogiston and changed its name to caloric; but fire matter is no longer the factor which determines the inflammability of substances. It is their ability to unite with the base of vital air; and this air is composed of a base called osygen, held in solution by caloric and light. Fourcroy said that this caloric, which Lavoisier admits as a component of vital air, "joue à-peu-près le même rôle que le phlogistique de Stahl, ou la lumière fixée de Macquer. ..."[132]

During the process of combustion, vital air is decomposed and heat and light are released. Thus what Stahl attributed to the combustible substance, modern doctrine "transporte à l'air vital. ..."[133] Following the arguments of Stahl,

> l'air vital est le véritable & le seul corps combustible. Cette théorie semble ne pas détruire la présence du phlogistique dont la lumière [and caloric] joue ici le rôle, mais elle differe de celle de Stahl par le lieu du phlogistique ou du feu fixé, que nous admettons dans le corps qui sert à la combustion tandis que Stahl l'admettoit dans le corps combustible.[134]

Fourcroy freely admitted the dependence of the new theory upon the old and those elements of the old which were modified and taken over

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[131] Ibid., I, 141.

[132] Ibid., p. 146.

[133] Ibid., p. 196.

[134] Ibid., II, 304.

into the new doctrine. He also admitted that no only had nothing been demonstrated positively concerning the nature of heat,[135] but also that the same objections which contemporary chemists made concerning phlogiston apply to oxygen as well. Both of these substances are unknown in the pure form and both pass from one combination to another without separating into their state of purity.[136]

In his Philosophie chimique of 1792, Fourcroy abandoned the restrictive definition of caloric which he employed in his earlier works and applied the term to indicate the matter of heat both free and combined.[137] Heat, he said, is an effect produced by a substance called caloric. Caloric penetrates substances, separating their molecules, and it may combine with these molecules.[138] In this and in his subsequent publications, Fourcroy abandoned his earlier distinction between heat matter in the free state and caloric, heat matter in the state of combustion, and used caloric to designate both states of heat.

Fourcroy's ideas expressed in his Philosophie chimique differ from his earlier views in that they are more definitely in keeping with Lavoisier's explanations of heat phenomena. He repeated Lavoisier's explanation of the change from a solid to a liquid as being different from the change from a liquid to a gas. For example, Fourcroy said that "les liquides sont des combinaisons de solides avec le calorique, & les gaz

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[135] Ibid., I, 118. [136] Ibid., II, 304.

[137] Antoine François de Fourcroy, Philosophie chimique, ou vérités fondamantales de la chimie moderne, disposées dans un nouvel ordre (Paris, 1792), cited hereafter as Philosophie chimique (1792).

[138] Ibid., p. 9.

sont des dissolutions de différens corps dans le calorique. ..."[139] The process of combustion is the release of heat and light due to the union of the base of vital air with the combustible substance. Vital air should be regarded as a base "fondue dans les deux dissolvans, le calorique & la lumière ...," and combustion is a "précipitation plus ou moins complette de l'oxigène [the base] de ses deux dissolvans."[140] Caloric then is what gives vital air the form of an elastic fluid, and vital air is the origin of the heat produced during combustion.[141]

In his Elémens of 1789, Fourcroy had stated that heat and light are different substances.[142] He expressed the same idea in his Philosophie chimique in 1792 when he said that "il n'est pas démontré qu'il [caloric] soit le même que lumière; plus on avance & plus on trouve de différences dans l'action de ces deux corps."[143] An edition of Fourcroy's Philosophie chimique appeared in 1795 containing notes by Jean Baptiste van Mons (1765-1842), a Belgian and an early adherent to Lavoisier's views who was a professor in Brussels and later an editor of the Annales de chimie.[144] Except for van Mons's notes, the edition is unchanged from that of 1792. Van Mons attacked Fourcroy's views on the relationship between heat and light. To a passage in which Fourcroy

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[140] Ibid., p. 19. [141] Ibid., p. 17.

[142] Elémens de chimie (1789), I, 121-133; see p. 165, above.

[143] Philosophie chimique (1792), p. 13.

[144] Antoine François de Fourcroy, Philosophie chimique, ou vérités fondamantales de la chimie moderne, disposées dans un nouvel ordre (Nouvelle édition, augmentée de notes et d'axiomes tirés des dernières découvertes par J. B. van Mons; Bruxelles, An III [1795]), cited hereafter as Philosophie chimique (Nouvelle ed.; 1795).

that heat and light are different, van Mons added in a note,

> Mais une plus grande analogie dans les effets rend, à mon avis, probable que la lumière n'est qu'une modification du calorique, ou le calorique une modification de la lumière, et que ces deux matières sont de nature indentique.[145]

In another note, van Mons spoke of "la maitère du feu à l'état de lumière ... [and] cette même matière à l'état de calorique. ..."[146]

In his Systême des connaissances chimiques of 1801, Fourcroy reversed his field and said that heat and light are two effects or modifications of the same substance.[147] Some physicists, he said, have established a relationship between light and caloric and conclude that these are merely effects due to modifications of a single substance. This theory

> est fondée sur un grand nombre d'expériences; elle explique naturellement et simplement la plupart des phénomènes; elle est d'accord avec la sublime économie de la nature, qui multiplie les effets beaucoup plus que les corps qui les produisent.[148]

The single substance of which caloric and light are modifications is "le feu lui-même."[149] In its appearance as caloric, fire matter is

> plus divisé, plus éparpillé, doué d'un mouvement plus lent, il frappe moins les corps, il les meut moins vivement, il faut qu'il s'y accumule peu à peu pour y produire des effets sensibles. ...[150]

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[145] Philosophie chimique (Nouvelle ed.; 1795), p. 15, note.

[146] Ibid., p. 21, note.

[147] Antoine François de Fourcroy, Systême des connaissances chimiques et de leurs applications aux phénomènes de la nature et de l'art (10 vols.; Paris, An IX [1801]). Partington and McKie erroneously indicate that Fourcroy did not equate heat and light until 1803; James R. Partington and Douglas McKie, "Historical Studies on the Phlogiston Theory: IV. Last Phases of the Theory," Annals of Science, IV (1939), 140-414.

[148] Systême, I, 131. [149] Ibid., p. 132. [150] Ibid.

When fire matter appears as light, it is

> plus dense, plus actif, plus rapidement agité; il frappe les corps avec énergie, il y produit un effet quelconque au premier choc.[151]

Thus fire matter can appear as caloric when it moves "doucement ou lentement" or as light when it moves "brusquement," or fire can appear in both forms at the same time, depending upon the quantity of movement which is imparted to it.[152]

Where he had formerly cited the differing chemical and physical effects of heat and light as indicating the existence of two different matters, Fourcroy stated that these effects offer no objection to the idea that heat and light are modifications of a single substance. In addition, there are several phenomena which the old idea could not handle but which can be explained with the new theory. Specifically he cited radiant heat, a phenomenon "inapprécié jusqu'ici," as being readily handled by the new theory. In the form of radiant heat, caloric has "un mouvement plus violent et plus rapide que celui qui le constitue chaleur ordinaire ... ," and thus it assumes some of the properties of light.[153]

Although Fourcroy's explanations are somewhat more positive and concise in the Systême than in his earlier works, the ideas expressed are fundamentally the same. The constancy of temperature during change of state is due to caloric being "réellement" fixed in the substance.[154] Although liquids are a true combination of caloric with a solid, gases are "dissolutions dans le calorique."[155] Caloric molecules obey the laws of attraction, and the combination of caloric with molecules of other

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[151] Ibid. [152] Ibid. [153] Ibid., pp. 132-134.

[154] Ibid., p. 123. [155] Ibid., pp. 134-135.

substances causes a great "ressort" in the molecules.[156] It is this elasticity which separates the molecules of a substance and, when increased by friction of percussion, causes heat.[157] Because these phenomena can be explained by means of the elasticity of caloric particles, there is no need, to assume a repulsive force among these particles.[158]

> Tout ce qui précède prouve que le calorique n'est point une simple modification des corps, que la chaleur ne consiste pas, comme l'avaient pensè quelques philosophes, dans le mouvement plus ou moins rapide des molécules des corps, qu'il existe comme corps particulier, non pondérable, très-élastique, très-compressible, très-dilatable, obéissant à l'attraction de composition, entrant sans cesse dans des combinaisons, ou se séparant dans d'autres; saturant les corps à sa manière; changeant leur état et leurs propriétés, ne se mettant en équilibre, comme on l'a dit, que dans des corps qui en sont déja saturés, changeant sans cesse de dimension et de volume, ayant lui-même un mouvement ou une vîtesse très-variables, suivant toutes les impressions qu'il reçoit, toutes les attractions dont il est sans cesse agité; répandu dans l'espace avec une immense libéralité par la nature, et jouant un grand rôle dans tous les phénomènes.[159]

Fourcroy's Systême of 1801 marks the final development of ideas on caloric and heat phenomena. He revised the 1806 edition of his Philosophie chimique to conform with the ideas expressed in his Systême.[160] His writings show a progression of ideas toward an almost total acceptance of Lavoisier's explanations of heat phenomena. His acceptance of a material theory of heat paralleled his acceptance of the oxidation theory, although the former came after the latter. He thought that the most telling argument against the motion theory of heat is the quantities of heat required to raise temperatures and to change the states of substances.

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[156] Ibid., p. 126.

[157] Ibid., pp. 126, 130, 133.

[158] Ibid., p. 130.

[159] Ibid., pp. 129-130.

[160] Antoine François de Fourcroy, Philosophie chimique, ou vérités fondamentales de la chimie moderne, destinées à servir d'élémens pour l'étude de cette science (3d ed.; Paris, 1806).

These quantities are constant for any particular substance but different for different substances. Fourcroy felt that these phenomena show that caloric, like any other chemical constituent of a substance, obeys the laws of attraction and elective affinity. As he expressed it,

> Observons en passant que cette attraction, veriée pour chaque corps, est une preuve directe de l'existence du calorique, et une réfutation de l'hypothèse dans laquelle on ne le considère que comme une modification des corps.[161]

Of Lavoisier's followers, Séguin and Fourcroy were two of the most prolific in their discussion of heat theory. Others were much less detailed. Jean Antoine Claude Chaptal de Chanteloup (1756-1832), a wealthy industrialist as well as a physician, chemist, and civil servant, was primarily interested in applied chemistry. However, his chemistry text of 1791 contains a short discussion of heat theory.[162]

Chaptal shows little variation from Lavoisier's views. Heat fluid, he said, acts like any other constituent principle of substances.[163] He explained heat of friction or compression as caused by caloric being squeezed from substances like water from a sponge.[164] Caloric can be free or combined, and what is called latent heat is caloric which has contracted a true chemical union with some substances and has become insensible.[165] This chemical union takes place when substances change

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[161] Ibid., pp. 95-96.

[162] Jean Antoine Claude Chaptal de Chanteloup, Elements of Chemistry, [trans. W. Nicholson] (3 vols.; London, 1791). This is a translation of the first French edition (1790). In the third edition of Nicholson's translation (3 vols.; London, 1800), the section on heat is unchanged.

[163] Elements of Chemistry (1791), I, 28.

[164] Ibid., pp. 66-67. [165] Ibid., pp. 66, 77.

from a solid to a liquid and from a solid or liquid to the aeriform state.[166]

Chaptal apparently did not agree with Lavoisier's idea that aeriform fluids are no different from vapors. He cited vapors as an example of heat existing in the state of simple mixture. ". . . [It] would be an abuse of words to call so weak an union by the name of combination: for, as soon as the heat becomes in a situation to combine with other bodies, it abandons the water, which returns to a liquid state."[167]

Chaptal repeated this discussion unchanged in the second edition (An III) of his text.[168] However, in the third edition (An IV), his doubts about combination of caloric in the formation of vapors was extended to apply to all changes of state.[169] In the first and second editions he had said that heat is absorbed and becomes combined in changes of state. In the third edition, however, he said only the caloric is absorbed during these changes.[170]

Mathurin Jacques Brisson (1723-1806), professor of physics at the Collège de Navarre, the Ecole Centrale, and the Lycée Bonaparte, had advocated the fire-in-motion theory in 1781.[171] In his physics text of

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[166] Ibid., pp. 77-80. [167] Ibid., p. 77.

[168] Jean Antoine Claude Chaptal de Chanteloup, Elémens de chymie (2d ed.; 3 vols.; Paris, An III [1794/1795]).

[169] Jean Antoine Claude Chaptal de Chanteloup, Elémens de chymie (3d ed., reviewed and enlarged; 3 vols.; Paris, An IV-An V (1795-1796)).

[170] Ibid., I, 69, 70.

[171] Mathurin Jacques Brisson, "Feu," Dictionnaire raissoné de physique (3 vols.; Paris, 1781), I, 603-605.

1799, however, he expounded the caloric theory [172] Brisson accepted Lavoisier's idea explaining the states of matter in terms of the ratio between the mutual attraction of the molecules of a substance and the repulsion due to heat, this ratio modified by the effects of atmospheric pressure.[173] Caloric can be either free or combined.[174] It is combined in the permanently elastic fluids; but caloric remains free in the non-permanently elastic fluids because they are condensable by cold, and permanent fluids are not.[175] He explained evaporation by the tendency of caloric particles to equilibrium. As the caloric particles leave a liquid, they combine with some less adherent particles of the liquid and carry them away.[176] The reason the temperature of liquids remains constant as they boil is that caloric, combined with the particles of vapor, leaves the liquid at the same rate it enters.[177] Caloric and light, he said, are the same substance differently modified.[178]

Edme Jean Baptiste Bouillon-Lagrange (1764-1844), Fourcroy's assistant and later professor at the Ecole de Pharmacie, gave a superficial account of the caloric theory in his chemistry text of 1800.[179]

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[172] Mathurin Jacques Brisson, Traité élémentaire, ou principes de physique fondés sur les connoissances les plus certaines, tant anciennes que modernes, et confirmés par l'expérience (3d ed., reviewed, corrected, and enlarged; 3 vols.; Paris, An VIII [1799/1800]).

[173] Ibid., II, 2-4. [174] Ibid., p. 5 [175] Ibid., pp. 6-7.

[176] Ibid., p. 173. [177] Ibid., pp. 220-221. [178] Ibid., p. 194.

[179] Edme Jean Baptiste Bouillon-Lagrange, A Manual of a Course of Chemistry, or a Series of Experiments and Illustrations Necessary to Form a Complete Course of That Science (2 vols.; London, 1800). Cf. Edme Jean Baptiste Bouillon-Lagrange, Manuel d'un cours de chimie, ou principes élémentaires, théoriques, et pratiques de cette science (2d ed., enlarged; 3 vols.; Paris, An IX (1801)).

Bouillon-Lagrange was primarily interested in chemical techniques and gave little space to discussing theory. He treated heat primarily as an agent in chemical processes. Caloric can be combined as a constituent, or it can be merely interposed.[180] It is united to all aeriform fluids, and the release of caloric during combustion occurs when the base of oxygen gas combines with the combustible.[181]

Charles Louis Cadet de Gassicourt (1769-1821), a barrister and son of the chemist Louis Claude Cadet de Gassicourt (1731-1799), gave a variant explanation of state change in his chemical dictionary, published in 1803.[182] In combining with substances, caloric "exerce sur leurs molécules une force repulsive qui les écarte. . . ."[183] When a solid absorbs all the caloric it can contain, it changes into a liquid.[184] At this point, expansion is such that the molecules of the substance "roulent les unes sur les autres. . . ."[185] When changed to a liquid, the heat capacity of the substance changes. When the heat capacity of the liquid is satisfied, the substance changes into an elastic fluid.[186] The constant temperature which exists during change of state is like saturating an acid with an alkali.[187] Cadet thought that heat waves observed in air above a heated substance demonstrate that heat is a substance.[188]

The chronological development of the ideas of Lavoisier's followers exhibit in general the same characteristics. The writings of

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[180] Course of Chemistry, I, 21. [181] Ibid., pp. 40-43.

[182] Charles Louis Cadet de Gassicourt, Dictionnaire de chimie, contenant la théorie et la pratique de cette science, son application à l'histoire naturelle et aux arts (4 vols.; Paris, An XI (1808)).

[183] Ibid., I, lxxxix. [184] Ibid., II, 28. [185] Ibid., I, lxxxix.

[186] Ibid., II, 28. [187] Ibid., p. 29. [188] Ibid., p. 31.

Séguin and Fourcroy show a progression toward an almost total acceptance of Lavoisier's explanation of heat phenomena. A curious aspect of this alteration in ideas is in explanations of change of state. In almost every case, there is a switch from a chemical explanation involving the chemical combination of caloric to a more physical explanation involving forces and pore-space.

The same sort of variation is seen in the writings of Lavoisier himself. His initial explanations involved the idea of combination. Beginning in 1782, however, he began to explain these phenomena in terms of a balance of forces, an explanation which received more and more emphasis in his subsequent writings. This is particularly noticeable in his explanation of the formation of gases, a process which, in his later writings, he repeatedly implied is different from the change of a solid into a liquid.

The progression of ideas is well illustrated in the writings of Séguin. He described phenomena, explicable in terms of the idea of latent heat, as caused by caloric becoming truly combined and thereby losing all its distinctive properties. Later, however, he credited these same heat phenomena to the idea that the mutual affinity among molecules no longer offers an obstacle to the introduction of caloric. This idea is almost identical to that of Herman Boerhaave.[189] Fourcroy's ideas show a similar change. From describing all changes of state as due to the chemical combination of caloric, he later described fusion as caused by combination of caloric and vaporization as due to solution in caloric.

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[189] See quotation, p. 23, above.

A comparison of the first three editions of Chaptal's text, shows that his explanations in terms of combination become less frequent in subsequent editions and are completely absent in the third. He denied the combination of caloric in vapors, which, he said, are different from permanently elastic airs. The distinction between vapors and airs was also maintained by Brisson. This was a complete departure from Lavoisier's views. He had claimed that the permanently elastic fluids are no different from vapors and that a considerable quantity of caloric is combined in the formation of both. This idea was fundamental to his explanation of the heat of combustion. If this heat derives from oxygen gas, then the question arises as to the reason for the presence of caloric in oxygen gas in the first place; and the seemingly obvious analogy was drawn to the absorpiton of heat in the formation of vapors. Once the oxidation theory was established, however, some of Lavoisier's followers abandoned this line of reasoning. Caloric is combined in permanently elastic fluids, but not in vapors.

In contrast to these evolving views on changes of states, explanations of the chemical production of heat remained virtually unchanged. Chemical heat was explained in terms of combined caloric, as it was originally explained by Lavoisier; and apparently none of his followers saw fit to change this idea.

CHAPTER VI

OPPOSITION TO THE CALORIC THEORY: PHLOGISTON IS NEITHER FIRE NOR CALORIC

Belief in the caloric theory of heat included an acceptance of Lavoisier's idea that the heat of combustion derives from oxygen gas, the base of which unites with the combustible substance. A belief in phlogiston would seem to indicate an automatic rejection of the caloric theory; but this is not necessarily the case. As long as phlogiston itself was not considered to be the same as fire matter, that is, the same as the material cause of heat, it was possible for a phlogistonist to accept a great deal of the caloric theory while still maintaining that the release of phlogiston is essential to the process of combustion.

An example is Joseph Priestley. In the early editions of his Experiments and Observations on Air he had indicated belief in a vibratory theory of heat.[1] Although these editions contain his only detailed discussion of the nature of heat, one can infer his ideas on the subject from some of his subsequent writings. By at least 1783, Priestley had changed his statements on the nature of heat and used explanations based on the idea that heat is a material substance.

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[1] See pp. 81-83, Chapter III, above.

In discussing some experiments on the transformation of water into a permanently elastid fluid by heating it to a red heat, Priestley said ". . . I imagined by this means the matter or principle of heat was so intimately combined with it [water], as not to be separated from it by cooling, as in the case of steam."[2] He admitted that it might be difficult for many persons to accept this explanation; however,

> admitting that this conversion is effected by the intimate union of what is called the principle of heat with the water, it appears to me to be sufficiently analogous to other changes, or rather combinations of substances.
>
> It is true, that steam is a thing very different from air, . . . but then, though it has acquired sensible heat, it has got no latent heat so intimately combined with it as it is with air. . . .[3]

Priestley gave as a possible explanation a suggestion of James Watt's that the transformation is caused by phlogiston being transmitted from the water to the external air, and "the water, thus dephlogisticated, was capable of being converted into respirable air by the intimate union of the principle of heat."[4]

In the 1790 edition of his Observations on Air, Priestley discounted this particular explanation of the transformation, but he restated the idea that heat substance is a constituent of all kinds of air.[5]

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[2]Joseph Priestley, "Experiments Relating to Phlogiston and the Seeming Conversion of Water into Air," Philosophical Transactions of the Royal Society of London, LXXIII (1783), 418.

[3]Ibid., pp. 428-429.

[4]Ibid., p. 431; cf. Joseph Priestley, "Expériences relatives au phlogistique et à la conversion apparente de l'eau en air," trans. Gibelin, Observations sur la physique, XXVII (1785), 414.

[5]Joseph Priestley, Experiments and Observations on Different Kinds of Air, and Other Branches of Natural Philosophy Connected with the Subject (3 vols.; Birmingham, 1790), II, 407-435.

He had suggested earlier that inflammable air might contain some heat in it;[6] and in this 1790 edition he extended this idea to all airs. In some instances, he said, the electric spark and red heat produce the same effects, that is, both can vaporize the water and phlogiston contained in some substances. However, the effect of the electric spark is due to the heat which the spark produces. In the action of both red heat and an electric spark,

> . . . something communicated by heat, seems to enter as a constituent principle into every species of air . . . The element of heat, therefore, called by Dr. Black latent heat, extremely obscure as the subject is seems to enter into the composition of all kinds of air.[7]

In his last stand against the new chemistry, Priestley was most explicit in stating the material theory of heat, this despite an attack on the idea which he included at the end of this essay:[8]

> It is not denied that light and heat, both of which are allowed to be substances, tho the weight of them cannot be ascertained, pass thro' glass. They both have certain properties, and are transferable from one substance to another, according to their known affinities. And why may not this be the case with phlogiston also.[9]

Priestley's almost casual references to the nature of heat not only show that he utilized the idea that heat is a material substance, but they also indicate that he accepted more of Lavoisier's views than he perhaps realized. Priestley credited Joseph Black with the idea that

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[6]Joseph Priestley, "Experiments and Observations Relating to Air and Water," Philosophical Transactions of the Royal Society of London, LXXV (1785), 280.

[7]Priestley, Experiments on Air (1790), III, 539-540.

[8]Joseph Priestley, The Doctrine of Phlogiston Established and That of the Composition of Water Refuted (Northumberland, 1800); see p. 83-84, Chapter III, above.

[9]Ibid., p. 35.

heat matter forms a constituent part of all elastic fluids, but the assumption that there is no basic difference between vapors and permanently elastic fluids is an idea created by Lavoisier and is fundamental in his oxidation theory. Priestley's suggestion that the production of air by the passage of steam over hot iron is due to a mutual exchange of phlogiston and heat matter indicates that he still adhered to his earlier view that phlogiston is not fire matter, and that heat matter and phlogiston are entirely different substances.[10]

Similar to Priestley in his discussions of heat was the Irish chemist Richard Kirwan (1733-1812). Kirwan did not address himself directly to the question of the nature of heat; but his ideas concerning heat are apparent in his writings on other subjects. In his discussion of the production of water by the inflammation of dephlogisticated and inflammable airs, Kirwan revealed his belief in the existence of a material heat substance and that this substance is a constituent of "rarefied" objects. When these rarefied objects unite, heat is released, the amount depending upon the intimacy of the new combination and the density of the compound.[11]

Kirwan was convinced that water is truly formed by the inflammation of dephlogisticated air and phlogiston, which he equated to inflammable air. In this process, both substances give off their "specific fire" which is the great obstacle to their becoming united. When

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[10]See pp. 81, above.

[11]Richard Kirwan, "Remarks on Mr. Cavendish's Experiments on Air," Philosophical Transactions of the Royal Society of London, LXXIV (1784), 154-169.

this fire is given off, it is

> converted into sensible heat (a circumstance which, in my opinion, constitutes the very essence of flame); the resulting compound having then lost the greatest part of its specific fire, is necessarily reduced, according to Dr. BLACK'S theory, into a denser state, which the present experiment shews to be water; whereas, in common cases of combustion, the phlogiston being denser and less divided, unites less intimately with the dephlogisticated part of common air, consequently expels less of its specific fire, and therefore forms less dense compounds, viz. fixed and phlogisticated air. . . .[12]

Kirwan added that Henry Cavendish did not agree that inflammable air is pure phlogiston on the grounds that inflammable air does not immediately unite with dephlogisticated air when the two airs are mixed. Kirwan said that the reason that the two airs do not unite is "on account of the specific fire which they contain, and must lose, before such union can take place. . . ."[13]

Kirwan indicated his acceptance of Lavoisier's explanation of absorption or release of heat during chemical reaction as being due to the relative densities of substances before and after a chemical reaction.[14] He described combustion as "the expulsion of heat and light from the pure air . . ." which unites with the combustible.[15]

One of the more influential works of the last quarter of the eighteenth century was one written by Adair Crawford (1748-1795), London

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[12] Ibid., p. 167.

[13] Ibid., p. 168; cf. Richard Kirwan, "Remarques sur les expériences de m. Cavendish sur l'air, adressées à m. Banck," trans. Angulo, Observations sur la physique, XXVI (1785), 423-424.

[14] Richard Kirwan, An Essay on Phlogiston and the Constitution of Acids (London, 1787), pp. 21-22; for Lavoisier's views, see pp. 122-123, Chapter V, above.

[15] Ibid., p. 30.

physician and later professor of chemistry at the Royal Military Academy, Woolwich. Although Crawford's views never attained wholesale acceptance, his ideas were widely discussed and many facets of his theory were influential in the thinking of phlogistonists and antiphlogistonists alike.[16]

Crawford opened his book on animal heat in good Boerhaaveian fashion; he completely ignored the question of the nature of heat and began by discussing the means which are available to determine whether heat is present or not. Heat is known by its effects; and one of the most striking effects is that different substances acquire different temperatures when the same amount of heat is applied to them. "It has been found by experiment that in bodies of different kinds, the quantities of absolute heat may be unequal, though the temperatures and weights be the same."[17] This effect is measured by the temperature change that two substances undergo when the same quantities of heat are added to them. The cause of this difference is that "some [substances] have the power of collecting and retaining that element [heat] in greater quantity than others." He named these powers the "capacities of bodies for containing heat. . . ."[18]

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[16]Adair Crawford, Experiments and Observations on Animal Heat and the Inflammation of Combustible Bodies, Being an Attempt to Resolve These Phenomena into a General Law of Nature (2d ed., enlarged; London, 1788). The first edition was published in 1779. For a discussion of Crawford's explanation of animal heat see Everett Mendelsohn, Heat and Life: The Development of the Theory of Animal Heat (Cambridge, Mass., 1964), pp. 123-33, 154-59, and G. J. Goodfield, The Growth of Scientific Physiology: Physiological Method and the Mechanist-Vitalist Controversy, Illustrated by the Problems of Respiration and Animal Heat (London, 1960), pp. 45-55. For a short discussion of Crawford's general theory see James R. Partington and Douglas McKie, "Historical Studies on the Phlogiston Theory: III. Light and Heat in Combustion," Annals of Science, III (1938), 346-350.

[17]Animal Heat, p. 3. [18]Ibid., p. 7.

If a given quantity of heat is applied to two objects, the greater temperature increase indicates a lesser heat capacity, whereas a lesser temperature increase indicates a greater heat capacity. Crawford concluded that the temperature of a substance depends upon two things, the quantity of heat present and the capacity of the substance to contain heat; and change in either the quantity of heat or heat capacity of the substance may change the temperature.[19]

> If, for example, a body of a given weight be supposed to have a capacity as one, a quantity of absolute heat as 10, and a temperature which computed from the point of total privation [of heat] is also as 10; and if the capacity of the body be conceived to be suddenly doubled, the same quantity of absolute heat which formerly raised it to the temperature of 10, will now be sufficient to raise it only to the temperature of five.[20]

Crawford believed, as had so many before him, that substances at ordinary temperatures contain a considerable quantity of heat in them. He also believed that this quantity is limited, that in theory at least there exists a temperature at which all heat is removed. It is clear

> that heat is contained in considerable quantities in all bodies, when at the common temperature of the atmosphere. It is plain, however, that the quantity of heat inherent in each individual body is limited. This I think must be admitted, whatever be the hypothesis which we adopt concerning the nature of heat, whether we conceive it to be a force or power belonging to bodies, or an elementary principle contained in them.[21]

Most of Crawford's ideas on heat capacity came from William Irvine (1743-1787) who taught chemistry at the University of Glascow.[22]

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[19] Ibid., p. 9. [20] Ibid., p. 10. [21] Ibid., p. 15.

[22] James R. Partington, A History of Chemistry (3 vols.; London, 1961-1964), III, 154-55, 156-57; cf. Andrew Kent, "William Irvine, M.D.," pp. 140-150 in An Eighteenth Century Lectureship in Chemistry: Essays and Bicentenary Addresses Relating to the Chemistry Department (1747) of Glasgow University (1451), ed. Andrew Kent (Glasgow, 1950).

Following Irvine, Crawford assumed that the capacity of a substance to contain heat represents a certain quantity of heat contained in the substance.[23] This assumption is supported by the decrease in heat capacity accompanied by a loss of heat when water, for example, freezes, and a corresponding increase in heat capacity and absorption of heat when ice melts. Heat capacity is permanent when the same quantity of heat raises the temperature of an object the same number of degrees at all temperatures;[24] and the heat capacities of all substances are constant between the freezing and boiling points of water. Crawford extrapolated these data and deduced that this constancy of heat capacity also holds true for the entire scale of heat as long as no change of state occurs.[25]

These then are the basic elements of Crawford's theory: there exists in substances at ordinary temperatures a substantial but limited quantity of heat. The heat capacity of substances is determined by the temperature change accompanying the addition or subtraction of a given quantity of heat, and this capacity represents a certain quantity of heat contained in the substance. The heat capacities of substances are constant at all temperatures as long as no change of state occurs.

It is well known, Crawford said, that heat is absorbed or given off during changes of state without a change in temperature.[26]

> From the experiments of Dr. Irvine, there is the utmost reason to believe, that if by a change of temperature the forms of bodies be altered, their capacities for heat are increased or diminished, in consequence of which they must necessarily absorb or evolve heat.[27]

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[23] Animal Heat, p. 10.

[24] Ibid., p. 53.

[25] Ibid., p. 65.

[26] Ibid., pp. 71-72.

[27] Ibid., pp. 84-85.

Crawford recognized that Deluc, Lavoisier, and Laplace think that fire may be chemically combined with substances; but he said that he knew of no experiments which demonstrate that this combination takes place, Lavoisier's and Laplace's experiments notwithstanding.[28] In order to show that heat does combine with substances, it would be necessary to show either that heat is produced without a change in heat capacity, or that the change in capacity is not proportional to the amount of heat produced. Crawford said that Lavoisier and Laplace had offered evidence to show that the change in capacity is not proportional to the amount of heat evolved; but even they admitted that their results could be due to experimental error.[29] Crawford claimed that it has been shown that the heat involved in change of state is "partly" due to change in capacity; "It is, therefore, more agreeable to the simplicity of nature to conclude that the phaenomena arise solely from that cause."[30]

Crawford thus admitted that he had no proof of this theory of capacity change, but, he said, neither did the advocates of the idea of combination. As both sides agreed that capacity change could account for some of the heat transferred, Crawford felt that it was better to accept his explanation as the sole cause rather than to assume some other cause

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[28] Crawford was referring to the Lavoisier and Laplace memoir of 1783; Antoine Laurent Lavoisier and Pierre Simon, marquis de Laplace, "Mémoire sur la chaleur," Mémoires de l'Académie Royale des Sciences, 1780 (1784), pp. 355-408. Although this paper contains no experiments designed to prove the combination of heat matter, the authors did state in one passage at least that heat is combined (p. 399).

[29] Animal Heat, pp. 372-374; see pp. 117-118, Chapter IV, above.

[30] Ibid., p. 377.

which was completely without foundation. He admitted that there may be some attraction between fire and other substances. However, this attraction cannot result in a true chemical union. Here in his final jab at the proponents of the idea of combination, Crawford exhibits a hallmark of the new chemical attitude:

> For, in chemical combination, the elements acquire new properties, and either wholly, or in part, lose those by which they were formerly characterized. . . . [And] we have no sufficient evidence for believing that fire, in consequence of its union with bodies, does, in any instance, lose its distinguishing properties.[31]

Crawford's belief that heat capacities represent a certain quantity of heat contained in substances and that capacities are constant at all temperatures as long as no change of state takes place gave him the possibility of computing the temperature of the total privation of heat.

As an example of the technique of computing absolute zero, Crawford discussed the formation of water by igniting pure and inflammable air.

> It is now generally believed that aqueous vapour is composed of pure and inflammable air, which in the process of combustion intimately unite with each other, and at the same time give off a large quantity of elementary fire.[32]

Knowing the heat capacity of the gas mixture before combustion and determining the heat evolved, by means of water-bath calorimeter, he computed the number of degrees which the heat given off would have raised the

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[31] Ibid., p. 437. Partington and McKie erroneously claim that Crawford's denial of the forces of elective attraction to explain heat transfer was due solely to his feeling that there is no proof that heat is a substance; Annals of science, III (1938), 349. This quotation seems to indicate Crawford had other reasons.

[32] Ibid., p. 253.

temperature of the gas mixture.

> It was shown, that the airs previously to their combustion contained a quantity of heat sufficient to raise them 1333 degrees. If we suppose, that when they were fired by the electric spark they gave off the whole of the heat which they contained; it will follow that the point of total privation, or the degree of cold to which they must be reduced in order to deprive them wholly of their heat, is 1333 degrees below the common temperature of the atmosphere [50°F].[33]

However, part of the heat is absorbed by the water formed, and thus the 1333 degrees represents the difference between the absolute heat of the gas mixture and that heat contained in an equal weight of water.

Crawford thought that capacity represents a certain quantity of heat contained in the substance and he knew that a change in capacity was accompanied by the release of a certain quantity of heat. He concluded that the change in heat capacities is proportional to the quantity of heat given off during combustion. The capacity of the gas mixture was 7.11, and the capacity of water is 1.0; thus the change of capacity during ignition is 6.11. Since this change corresponds to 1333 degrees of heat, dividing 1333 by 6.11 gives 218 degrees for each unit of capacity. This 218 degrees is also the quantity of heat absorbed by the water. Therefore the total quantity of heat evolved by the combustion equals 1333 plus 218, or 1551 degrees. Thus 1551 is the total quantity of heat contained in the gas mixture measured from "the point of total privation."[34]

An example of his use of absolute zero is in his computations of the amount of heat in water vapor. As water at atmospheric temperature contains 1550 degrees of heat, 100 degrees must be added to raise

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[33] Ibid., pp. 263-264. [34] Ibid., pp. 264-265.

it to the boiling point, and 914 degrees, equal to the heat of vaporization, must be added also.[35] Thus steam at the boiling point contains 2564 degrees of absolute heat.

The "true zero," as he called it, should be the same regardless of how it is derived or what particular transformations are used as a basis for the data.

> It was before shown that all bodies, which have a common temperature, must have the same number of degrees of sensible heat, . . . estimated from the point of total privation. If, therefore, the entire quantity of sensible heat contained in air, at the common temperature of the atmosphere [50°F], be 1550 degrees, it will follow that the number of degrees of heat, in all bodies at the same temperature, must likewise be 1550; and consequently this will be the point to which, if bodies were to be refrigerated, they would become absolutely cold.[36]

Crawford admitted that Lavoisier's and Laplace's experiments show that the computed zero is not constant. But, Crawford added, they admit that the variations observed could be due to experimental error. He himself admitted that his own experiments were not accurate enough to determine if the zero calculated from different reactions is constant, but he said that his variations are entirely explainable by experimental error.

Crawford and Lavoisier agreed that the heat of combustion derives from pure air that unites with the combustible substance. Crawford burned various substances with a measured quantity of pure air in each case and found that the quantity of heat released is the same for the various substances. As the quantity of heat is proportional to the quantity of pure air, the heat must come from that air:[37]

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[35] Ibid., pp. 269-270 [36] Ibid., pp. 267-268.

[37] Ibid., pp. 351-352.

> Hence we infer, that the heat which is produced by combustion, is derived from the air, and not from the inflammable body.
>
> For inflammable bodies contain little absolute heat; atmospherical air, on the contrary, abounds with this principle.[38]

Crawford supplied further support for this theory from his own concept of capacity changes and from the heat capacities of various substances, which he had determined. For him, the only factors determining if heat would be generated or not were the changes in capacity which take place and the quantity of matter involved in the reaction.[39] He found that during combustion and calcination the heat capacity of a substance calcined or burned is increased. Thus this substance cannot possibly give off heat, in fact it absorbs heat.[40] In these same processes, however, the heat capacity of the air decreases; and it decreases more than the capacity of the substance burned or calcined increases. Thus heat is evolved.[41]

In spite of his agreement with Lavoisier's views on the role of pure air in combustion and calcination, Crawford saw no reason to reject phlogiston, which he equated with inflammable air.[42] His comparison of the heat capacities of substances before and after combustion and calcination led him to the conclusion that the loss of phlogiston causes an

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[38] Ibid., pp. 368-369

[39] Ibid., p. 379.

[40] Ibid., p. 369.

[41] Ibid., p. 419.

[42] Ibid., pp. 280, 307. Mendelsohn remarks that Crawford used the language of phlogiston but "does not seem to be hampered by it" (Heat and Life, p. 138). Mendelsohn implies that Crawford's use of this language was because "he was an Englishman and a friend of Priestley . . ." (ibid.). The similarity between Crawford's and Lavoisier's ideas is due to Crawford's concept of phlogiston as being different from fire matter.

increase in heat capacity and the combination of phlogiston causes a decrease in capacity. He concluded that heat and phlogiston tend to be exclusive of each other and to mutually replace each other in chemical reactions.[43] Thus

> we may conclude, in general, that the comparative heats [capacities] of bodies, supposed to contain phlogiston, are increased by the processes of calcination and of combustion.
>
> It follows, that when an inflammable body is deprived of its power of supporting flame, by the process of combustion, it absorbs a quantity of absolute heat. . . .[44]

The same is true for the reverse process, that is, heat is given up when a substance recovers its inflammability.

Crawford's tables of heat capacity to indeed confirm this thesis; the calces of metals have a greater heat capacity than the metals themselves.[45] Furthermore, his concept of capacity change agrees with the theory that pure air combines during combustion and calcination. Pure air shows a decreased heat capacity when it unites with inflammable air (phlogiston) to form water or fixed air. At the same time, pure air gives up its heat.[46]

Up to this point, Crawford had made no explicit statement regarding the nature of heat, although from some expressions he used, it is clear that he had a material substance in mind; and he frankly admitted it:

> It is true, I have, in some places, made use of expressions, which seem to favour the former of these opinions [that heat is a substance].

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[43] Antoine Baumé in his Chymie expérimentale et raisonnée (4 vols.; Paris, 1774) had expressed a similar idea; see p. 46, Chapter II, above.

[44] Animal Heat, pp. 305-306.

[45] Ibid., pp. 489-491.

[46] Ibid., pp. 307, 352.

> But my sole motive . . . was, because it appeared to be more simple and natural, and more consonant to the facts which had been established by experiment. At the same time, I am persuaded, that it will be found to be a very difficult matter to reconcile many of the phenomena with the supposition, that heat is quality. It is not easy to conceive, upon this hypothesis, how heat can be absorbed in the processes of fusion, evaporation, combustion [&c.]. . . .
>
> Whereas if we adopt the opinion, that heat is a distinct substance, or an element sui generis, the phenomena will be found to admit of a simple and obvious interpretation.[47]

Crawford's ideas were introduced to the continent by Joao Jacinto Magalhaens (1722-1790), or Magellan as he is usually called.[48] Magellan, a descendant of the Portuguese Navigator, was an Augustinian prior who left the Church and Lisbon for England in 1764. He became a Fellow of the Royal Society in 1774. In 1780, the year after the first edition of Crawford's work on animal heat, Magellan published an account of Crawford's views.[49] A shortened form of this work appeared the following year in the Observations sur la physique.[50]

Magellan thought that Crawford's work had founded a new branch of physics:

> C'est à la publication de l'excellent Ouvrage du Docteur Adair Crawford, sur la chaleur animale, & sur l'ignition ou inflammation des corps (qui selon lui, dépendent toutes deux d'un seul & même principe), qu'on doit la naissance de cette branche de physique, qui par la nouveauté & l'evidence de ses principes, doit faire époque dans la philosophie modern.[51]

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[47] Ibid., pp. 435-536.

[48] He signed the register of the Royal Society as "John Hyacinth Magalhaens."

[49] John H. Magellan, Essai sur la nouvelle théorie du feu élémentaire et de la chaleur des corps (London, 1780), cited in Douglas McKie and Niels H. de V. Heathcote, The Discovery of Specific and Latent Heats (London, 1935), p. 40.

[50] John H. Magellan, "Essai sur la nouvelle théorie de feu élémentaire & de la chaleur des corps," Observations sur la physique, XVII (1781), 375-386.

[51] Ibid., p. 375.

Crawford's book, which Magellan described as "cet Ouvrage precieux," was so generally approved and in such demand that a second edition had to be printed almost immediately.[52] The basis of Crawford's theory is the work of Joseph Black and especially that of the Swedish chemist, Johann Karl Wilcke (1732-1796).[53] Magellan felt that the honor for the discovery of latent heat should go to the Swedish professor rather than to Black, because "C'est à ceux qui publient leurs propres découvertes, & même celles des autres, que le public en est redevable."[54]

In discussing the details of Crawford's ideas, Magellan remarked that Crawford had not committed himself on the question of the nature of heat. However, Magellan thought that Crawford's work had established without question that heat is a material substance:

> Le Docteur Crawford a parlé d'une manière problématique sur la question, si la chaleur absolue (ou la feu) est une substance sui generis; ou si elle est seulement une qualité ou modification des autres substances. La grande modestie de l'Auteur l'a porté, sans doute, à ne pas donner son opinion sur cet article: mais il me paroît indubitablement établi par toutes les expériences, qui servent de base à cette théorie, que le feu est un élément ou substance sui generis; je regarderai cette assertion comme un fait démontré, dans ce que je vais dire sur ce sujet.[55]

Magellan continued by defining various terms used in this "new" field of physics. He defined "chaleur absolue" as the elementary fire found in all substances. He said that "chaleur spécifique"[56] is the

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[52] Ibid., Magellan must have meant a second printing rather than a second edition.

[53] For a discussion of Wilcke's ideas, see McKie and Heathcote, Latent Heats, pp. 78-108.

[54] Magellan, Observations sur la physique, XVII (1781), 376.

[55] Ibid.

[56] Ibid. Its appearance in the 1780 edition is purportedly the

quantity of absolute heat which belongs to each element or particle of a substance. Specific heat is the numerical proportion of particles of elementary fire which belongs to each specific part of a substance. Sensible heat is the proportional excess of the amount of absolute heat over the quantity of specific heat. The quantity of absolute heat which accumulates in a substance and which causes sensible heat is always proportional to the quantity of specific heat in the substance. Equal quantities of absolute heat will increase the quantity of sensible heat in a proportion that is inverse to the specific heats of the substances.[57]

Magellan described the method of mixtures for determining specific heats and gave a table of specific heats derived from the work of Richard Kirwan. Water was used as a standard of comparison with a specific heat of "1,000."[58]

Magellan noted that the difference between specific heat of a liquid and the corresponding solid is very great, although he did not explicitly attribute state change to changes in specific heat. However, he did say that a liquid contains more heat than the corresponding solid, and a vapor more than the liquid, and he denoted that quantity of heat absorbed during changes of state as degrees of specific heat. He also said that the heat absorbed in those changes is responsible for the

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first use of this term; McKie & Heathcote, Latent Heats, p. 42.

[57]Magellan, Observations sur la physique, XVII (1781), 376-377.

[58]Ibid., pp. 377-380; table, p. 384. Its appearance in the London edition of 1780 was the first published table of specific heats; McKie and Heathcote, Latent Heats, p. 43.

difference in the specific heat of the solid, for example, as compared to that of the liquid.[59]

Magellan objected to the terms "latent" or "hidden" used by Black's students to denote the heat absorbed or given off during changes of state. These terms, "ressemblent trop au langage des Péripatéticiens." Furthermore, the heat is not strictly latent, "puisqu'elle [heat] produit l'effet sensible de fluidité & de vapeur. ..."[60]

In the sequel to the first article, Magellan discussed Crawford's idea on the mutual exchange of heat and phlogiston.[61] A comparison of the specific heats of metals with those of their calces shows that the specific heats of the calces are greater than those of the corresponding metals. This demonstrates that there is a mutual exchange which takes place between phlogiston and heat, that the specific heat of a substance is decreased by adding phlogiston and increased by the separation of phlogiston. This same relationship is also found in the process of combustion. Common air has a greater specific heat and contains little phlogiston whereas fixed air has a lesser specific heat and contains a great deal of phlogiston:

> On sait d'ailleurs que les combustibles n'ont que très-peu de chaleur & beaucoup de phlogistique. Ainsi, à mesure que celui-ci [phlogiston] commence à se dégager, l'air le reçoit avidement, comme il est montré

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[59]Magellan, Observations sur la physique, XVII (1781), pp. 380-382.

[60]Ibid., p. 381; cf. p. 385.

[61]John H. Magellan, "Suite de mémoire de m. H. Magellan sur le feu élémentaire et la chaleur, sommaire de l'ouvrage du docteur Crawford," Observations sur la physique, XVII (1781), [411]-422.

[62]Ibid., pp. [411]-413.

par les expériences du Docteur Priestley, & toute sa chaleur tend à former la flame & l'ignition.[63]

Crawford's ideas were widely discussed. Priestley had mentioned the idea of mutual replacement of phlogiston and heat to explain the transformation of water into a permanently elastic fluid. He said that this explanation had been suggested by James Watt (1736-1819).[64] Later on, Watt himself, although not mentioning Crawford by name, described the composition of dephlogisticated air as water deprived of its phlogiston and united to elementary heat. When phlogiston is exchanged for the heat, water and heat are released.[65] However, as he believed inflammable air to be the same as phlogiston, he questioned whether heat and phlogiston, are truly mutually exclusive. Inflammable air (phlogiston) is patently a gas, and according to Black's theory of latent heat, it should contain a large quantity of heat matter in it.[66]

Kirwan also accepted the theory of mutual replacement, an idea which he credited Crawford with originating.[67] Kirwan also indicated

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[63] Ibid., p. 412.

[64] See p. 183, above. Magellan also thought this transformation agreed perfectly with Crawford's theory; John H. Magellan, "Extrait d'une lettre de m. Magellan à m. le chevalier de Bory, de l'Académie des Sciences, 6 mai 1783, sur la conversion de l'eau en air par Priestley, sur l'étoile algol, & sur un nouvel echappement libre," Observations sur la physique, XXII (1783), 465-468.

[65] James Watt, "Thoughts on the Constituent Parts of Water and of Dephlogisticated Air, with an Account of Some Experiments on That Subject," Philosophical Transactions of the Royal Society of London, LXXIV (1784), 333.

[66] Ibid., pp. 352-353.

[67] Richard Kirwan, "Notes on the Preceding Work," in Karl Wilhelm Scheele, Chemical Observations and Experiments on Air and Fire, trans. J. R. Forster (London, 1780), p. 228; cf. Richard Kirwan,

his acceptance of Crawford's explanation of heat produced and absorbed in chemical reactions as due to changes in the heat capacities of the substances involved. He specifically referred to this idea in explaining some heat phenomena associated with the decomposition of acids.[68] His explanation of the cold produced by evaporation illustrates his use of the concept of capacity change:

> . . . [The] attraction of the particles of liquids decreases as their points of contact diminish, and thereby their capacity for receiving the matter of heat, (which is the same as that of light) increases; by this increased capacity, the matter of heat or fire contained in the neighbouring bodies, which, like all other fluids, flows where it finds least resistance, is determined to flow towards the vapour; and consequently those bodies are cooled, though the vapour is not heated; because the re-action of its particles is barely equal to that which it had before its capacity was increased.[69]

He agreed with Lavoisier that the densities of substances before a reaction compared with their densities after the reaction would in general determine whether heat would be absorbed or released. But Kirwan thought the basic cause of the temperature change is to be found in the change in heat capacity which occurs. The initial cause is a change in capacity which produces an absorption or release of heat matter. This in turn causes a more dense or rarefied state. In general, dissolutions will result in an absorption of heat and precipitations in a release of heat.[70]

"Troisième et dernière suit de la dernière partie des expériences et observations de m. Kirwan sur les affinités, &c.," trans. Madame P***, de Dijon, Observations sur la physique, XXVIII (1786), 100.

[68] Richard Kirwan, "Expériences et observations sur les forces attractives des acides minéraux," Observations sur la physique, XXVII (1785), 330-331.

[69] Richard Kirwan, An Estimate of the Temperature of Different Latitudes (London, 1787), p. 12.

[70] Kirwan, Observations sur la physique XXVII (1785), 335; cf. Kirwan, Essay on Phlogiston, p. 72.

Kirwan combined the idea of mutual exchange of heat matter and phlogiston with the idea of capacity change to explain the release of phlogiston caused by the action of light. Light has the property of increasing the capacity of substances for fire matter. This increased capacity results in an absorption of heat and a concomitant release of phlogiston.[71]

In the discussion of chemistry in the second edition of the Britannica, the author remarked that phlogiston is different from fire matter because "the phlogiston is always displaced, and to appearance destroyed by fire; which it could not be if itself were either heat or light."[72] The Britannica gave a resume of Crawford's general theory of heat and its application to animal heat.[73] With regard to theories of animal heat, the author remarked that Crawford's theory "seems to be the best that hath yet appeared."[74]

Thomas Henry (1734-1816), Manchester chemist, surgeon, and Fellow of the Royal Society, supported Crawford's views in the former's translation of Lavoisier's Essays on Air and Acids.[75] In the preface, Henry explained that he believed in phlogiston. He said that Crawford

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[71] Kirwan, Essay on Phlogiston, p. 72.

[72] "Chemistry," Encyclopaedia Britannica (2d ed., enlarged; 10 vols.; Edinburgh, 1778-1783), III (1778), 1807. Articles discussing heat in this edition were probably written by James Tytler (1747?-1805); see n. 2, p. 104, Chapter IV, above.

[73] "Heat," Britannica, V (1780), 3552-3554.

[74] Ibid., p. 3554.

[75] Antoine Laurent Lavoisier, Essays on the Effects Produced by Various Processes on Atmospheric Air, with a Particular View to an Investigation of the Constitution of the Acids, trans. Thomas Henry (Warrington, 1783).

had shown that substances containing much phlogiston contain little "absolute fire," because these two principles repel each other.[76] "That truly ingenious philosopher Dr. Crawford" had also shown that dephlogisticated air contains a large portion of absolute heat which is released when phlogiston unites with the air.[77]

Isaac Milner (1750-1820), Jacksonian Professor of Natural Philosophy at Cambridge, discussed Crawford's theory in his chemistry's lectures for 1784-1788. He listed Crawford's views as comprising one of the three main theories of heat. Milner believed in the vibrational theory; but he said that most natural philosophers had rejected this view, and that no one had attempted to support it "since the Publication of Dr Crawford's system. . . ."[78]

Tiberius Cavallo (1749-1809), natural philosopher and member of the Royal Society, accepted phlogiston as the cause of inflammability.[79] He sidestepped the question of the relation between phlogiston, light, and heat, and referred his readers to Crawford's "ingenious hypothesis," which he briefly summarized.[80] Similar advice was offered by Richard Watson (1773-1816), one-time professor of chemistry at Cambridge and later Bishop of Llandaff.[81] Although Watson advocated the vibratory

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[76] Ibid., p. xvi.

[77] Ibid., note, p. 14.

[78] Isaac Milner, MS notes, quoted in L. J. M. Coleby, "Isaac Milner and the Jacksonian Chair of Natural Philosophy," Annals of Science, X (1954), 243-244.

[79] Tiberius Cavallo, A Treatise on the Nature and Properties of Air and Other Permanently Elastic Fluids, to Which Is Prefixed an Introduction to Chemistry (London, 1781), pp. 17-19.

[80] Ibid., pp. 19-21.

[81] Richard Watson, Chemical Essays (5 vols.; Cambridge, 1781-

theory of heat,[82] he advised his readers who wished to learn more about heat theory to read Crawford's work.[83]

The noted Swedish chemist Torbern Bergman cited the idea that phlogiston and fire are contraries and are mutually exclusive.[84] He remarked that although phlogiston and specific fire do seem to vary inversely, there is no mutual repulsion between them.[85] Crawford was praised by Gioachimo Carradori (1758-1818) as having done great work in the field of heat phenomena.[86] William Hamilton, physician to London Hospital and lecturer on chemistry, in his translation of Berthollet's Art of Dyeing, claimed that Crawford had proven that both the heat of respiration and the heat of combustion comes from pure air and had published this theory before Lavoisier.[87]

Crawford was cited with approval several times in the Mathematical and Philosophical Dictionary of Charles Hutton (1737-1823).[88]

1787 [Vol. V: London]). Watson's discussion of heat is unchanged through the third edition (5 vols.; London, 1784-1788) and a 1791 Dublin edition (2 vols.).

[82] Ibid., I, 157. [83] Ibid., p. 164, note.

[84] Torbern Olof Bergman, A Dissertation on Elective Attractions, trans. Translator of Spallanzani's Dissertations [T. Beddoes] (London, 1785)," p. 232.

[85] Ibid., pp. 254-255.

[86] Gioachimo Carradori, "Extrait d'un ouvrage qui a pour titre, la theoria del calore, en deux volumes," Observations sur la physique, XXXIV (1789), 271.

[87] Claude Louis Berthollet, Elements of the Art of Dyeing, trans. William Hamilton (2 vols.; London, 1791), I, 168-169, note. Mendelsohn speaks of Lavoisier and Crawford as co-founders of the oxidation theory of combustion and animal heat (Heat and Life, p. 164).

[88] Charles Hutton, A Mathematical and Philosophical Dictionary, Containing an Explanation of the Terms and an Account of the Several

Crawford's views were listed along with the views of many others. Hutton described Crawford's idea on the mutual replacement of heat and phlogiston as offering a "very plausable" explanation of animal heat. He mentioned that some persons objected to this explanation, but he added that there was no regular, systematic theory available which could replace Crawford's.[89] Hutton's explanation of the heat of combustion was also taken from Crawford. Hutton explained that the heat derived from the air is the result of capacity change.[90]

William Nicholson (1753-1815), London scientist, inventor, and editor, praised Crawford's book on heat:

> This most valuable performance contains the theory, and most of the facts, relating to heat; and deserves to be made part of the library of every natural philosopher.[91]

Nicholson frequently cited Crawford in his discussion of heat. He explained latent heat phenomena entirely in terms of capacity changes,[92] and he thought that the quantity of heat involved in changes of capacity offered a mode of computing absolute zero.[93] He explained the heat evolved during combustion as due to the decrease in the heat capacity

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Subjects Comprized under the Heads Mathematics, Astronomy, and Philosophy, Both Natural and Experimental, with an Historical Account of the Rise, Progress, and Present State of These Sciences, Also Memoirs of the Lives and Writings of the Most Eminent Authors, Both Ancient and Modern, Who by Their Discoveries or Improvements Have Contributed to the Advancement of Them (2 vols.; London, [1795-1796]).

[89] Ibid., I, 589-590. [90] Ibid., p. 590.

[91] William Nicholson, The First Principles of Chemistry (2d ed., with improvements; London, 1792), p. 12, note. The section on heat is unchanged in the third edition (1796).

[92] Ibid., pp. 15-16, 20. [93] Ibid., pp. 16-17.

of the air that combines with the combustible substance.[94]

The Swedish chemist, Johan Gadolin (1760-1852), a student of Bergman's and an acquaintance of Crawford's, accepted the theory that changes in specific heat explained latent heat phenomena. He also accepted Crawford's mutual replacement theory until 1789 when he abandoned phlogiston in favor of Lavoisier's oxidation theory.[95]

> If the specific heat depends on the degree of coherence of the parts of the body, then it must be that a change in the state of the body or of the union between its parts, is accompanied by a change in the specific heat. . . . Likewise phlogiston loses to a remarkable degree its power of attracting heat when it is present in either a solid or a liquid; or rather, it very often diminishes by its union the specific heat of the other bodies with which it is united.[96]

Latent heat phenomena indicate

> that a definite supply of latent heat is contained in all bodies and that it is greatest in elastic fluids, least in solids. There is every justification for believing that the latent heat in bodies . . . in no way differs from the specific heat of the bodies. . . . There seems to be scarcely any room for doubt that sensible heat ought to arise when a change in the specific heat of a body occurs as a result of a change in its state or form.[97]

Gadolin accepted Crawford's idea that specific heats represent a certain quantity of heat contained in substances and that by equating the change in specific heat during changes of state to the amount of

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[94] Ibid., p. 33. Nicholson expressed his support of the concept of capacity change as early as 1787; An Introduction to Natural Philosophy, Illustrated with Copper Plates (2 vols.; 2d ed., with improvements; London, 1787), pp. 116-26. This discussion remains virtually unchanged through the 5th edition (2 vols.; London, 1805).

[95] Partington, History of Chemistry, III, 235.

[96] Johan Gadolin, Dissertatio chemio-physica de theoria caloris corporum specifici (Åbo, 1784), p. 16, translated in McKie and Heathcote, Latent Heats, p. 114.

[97] Gadolin, Dissertatio de theoria caloris, p. 21, translated in McKie and Heathcote, Latent Heats, p. 115.

heat released or absorbed, one can compute absolute zero. In the 1788 edition of his Animal Heat, Crawford appended "Results of Mr. Gadolin's Experiments on the Absolute Heat of Bodies, Published in the Memoires of Stockholm for 1784."[98] However, the variations in values of absolute zero, which theoretically should be uniform, caused Gadolin to abandon his attempts to calculate this value and to conclude eventually that specific heats do not represent a quantity of heat contained in substances.[99] However, he continued to maintain Crawford's view that caloric does not combine with other substances to cause changes of state.[100]

The Scotsman Patrick Wilson (1743-1811), a fellow student of Crawford's and professor of astronomy at the University of Glasgow, expressed belief in Crawford's idea of mutual replacement of phlogiston and heat.[101] He also accepted Crawford's use of capacity change to explain changes of state, as did the German apothecary and physician Johann Wilhelm Ritter (1776-1810).[102] Johann Tobias Mayer (1752-1830), at the time professor of physics at Erlangen, also invoked the theory of capacity

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[98]Crawford, Animal Heat, pp. 467-481.

[99]Johan Gadolin, "Extrait d'une lettre écrite à m. Guyton (cidevant de Morveau)," Annales de chimie, XI (1791), 27; cf. Johan Gadolin, "Disquisitio de theoria caloris corporum specifici," Nova acta regiae societatis scientiarum Upsaliensis, V (1792), 1, cited in McKie and Heathcote, Latent Heats, p. 137.

[100]Gadolin, Annales de chimie, XI (1791), 27-28.

[101]Patrick Wilson, "Experiments and Observations Upon a Remarkable Cold Which Accompanies the Separation of Hoarfrost from a Clear Air [1784]," Transactions of the Royal Society of Edinburgh, I (1788), p. 149.

[102]Johann Wilhelm Ritter, "Einige Bermerkungen über die Cohäsion, und über den Zussammenhang derselben mit dem Magnetisums," Annalen der Physik, IV (1800), 14.

and the idea that heat involved in changes of state is not chemically combined with the substance.[103]

Mayer said that the reason latent heat is not combined is that this heat can be added or removed by mere alterations of external temperature; this is not true for the permanently elastic fluids. In this he agreed with Gadolin. The idea that heat combines with substances during changes of state was one feature of the caloric theory and originally a fundamental one, even though some of Lavoisier's followers later gave it up. It is by no means certain that the denial of this idea was primarily due to Crawford's influence; but Crawford was widely read, and he emphatically denied the theory of combination. Crawford had argued that the three states are caused by a mere separation of particles; change of state is not the fundamental alteration which would result if chemical combination of heat matter took place.[104] Magellan implied a similar argument when he objected to the use of the term latent heat on the grounds that the effects are visible not hidden.[105]

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[103]Johann Tobias Mayer, "Eleber die Geseze und Modificazianum des Warmestoffs, c'est-à-dire, sur les loix & les modifications du calorique, par J. T. Mayer, à Erlangue 1791, in -8°, 288 pag." reviewed in Annales de chimie, XVIII (1793), 111. John Elliot (1747-1787), London physician and apothecary, accepted Crawford's views; Partington and McKie, Annals of Science, III (1938), 352. Guyton de Morveau did the same, before his conversion to Lavoisier's theory (ibid., pp. 353-354). Johann Gottfried Leonhardi (1746-1823), professor at Leipzig and later at Wittenberg, accepted Crawford's ideas on the relationship between heat and phlogiston; James R. Partington and Douglas McKie, "Historical Studies on the Phlogiston Theory: IV. Last Phases of the Theory," Annals of Science, IV (1939), 120. William Cleghorn (1754-1783), in his inaugural dissertation delivered at Edinburgh in 1779, accepted Crawford's ideas on the mutual exchange of heat and phlogiston; Douglas McKie and Niels H. de V. Heathcote, "William Cleghorn's De igne (1779)," Annals of Science, XIV (1958), 31, 33, 35.

[104]See pp. 189-191, above, Chaptal's ideas, p. 177, above, and those of Brisson, p. 178, above.

[105]See p. 199, above.

Much the same argument was presented by Jean Claude de Lamétherie (1743-1817), editor of the Observations sur la physique. Lamétherie said that specific heat and latent heat are the same thing. Changes of state are caused by specific heat; and this heat is not combined because the fundamental natures of the substances are not changed by a mere change of state.[106] The Genevan Marc Auguste Pictet (1752-1825) stated that combined caloric is retained by chemical affinity and can be removed only by chemical decomposition. As latent heat can be removed by mere cooling, it is not combined. This is what differentiates aeriform fluids from vapors.[107]

The extent of contemporary familiarity with Crawford's views is also apparent among those who disagreed with him. Lavoisier and Laplace devoted considerable space in their 1783 memoir to refuting various elements of Crawford's theory, particularly the theoretical bases upon which calculations of absolute zero were made. The wide divergence among the

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[106]Jean Claude de Lamétherie, "Discours préliminaire contenant un précis des nouvelles découvertes," Observations sur la physique, XXVIII (1786), 12, 14. Cf. Jean Claude de Lamétherie, "Discours préliminaire," Journal de physique, III [XLVI] (1798), 18-19. See pp.223-224, 227-229, below for a more detailed discussion of Lamétherie's views.

[107]Benjamin Thompson, count Rumford, "An Inquiry Concerning, &c., recherche sur la source de la chaleur qu'excite le frottement," trans. M. A. Pictet, Journal de physique, IV [XLVII] (An VI [1798]), 29, note. Cf. Lamétherie, Observations sur la physique, III [XLVI] (1798), 18-19. Friedrich Albert Carl Gren (1760-1798), a professor at the University of Halle and a popular lecturer on chemistry, also contrasted latent heat with chemically bound heat. The former is only loosely attached; Grundriss der Naturlehre in seinem mathematischen und chemischen Theile, neu bearbeitet (Halle, 1793), p. 542, cited in James R. Partington and Douglas McKie, "Historical Studies on the Phlogiston Theory: II. The Negative Weight of Phlogiston," Annals of Science, III (1938), 50.

computed values, which in theory should be equal, led Lavoisier and Laplace to conclude that the theoretical foundations of the calculation method could not be verified, and that heat capacities are not constant at all temperatures. Indeed, as specific heat should bear a relation to the pore space in the substance, increased volume resulting from increased temperature should result in absorption of a certain amount of heat which does not affect a thermometer. Thus, Lavoisier said, specific heat cannot represent a certain quantity of heat contained in substance. Furthermore, knowing the specific heats (Crawford's heat capacity) of substances before and after a chemical reaction did not enable one to predict the resulting temperature change.[108] The authors thus implied that heat evolved or absorbed in chemical reactions cannot be explained in terms of change in heat capacity.

In his memoir of 1783, Lavoisier offered an explanation of specific heats in terms of the pore space existing within a substance. Changes in the pore space should cause corresponding changes in specific heat.[109] This was an attempt to explain the capacity changes, which accompany changes of state, as effects of a separation or contraction among molecules, rather than capacity change causing the separation or contraction. Lavoisier did admit later that Crawford's theory is very

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[108] Lavoisier and Laplace, Mémoires, 1780 (1784), pp. 382-385; see pp. 117-118, Chapter IV, above.

[109] Antoine Laurent Lavoisier, "Réflexions sur le phlogistique, pour servir de développement à la theorie de la combustion & de la calcination publiée en 1777," Mémoires de l'Académie Royale des Sciences, 1783 (1786), pp. 527-28, 531-32, 534; see pp. 121-122, Chapter IV, above; cf. Antoine Laurent Lavoisier, Traité élémentaire de chimie, présenté dans un ordre nouveau et d'après les découvertes modernes, avec figures (2 vols.; Paris, 1789), pp. 18-19.

plausible regarding the change from liquid to a gas because of the patent volume change. He denied, however, that the theory could explain the change from solid to liquid because of the absence of a sufficient volume change.[110]

Armand Séguin devoted a substantial portion of two lengthy articles in the Annales de chimie to arguing against Crawford's views.[111] Séguin's arguments differ little from those of Lavoisier and Laplace.

Although Lavoisier and Séguin disclaimed any validity for Crawford's views, neither were loath to cite him in support of their own theories. Lavoisier credited Crawford as agreeing with him that pure air is the source of heat derived during combustion and respiration, although he admitted that they disagreed on the mechanism.[112] Séguin said the same thing.[113] He also explained the blood's role in maintaining animal

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[110]Antoine Laurent Lavoisier, Mémoires de chimie (2 vols.; [Paris?, 1805?]), I, 7, 286-287; see p. 133, Chapter IV, above.

[111]Armand Séguin, "Observations générales sur le calorique & ses différens effets, & réflexions sur la théorie de mm. Black, Crawfort, Lavoisier, & de Laplace, sur la chaleur animale & sur celle qui se dégage pendant la combustion, avec un résumé de tout ce qui a été fait & écrit jusqu'à ce moment sur ce sujet," Annales de chimie, III (1789), 163, 169, 177-179, 231; Armand Séguin, "Second mémoire sur le calorique," Annales de chimie, V (1790), 231-57; see pp. 152-153, 156-157, Chapter V, above. Cf. Séguin's discussions of Crawford in Lavoisier's Mémoires de chimie, I, 174, 192-194, 198.

[112]Lavoisier, Mémoires, 1780 (1784), p. 394. See Mendelsohn, Heat and Life, pp. 150-151, for Lavoisier's and Laplace's use of capacity change to explain absorption of heat by arterial blood; see Goodfield, Scientific Physiology, pp. 55-59, for a comparison of the animal heat theories of Crawford and Lavoisier.

[113]Séguin, Annales de chimie, V (1790), 259; Armand Séguin, "Observations générales sur la respiration et sur la chaleur animale, lues à la Société Royale de Médecin, le 22 mai 1790," Observations sur la physique, XXXVII (1790), 469-471. The essence of this last article

heat as caused by caloric being given off by the blood when its heat capacity is decreased by the absorption of hydrogen. This takes place when the blood is transformed from arterial to venous.[114] Jean Henri Hassenfratz (1755-1827), one-time secretary to Lavoisier and later professor of physics at the Ecole Polytechnique, in setting forth his own views, cited Crawford and Lavoisier as agreeing on the cause of animal heat.[115]

Many persons accepted Lavoisier's and Laplace's censoring of Crawford's theoretical bases for the computation of absolute zero. Jean André Deluc (1727-1817) dismissed Crawford's ideas on absolute zero as having been proved false by Laplace and Lavoisier.[116] Deluc also said that Crawford's explanation of changes of state as due to changes in heat capacity is wrong because it supposes that heat diminishes only after the vapor is formed and thus does not explain the change of state itself.[117] Gehler's Wörterbuch of 1798 credits both Deluc and Lavoisier

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was reprinted in Armand Séguin, "Mémoire sur la respiration et sur la chaleur animale, lu à la Société de Medecin en mai 1790," Annales de chimie, XXI (1797), 225-234.

[114]Séguin, Observations sur la physique, XXXVII (1790), 471; Séguin, Annales de chimie, XXI (1797), 231-232; cf. Crawford, Animal Heat (1788), pp. 361-362. See Mendelsohn, Heat and Life, pp. 161-62, for the influence of Crawford on Séguin.

[115]Jean Henri Hassenfratz, "Mémoire sur la combinaison de l'oxigène avec le carbone & l'hydrogène du sang, sur la dissolution de l'oxigène dans le sang, & sur la manière dont le calorique se dégage," Annales de chimie, IX (1791), 261-262.

[116]Jean André Deluc, "Trente-unième lettre de m. de Luc, à J. C. Delamétherie, sur les fluides expansibles," Observations sur la physique, XLIII (1793), 36.

[117]Ibid., cf. Séguin, Annales de chimie, III (1789), 177-178, who said the same thing.

with having shown Crawford's ideas on heat capacities to be wrong.[118] Gehler also objected to Crawford's idea that the amount of phlogiston in a substance is inversely proportional to the heat capacity of the substance. There are exceptions to the rule of inverse proportions. For example, coal ashes containing little phlogiston have a heat capacity which is less than the original coal, whereas it should be more if Crawford's theory were correct.[119]

Ludwig Achim von Arnim (1781-1831) thought that all concepts of heat capacity and specific heats are uncertain.[120] He singled out Crawford's concept that capacities are constant at all temperatures as being particularly suspect.[121] William Henry (1774-1836) described Crawford's assumption that heat capacity is constant unless a change of state occurs as completely arbitrary and his calculations of absolute zero as baseless.[122] Henry's discrediting Crawford was due to Henry's attack on the

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[118]Johann Samuel Traugott Gehler, Physikalisches Wörterbuch, oder Versuch einer Erklärung der vornehmsten Begriffe und Kunstwörter der Naturlehre, mit kurzen Nachrichten von der Geschichte der Erfindungen und Beschreibungen der Werkzeuge, begleitet in alphabetischer Ordnung (New ed.; 6 vols.; Leipzig, 1798-1801), IV, 566.

[119]Ibid., p. 581.

[120]Ludwig Achim von Arnim, "Electrische Versuche," Annalen der Physik, V (1800), 61.

[121]Ibid., p. 61.

[122]Humphry Davy, Benjamin Thompson, Count Rumford, and William Henry, "Giebt es eine Wärmemateria oder nicht?," Annalen der Physik, XII (1803), 560-561. This paper consists of extracts from articles previously published by the three authors cited. Henry's article originally appeared as "A Review of Some Experiments, Which Have Been Supposed to Disprove the Materiality of Heat [1801]," Memoirs of the Literary and Philosophical Society of Manchester, V (1802), 603-621.

reasonings of Benjamin Thompson, Count Rumford, and Sir Humphry Davy (1778-1829), both of whom attempted to eliminate altogether the concept of heat as a material substance. One of the basic arguments of both Rumford and Davy is based on a falsification of Crawford's concept of capacity change as causing a release of heat.

In an attempt to discredit the material theory, Rumford questioned whether the heat produced by friction could have come from the metal chips bored from a cannon tube.

> If this were the case, then, according to the modern doctrines of latent heat, and of caloric, the capacity for heat of the parts of the metal, so reduced to chips, ought not only to be changed, but the change undergone by them should be sufficiently great to account for all the heat produced.[123]

He found that no change in capacity had taken place, and thus "the heat produced could not possibly have been furnished at the expence of the latent heat of the metallic chips."[124] He then questioned the possibility of a change in the heat capacity of the cylinder itself. As the quantity of heat evolved did not diminish, there was no capacity change in the cylinder.[125]

Davy's argument is the same. If heat be considered a material substance, then the temperature of a substance can be increased only by the addition of heat from an external source, "unless their capacities are diminished from some cause. . . ."[126] Davy's experiment of melting

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[123]Benjamin Thompson, Count Rumford, "An Inquiry Concerning the Source of the Heat Which Is Excited by Friction," Philosophical Transactions of the Royal Society of London, LXXXVIII (1798), 81.

[124]Ibid., pp. 82-83. [125]Ibid., p. 88.

[126]Humphry Davy, "An Essay on Heat, Light, and the Combinations of Light [1799]," The Collected Works of Sir Humphry Davy, Bart., LL.D.,

by friction was designed to demonstrate that "Friction consequently does not diminish the capacities of bodies for heat."[127]

Henry's argument is that Crawford's theories can be falsified in terms of a material theory of heat. Thus it is meaningless to cite a refutation of Crawford's ideas on capacity as a basis for rejecting the hypothesis of heat as a material substance.

The Chevalier de Soycourt picked Crawford as an epitome of those who believe heat to be a material substance.[128] Soycourt attacked this "étrange doctrine" and especially all demonstrations of it based upon specific heats. The only sure sign of the presence of heat is expansion. Thus specific heats should be based upon volume changes rather than upon temperature change.[129]

Leopold Vacca Berlinghierei (fl. 1789-1807) attacked Crawford's theory of capacity on the grounds that some heat is combined with substances.[130] Crawford's method is very exact when dealing with the fire matter which acts on a thermometer, but it fails completely to account for heat evolved during combustion and respiration. Berlinghieri accepted and used Crawford's value for the heat capacity of air as

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F.R.S., Foreign Associate of the Institute of France, etc., ed. John Davy (9 vols.; London, 1839-1840), II, 10. This is the article extracted in the Annalen der Physik, XII (1803), 546-573.

[127]Collected Works, p. 12.

[128]Chevalier de Soycourt, "Mémoire de m. le Chevalier, sur les expériences données en preuve de la chaleur latente, couronné par l'Académie des Sciences de Rouen, le 27 juillet 1787, extrait," Observations sur la physique, XXXII (1788), 143-150.

[129]Ibid., pp. 144-145.

[130]Leopold Vacca Berlinghieri, "Mémoire sur la chaleur," Observations sur la physique, XXXV (1789), 117.

the quantity of heat contained in it. However, Berlinghieri's argument is that common air does not contain enough heat to account for all the heat produced during combustion.[131] Furthermore, as more heat is liberated in burning sulfur. than in burning carbon, then according to Crawford's theory, vitriolic acid should have less heat capacity than fixed air; but experiment shows that it does not.[132]

Berlinghieri's primary objection was that the formation of water vapor during respiration absorbs much more heat than is liberated by the change in capacity which occurs when vital air is changed into fixed air.[133] Here again he accepted Crawford's idea that capacity reflects a certain quantity of heat contained in a substance and the idea that a change in capacity does indeed produce an exchange of heat. Berlinghieri's argument was that these changes do not provide sufficient heat and thus some heat must be combined in the substance which unites with vital air.[134]

Hassenfratz came to Crawford's support, not because he adopted Crawford's theories, Hassenfratz said, but because not enough justice had been rendered to Crawford's intelligence and the sagacity with which he had made such a large number of ingenious experiments concerning heat.[135] Besides, Berlinghieri had attacked Lavoisier as well. Hassenfratz said

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[131] Ibid., p. 120. [132] Ibid., pp. 120-121.

[133] Leopold Vacca Berlinghieri, "Mémoire sur la nature de feu et du phlogistique," Observations sur la physique, XXXV (1789), 433.

[134] Ibid., pp. 433-434.

[135] Jean Henri Hassenfratz, "Observations de m. Hassenfratz relatives à un mémoire de m. Berlinghieri," Annales de chimie, III (1789), 262-263.

that Berlinghieri's arguments are valid only if it were assumed that the water exhaled during respiration is formed in a liquid state in the lungs and then transformed into a vapor; and there is no proof of this.[136] He suggested that persons who do not understand Lavoisier's doctrine should be sent to read his works. Berlinghieri, however, was not intimidated and he restated his argument that vital air cannot be the sole source of the heat evolved.[137]

Although Crawford did not think phlogiston to be the same as fire matter, he was a phlogistonist. Nevertheless, his theories and arguments were used by both sides. Stephen Dickson said that Crawford's tables of comparative heats do not correspond to the inflammabilities of the substances listed. This falsifies Stahl's idea that phlogiston and fire matter are identical.[138] Lamétherie complained that the anti-phlogistonist forces benefitted from Crawford's theory, especially Crawford's high value of the specific heat of pure air.[139] Crawford's value enables the anti-phlogistonists to say that heat and flame come from pure air and that combustibles contain only a small amount of specific or latent heat. He listed Crawford's demonstration of the high specific heat of pure air as one of the four fundamental experiments upon which the new

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[136] Ibid., pp. 263-264.

[137] Leopold Vacca Berlinghieri, "Réponse aux observations de m. Hassenfratz relatives à un mémoire de m. Vacca Berlinghieri," Observations sur la physique, XXXVI (1790), 58-61.

[138] Stephen Dickson, An Essay on Chemical Nomenclature (London, 1796), pp. 81-86.

[139] Jean Claude de Lamétherie, "Discours préliminaire," Observations sur la physique," XXXIV (1789), 25.

theory is based.[140] He did not doubt Crawford's value for the specific heat of pure air; but he denied that most of the heat and flame of combustion come from this air. If this were true, then heat and flame should result in all cases where pure air combines, but this is not the case. Lamétherie noted, however, that the latest edition (1788) of Crawford's book listed inflammable air as having a greater specific heat than pure air thus showing that all the heat evolved when inflammable and pure air are ignited cannot come from pure air alone.[141]

Claude Louis Berthollet (1748-1822), a student of Macquer's and supporter of Lavoisier mentioned Crawford's theory of capacity change in a footnote in his book on the art of dyeing. Although he refused to discuss the validity of Crawford's theory, he objected to phlogistonists's using Crawford's high value of the specific heat of hydrogen gas to undermine the oxidation theory.[142] Berthollet admitted that substances other than oxygen gas can furnish some heat when uniting with oxygen. But he objected to extending this argument to the point of denying that the heat comes principally from oxygen gas; and this was what was happening, and phlogistonists were citing Crawford as having demonstrated it.[143]

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[140] Ibid., p. 25.

[141] Ibid., pp. 29-30.

[142] Claude Louis Berthollet, Eléments de l'art de la teinture (2 vols.; Paris, 1791), p. 184, note.

[143] It is at this point in his translation of this work that William Hamilton inserted his defense of Crawford; see p. 204, above. Friedrich Albert Carl Gren objected to Crawford's idea of mutual replacement for failing to account for the production of light; Partington and McKie, Annals of Science, III (1938), 18; cf. Gren's other views, n. 107, above. Bryan Higgins (1737?-1820), M.D. who conducted public chemistry lectures in London, said that phlogiston and fire matter can combine and he objected to Crawford's views to the contrary; Partington and McKie, Annals of Science, III (1938), 344.

The extensive citations of Crawford and his ideas indicate that he was a major figure in late eighteenth-century heat theory. His work was one of the first successful attempts to propagate Joseph Black's ideas on latent heat and William Irvine's ideas on heat capacity, and to use these ideas to explain the vast range of heat phenomena from changes of state to combustion and animal heat. The publication of this work in 1779 preceded the appearance in 1780 of Lavoisier's early papers dealing with the same subjects.

Crawford's concept of phlogiston was such that he could easily incorporate into his system practically all of the experimental data associated with the new pneumatic chemistry. He seems to have been an obvious choice as a rallying point for those who were impressed by the force of Lavoisier's arguments and who were still reluctant to eliminate the properties of combustibles as being essential to the process of combustion. Joseph Priestley remarked in 1800 that "now that Dr. Crawford is dead, I hardly know of any person, except my friends of the Lunar society at Birmingham, who adhere to the doctrine of phlogiston."[144]

The similarity of Crawford's views to those of Lavoisier resulted not only in Crawford being supported by phlogistonists, but also in his subverting anti-phlogistonists. His fame was such to make him something of an authority on the subject of heat, a figure who had to be dealt with by anyone, including Lavoisier, who disagreed with him.

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[144]Priestley, Phlogiston Established, p. 2.

CHAPTER VII

OPPOSITION TO THE CALORIC THEORY: PHLOGISTON IS FIRE

One of Lavoisier's most inveterate opponents was Jean Claude de Lamétherie (1743-1817). As editor of the Observations sur la physique[1] from 1785 on, he effectively turned that publication into a sounding board for his own opinions and the opinions of others who opposed the new chemistry. His policy as editor of one of the foremost French chemical journals of his time was instrumental in causing Lavoisier to begin his own Annales de chimie in 1789.[2]

In stating his early views, Lamétherie followed the more or less standard phlogistic arguments. There are only two agents which can overcome the force of cohesion, fire and water.[3] Water acts only secondarily as it receives its liquidity from the fire that penetrates it. The air itself would perhaps crystallize if deprived of sufficient fire. For this reason, fire alone has the ability to dissolve substances and make them fluid.

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[1]In 1794 the title was changed to the Journal de physique.

[2]See Edward W. J. Neave. "Chemistry in Rozier's Journal: II. The Phlogiston Theory," Annals of Science, VII (1951), 101-106.

[3]Jean Claude de Lamétherie, "Mémoire sur la crystallisation," Observations sur la physique, XVII (1781), 252.

Fire has the property common to all other elements, it can combine itself with other substances. When combined it is known as phlogiston. When free, however, fire is the principle of all fluidity. It destroys the force of cohesion; it separates all united particles; and it agitates them into a rapid motion.[4] The activity of fire matter is due to the force and spherical shape of its particles. It is the only substance "fluide par lui-même."[5] Although fire matter may be combined in the form of phlogiston, the nature of the fire particles is not changed, and they always try to escape the combination. But in order to escape, "air" is needed for the fire to unite with.[6] Lamétherie felt that the caustic property of acids demonstrates the activity of fire matter, even when combined in the form of phlogiston.[7]

He equated fire matter with the element light.[8] He later credited Macquer with the idea.[9] He also accepted Scheele's idea that heat matter (matière de la chaleur) is fire matter united with pure air.[10] Lamétherie said that the reason he thought heat matter to be different from pure fire matter or light is that heat expands slowly whereas light expands with great speed. Air gives mass to fire and makes it difficult for the heat to traverse substances. It is also due to this mass

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[4] Ibid.

[5] Jean Claude de Lamétherie, "Réflexions sur les élémens," Observations sur la physique, XVIII (1781), 230.

[6] Ibid., p. 317.

[7] Ibid., p. 319.

[8] Ibid., p. 322.

[9] Jean Claude de Lamétherie, "Discours préliminaire contenant un précis des nouvelles découvertes," Observations sur la physique, XXVIII (1786), 11.

[10] Ibid.

that heat matter can destroy the cohesive force among particles.[11] He not only accepted Scheele's view on the nature of heat matter, but in the same article he expressed approval of Richard Kirwan's idea that phlogiston is nothing more than pure inflammable air.[12]

In 1787, the following year, Lamétherie restated his belief in Scheele's theory of heat.[13] After this date, he made no more claims that he accepted this theory. Scheele's views were mentioned without comment in 1791,[14] and in 1798 Lamétherie described them as having been proven wrong.[15]

Kirwan's views fared a little better. In 1787 Lamétherie stated that inflammable air, in addition to containing heat matter, contains a small amount of pure air.[16] He repeated this in another article the same year,[17] and he referred to the idea again in 1789.[18] In 1791 he described inflammable air as a mixture or compound of heat and light which together form the "principe inflammable."[19] In 1794 he stated that heat matter,

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[11] Ibid., pp. 11-12. [12] Ibid., p. 13.

[13] Jean Claude de Lamétherie, "Discours préliminaire," Observations sur la physique, XXX (1787), 33.

[14] Jean Claude de Lamétherie, "Discours préliminaire," Observations sur la physique, XXXVIII (1791), 15.

[15] Jean Claude de Lamétherie, "Discourse préliminaire," Journal de physique, III [XLVI] (1798), 20.

[16] Lamétherie, Observations sur la physique, XXX (1787), 33.

[17] Jean Claude de Lamétherie, "Lettre de m. de la Métherie à m. ***," Observations sur la physique, XXX (1787), 225.

[18] Jean Claude de Lamétherie, "Discours préliminaire," Observations sur la physique, XXXIV (1789), 33-34.

[19] Jean Claude de Lamétherie, "De la combustion," Observations sur la physique, XXXVIII (1791), 398.

when combined, "est le véritable oxigène ou principe de l'acidité dans le sens où on prend ce mot."[20] In 1795 he reverted to his old nomenclature: when heat matter is combined in substances, it is called the inflammable principle or phlogiston.[21] He repeated this in 1798.[22]

These frequent changes in opinion indicate that Lamétherie was willing to accept any reasonable theory as long as it enabled him to maintain the existence of a fire principle in substances other than pure air. And on this point he was unyielding. The latent heat of oxygen gas, the heat that is responsible for its aeriform state, cannot be the sole source of the heat produced during combustion.

Lamétherie staunchly maintained that the heat matter which causes changes of state is not combined with the substance. In 1781 he asserted that the mechanism of change of state is no different than that which causes substances to expand.[23] Fire matter penetrates without combining.[24] In 1786 he said that the term specific heat means the same as latent heat.[25] Although this heat is essential to substances, it is not combined with them, for substances can contain more or less of this heat matter without it changing their fundamental nature.[26]

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[20]Jean Claude de Lamétherie, "Discours préliminaire," Journal de physique, I [XLIV] (An II [1794]), 32.

[21]Jean Claude de Lamétherie, Théorie de la terre (3 vols.; Paris, An III (1795)), I, 99.

[22]Lamétherie, Journal de physique, III [XLVI] (1798), 20.

[23]Lamétherie, Observations sur la physique, XVIII (1781), 232-233.

[24]Ibid., p. 318.

[25]Lamétherie, Observations sur la physique, XXVIII (1786), 12.

[26]Ibid.

Fire matter can indeed combine with certain substances; but this combined fire is not the same as latent heat. For example, inflammable air contains a large quantity of the fire principle in it in a combined state, whereas pure air contains a large quantity of latent heat which is not combined.[27] When these two airs unite, heat is released from both of them, and thus the heat from pure air forms only part of the total heat released.[28] Acids, he continued, owe their activity to the heat matter they contain. But the heat matter released by acids in certain reactions is in a different form from that contained in pure air; for acids are active by themselves, whereas pure air is not.[29]

Lamétherie repeatedly insisted that the two forms, latent heat and combined heat, are different. Quick-line, he said, contains an active principle which is a modification of fire. Expose substances to fire and they acquire a certain degree of heat proportional to their specific heat. However, expose quick-lime to a high or low temperature and it still retains its burning quality. Hence the difference between free and combined fire.[30] The specific heat of pure air is indeed great, but specific heat indicates only the quantity of uncombined heat, not the quantity combined.[31]

Returning again to the heat of combustion, Lamétherie claimed that if pure air does indeed furnish all of the heat and flame observed, then heat and flame should appear in all cases where pure air combines;

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[27] Ibid., p. 14. [28] Ibid., pp. 16-17. [29] Ibid., p. 17.

[30] Lamétherie, Observations sur la physique, XXX (1787), 223.

[31] Jean Claude de Lamétherie, "Discours préliminaire," Observations sur la physique, XXXII (1788), 15.

but this is not the case. Furthermore, other fluids are rendered aeriform by heat, but they do not produce flame when they are condensed.[32]

As far as Lamétherie was concerned, the fundamental tenet of the new chemistry is that the flame of combustion comes uniquely from the heat or light released from pure air.[33] He admitted that Crawford's high specific heat of pure air seems to support this view, but he added that the latest edition of Crawford gave inflammable air an even greater specific heat.[34]

In 1791, Berthollet published a work on dyeing in which he gave a short discussion of the heat derived during combustion.[35] He said that although it is stated that vital air is the source of the heat of combustion, this statement is not to be construed as denying that some heat can be contributed by the substance which burns, "quoiqu'en fixant son attention sur la cause principale de ce phénomène, on se soit quelquefois contenté de l'indiquer seule."[36] It is probable and satisfying that the heat of combustion comes from vital air; but other substances can also contribute heat, and among these hydrogen is of the first rank.[37]

Lamétherie quoted Berthollet's statements regarding combustion as showing that at last the antiphlogistonists were listening to

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[32]Lamétherie, Observations sur la physique, XXXIV (1789), 29-30.

[33]Lamétherie, Observations sur la physique, XXX (1787), 29.

[34]Lamétherie, Observations sur la physique, XXXIV (1789), 25, 30; for his criticisms of Crawford, see pp. 217-218, Chapter VI, above.

[35]Claude Louis Berthollet, Eléments de l'art de la teinture (2 vols.; Paris, 1791).

[36]Ibid., I, 183, note. [37]Ibid.

reason.[38] This, he said, is what he had been advocating all the time: the heat of combustion does not derive entirely from pure air. He had stated previously that he felt the opposing doctrines were, in principle, not so far apart as one would think.[39] Now, he felt, the differences were to a large extent reconciled:

> Nous voilà donc d'accord. Toute cette fameuse dispute est terminée, & se réduit à une querelle de mots. On substitute le mot CALORIQUE COMBINE, à celui DE PHLOGISTIQUE OU PRINCIPE INFLAMMABLE; car par principe inflammable je n'ai jamais entendu que la substance qui dans la combustion fournit la flamme, ou la chaleur & la lumière; mais d'ailleurs on convient unanimement que dans la combustion, les corps combustibles fournissent de la lumière & de la chaleur; l'air pur fournit de la lumière & de la chaleur: il ne s'agira plus que d'en déterminer la quantité respective.[40]

But, Lamétherie said, he could not agree with Berthollet that it is the caloric which gives the elastic state to vital air that furnishes the heat and light of combustion. In the first place, caloric which is combined with vital air to give it the gaseous state is not sufficient to produce the effects attributed to it during combustion. Second, there are many phenomena in which pure air <u>not</u> in the elastic state produces the same effects as when it is in the elastic state, for example, pure air in gun powder and in fulminating calces. In all of these, great quantities of heat and light are produced, and yet pure air is not in an aeriform state. Similarly, all reactions with pure air <u>in</u> the aeriform state do not produce the same effects, for some reactions produce little light and others produce little heat. Finally, the caloric which holds pure air in its elastic state is no different from the

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[38] Lamétherie, <u>Observations sur la physique</u>, XXXVIII (1791), 394-395.

[39] Lamétherie, <u>Observations sur la physique</u>, XXX (1787), 31.

[40] Lamétherie, <u>Observations sur la physique</u>, XXXVIII (1791), 396.

caloric which forms other airs or gases. Why then, he asked, when these other substances cease to be elastic, do they not give up heat and light also.[41]

Furthermore, Lametherie said, it cannot be the caloric which is combined in substances that alone produces their portion of the effects of combustion; for in the new nomenclature, this caloric is only "latent heat" or "heat matter"; and in combustion, light as well as heat or caloric is produced; and light and heat, so the caloricists say, are different elements.

Lametherie felt that the elements light and heat, perhaps combined, are contained in combustible substances as a principle of inflammability, although he was indifferent to the names given to this principle. This principle acts like water in salts. Water of crystallization may be actually combined and separable only by decomposition. Water also may be in the form of what he called hygrometric water or "eau latente" which depends upon the humidity of the atmosphere and the capacity of the substance to attract this humidity. Latent or specific heat can vary in the same way, depending upon external temperature and the capacity of the particular substance for heat.

However, combined caloric, perhaps united with light, cannot vary in this manner. It cannot be removed unless some decomposition occurs, unless there is a change caused by different chemical affinities.[42] Latent heat cannot be combined, for simple change in external temperature

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[41] Ibid., pp. 396-397.

[42] Ibid., pp. 397-399.

is sufficient to remove it. Combined heat, on the other hand, requires a chemical transformation, a decomposition, to remove it.[43]

In 1798 Lamétherie summarized his argument against the then prevailing heat theory and presented his ideas on the possible states of fire matter or caloric.[44] He said that the molecules of fire matter have the greatest tenuity of all substances; they have a great force to expand all substances and a great force of repulsion among themselves. These properties are due to the spherical shape and "mouvement giratoire" of fire molecules.[45]

Fire matter can exist in three different states. Lamétherie equated "feu thermométrique" to caloric of the new chemistry. In this state, fire is a fluid expanded everywhere. It penetrates all substances and enters them without altering their nature. Fire, acting as caloric, causes substances to assume the three states of solid, liquid, and gas.

As caloric, fire is not combined, for a combination of substances can only be broken by another substance which has more affinity for one of the constituents than the constituents have for each other. But there is no need for new combinations to separate caloric from substances whether they be solid, liquid, or aeriform. All that is needed is to place these substances in a region which contains less external caloric. The reason some aeriform substances do not condense into liquids is because the degree of cold is insufficient, not because caloric is combined

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[43]For other arguments against the combination of heat in changes of state, see pp. 208-209, and n. 104, n. 107, Chapter VI, above.

[44]Lamétherie, Journal de physique, III [XLVI] (1798), 17-21.

[45]Ibid., p. 17.

in them. Fire in the state of caloric has different affinities for different substances. This affinity is called specific heat. Latent heat is only a modification of specific heat, and latent heat does not combine with substances to change their state.[46]

In addition to being free and uncombined, fire matter may combine with other substances and be disengaged from these substances by double elective affinities. When combined, fire can exist in two forms. Lamétherie described the first of these combined forms as fire acting as the principle of causticity. In this state, the fire particles retain part of their activity. As examples of substances containing caustic fire, he listed quick-lime, caustic alkalies, and acids. The second form of combined fire is fire acting as the inflammable principle. In this state, the fire matter has no activity. Examples of substances containing inactive fire are inflammable air, sulfur, carbon, in short, all combustibles. Combined fire is also called phlogiston.

Whether fire acts as the principle of causticity or as the principle of inflammability, it can be separated from the substance with which it is combined only by some chemical reaction. In this reaction, some other substance, for example, pure air, must have a greater affinity for the substance containing the combined fire matter than the fire matter has for the substance. In cases such as this, pure air unites with the substance and fire matter is expelled.[47]

In all of this, Lamétherie never questioned the existence of heat as a material substance. But he was never satisfied with the heat

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[46] Ibid., pp. 18-19. [47] Ibid., pp. 19-20.

theory associated with the new chemistry. Indeed, in 1802 he attributed the denial of the existence of this heat matter by "plusieurs physiciens célèbres" as evidence indicating the weakness of current theory and that ideas concerning caloric were "si peu avancées."[48]

Lamétherie was a confirmed phlogistonist. He was willing to accept a good deal of the new chemistry, but he insisted that the phenomenon of combustion depends to some extent upon the composition of the combustible substance. He eventually accepted the definition of combustion as the union of pure air with the combustible, with a concomitant release of heat and light; but the point of contention was the source of the heat and light released. He unfailingly denied the assertion that all the heat derives from pure air. This was the nub of his disagreement, and for this reason he regarded the heat theory associated with the new chemistry as the single foundation upon which the entire structure of the oxidation hypothesis rested.

Of similar mind was James Hutton (1726-1797). Both Hutton and Lamétherie thought that the oxidation theory was founded upon the belief that the latent heat of vital air is the source of heat released during combustion, that this heat is sufficient to account for all phenomena associated with this reaction, and that postulating a substance called phlogiston as a constituent part of the combustible is unnecessary to explain the phenomena observed.[49] And both agreed that this explanation

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[48]Jean Claude de Lamétherie, "Discours préliminaire," Journal de physique, LIV (An X (1802)), 14. He probably meant Count Rumford and Sir Humphry Davy.

[49]There is some indication that Lavoisier himself considered latent heat as fundamental to his theory. Sir James Hall (1761-1832),

was inadequate. Hutton thought that the trouble with the antiphlogistonists was that they had become so engrossed over the production of water from vital and inflammable air and over the weight relations involved that they had forgotten about the heat and light produced.[50] A similar complaint had been voiced by the committee appointed to report on the new nomenclature to the French Academy of Sciences.[51]

Hutton said that the antiphlogistonists explain the heat of combustion as being analogous to the release of heat by the condensation of steam. "Thus Calorique would be no other than what was termed by Dr Black the latent heat of those elastic fluids."[52] In other words, the latent heat of vital air is the same as the heat required to give the

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in a letter written in 1786 in which he described some conversations with Lavoisier, credited Lavoisier with saying "the whole [oxidation theory] is founded on the theory of Latent heat. . . ," and that "latent Heat and fix[ed] air are two of its [the new theory's] fondation stones"; quoted in Victor A. Eyles, "The Evolution of a Chemist, Sir James Hall, Bt., F.R.S., P.R.S.E., of Dunglass, Haddingtonshire, (1761-1832), and His Relations with Joseph Black, Antoine Lavoisier, and Other Scientists of the Period," Annals of Science, XIX (1963), 167, 169-170.

[50]James Hutton, Dissertations on Different Subjects in Natural Philosophy (Edinburgh, 1792), p. 180. For a brief survey of Hutton's views, see James R. Partington and Douglas McKie, "Historical Studies on the Phlogiston Theory: III. Light and Heat in Combustion," Annals of Science, III (1938), 366-370. The authors's claim (p. 368) that Hutton's theory is almost identical with Crawford's is an oversimplification. V. A. Eyles suggests that Hutton's writings in support of the phlogiston theory derived originally from a series of debates between him and Sir James Hall which took place during several meetings of the Royal Society of Edinburgh in 1788. Hall defended the new chemistry; Annals of Science, XIX (1963), 171-173.

[51]Louis Bernard Guyton de Morveau, et al., Méthode de nomenclature chimique proposée par mm. de Morveau, Lavoisier, Bertholet, & de Fourcroy, on y a joint un nouveau système de caractères chimiques, adaptés à cette nomenclature par mm. Hassenfratz & Adet (Paris, 1787), p. 249. The committee consisted of Antoine Baumé, Antoine Alexis Cadet de Vaux (1743-1828), Jean d'Arcet (1725-1801), Balthazar Georges Sage (1740-1824). Their report was printed in the Méthode de nomenclature chimique, pp. 238-252.

[52]Hutton, Dissertations, p. 183.

air the state of an elastic fluid. Can this heat, the heat of vaporization of vital air, account for the phenomena of combustion, and especially the combustion of vital and inflammable air?

In the first place, Hutton argued, the two airs do not unite when merely mixed. This failure to unite is not caused by the latent heat of the airs, as claimed by caloricists. Indeed to assume that it is "would plainly contradict every thing that we know."[53] For fluidity is no hindrance to chemical action, it is a necessary prerequisite, and elastic fluidity is no exception to this. For example, the latent heat of water does not prevent it from combining with lime or alkalies, even when the water is in the form of steam.[54] To say that the heat which keeps the two airs in the elastic state is different from latent heat "is giving up the argument."[55]

In the second place, he continued, assuming that the heat responsible for the elastic state of the two airs is in the form of latent heat, then how is it to be removed so that the airs can unite. By cooling, he asked? No, by increasing the heat. How is it possible for an increase in sensible heat to cause a release of latent heat? Clearly, the heat cannot be in the form of latent heat.[56]

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[53] Ibid., p. 185.

[54] Ibid., pp. 185-186, note.

[55] Ibid., p. 186.

[56] Ibid. Similar doubts regarding the reaction between vital and inflammable air had been raised by Gaspard Monge. Monge said that to assume an increase of heat should decrease the adherence of heat to the base of the two airs "est absolument contraire à ce qu'on observe dans toutes les opérations analogues se la Chimie"; see p. 141, Chapter V, above. The question of how the heat which causes substances to expand should cause air to become fixed was also raised by Friedrich Albert Carl Gren (1760-1798); see James R. Partington and Douglas McKie, "Historical

Hutton admitted that the assumption that elastic fluids contain latent heat is entirely consistent with Black's theory. However, the question is whether this heat is sufficient to account for combustion phenomena.

> That the latent heat of those aeri-form substances [vital and inflammable air] would be sufficient to heat a solid body, equal to the water, to the most intense degree of incandescency, will be readily granted, and is a conclusion that necessarily flows from the doctrine of latent heat. But it must be attended to, that, in the experiment we are considering, when the water is formed and heat appears, the two aeri-form fluids, or rather the water into which they are now changed, does not concrete into a solid substance; it is at first in the form of a vapour, which occupies as much space as the two aeri-form fluids did before they acted on one another, and which therefore must require the whole, or nearly the whole, of their latent heat, to give it that form, without being made sensibly hotter by it than they were before.[57]

He concluded that the explanation of heat of combustion as due to the latent heats of the fluids "is inconsistent with the doctrine of latent heat, which teaches that this heat never becomes sensible, except when the fluid containing it is condensed or congealed."[58] The production of heat and light in this case cannot come from caloric, at least not if caloric is supposed to be some known form of heat.

Argument concerning changes in volume or density forms the basis of Hutton's objection to explaining heat of combustion in terms of latent heat theory. For latent heat to become sensible, there must be condensation; and the quantity of latent heat released is proportional to the decrease of rarity or expansion. Hutton said that solids contain no

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Studies on the Phlogiston Theory: II. The Negative Weight of Phlogiston," Annals of Science, III (1938), 29.

[57]Hutton, Dissertations, pp. 189-190.

[58]Ibid., p. 190.

latent heat. Thus according to Lavoisier's theory, when iron or sulfur, for example, are burned, the heat released must come from vital air. If this were true, then inflammable air contributes none of the heat released in the production of water. Yet latent heat is proportional to the degree of expansion; and inflammable air, which is ten times more rare than vital air, should contain ten times more latent heat than vital air; but this is denied by the antiphlogistonists.[59]

Hutton also cited the reaction between niter and sulfur as releasing a great quantity of heat. Yet there is no condensation of air in this reaction, and both of these substances are solids, presumably containing no latent heat. He remarked that Lavoisier argued that the oxygen combined in acid of niter retains much of its caloric. Hutton replied that

> To suppose that a body [oxygen gas] should lose its state, not only of gas, but also of fluidity, and at the same time retain that quantity of heat by which those effects had been produced, is to feign a cause for a perceived effect, or gratuitously to suppose an effect without the smallest shadow of inductive reasoning, which physical science necessarily requires.[60]

Furthermore, in burning charcoal, a substance is expanded and evaporated instead of being condensed. For Hutton, these examples were sufficient to demonstrate that latent heat theory cannot explain the heat of combustion.

Hutton thought that the only adequate explanation of the phenomena of combustion is to assume the existence of a substance which

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[59] Ibid., pp. 191-192. See the arguments of Robert Kerr (1755-1813), pp. 244-245, below.

[60] Ibid., p. 194.

causes heat and light, but a substance which is not transferable as sensible heat is transferable, and which is different from that which expands substances and is the cause of fluidity.[61] Having shown that the heat of combustion cannot be the latent heat of vital air, Hutton said that

> . . . the French philosophers who deny phlogiston, must say what this calorique of theirs is; for, being neither sensible heat, heat of fluidity, nor that of fluid elasticity, it must either be a word to us without a meaning, or it must mean the same thing as our term phlogiston, which properly expresses an unknown cause producing light and heat.[62]

Arguments against phlogiston based upon its weightlessness are meaningless. "A blind man," Hutton said, "might as well pretend to judge of colours by his feeling, as a chymist to be sensible of phlogiston by his balance."[63] He admitted that the term phlogiston has been misapplied in the past. But to eliminate it because of this "would be like a noxious use of the pruning knife, lopping off the bearing branches with the useless wood."[64]

The release of phlogiston is the cause of the sensible heat and light of combustion; and as such its substantive nature cannot be much different from that matter which is the cause of sensible heat. Hutton considered phlogiston and heat (as well as electricity) to be different modifications of light, or "the solar substance" as he commonly called it.[65] Indeed, he thought these modifications to be convertible; heated substances emitting light are losing heat and cold substances receiving

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[61] Ibid., p. 199. [62] Ibid., p. 203. [63] Ibid., p. 204.
[64] Ibid., p. 211. [65] Ibid., pp. 266, 505-506.

light are being heated.[66] Light may be considered as "the matter of heat separated from bodies, and moving with extreme velocity."[67]

Although phlogiston and sensible heat are substantively the same, they are different in their actions. Sensible heat is a fluid which is transferable by simple change of temperature, a substance which can expand other substances and can produce changes of state. There is no justification to assume that sensible heat can act any other way.[68] Yet heat is released during combustion, a release which cannot be explained in terms of the known laws concerning sensible heat. Light matter is combined in substances in the form of phlogiston; in the form of heat, it is not combined. The heat of combustion is due to the release of phlogiston, combined light, from the combustible substance.[69]

Hutton believed that there are two fundamental forces or actions in nature. The first is the force of gravity or cohesion which tends to draw particles together, the second is the expansive force of heat matter which tends to separate particles.[70] Therefore, all substances are essentially composed of heat matter and gravitating matter in various proportions.[71] The volume of an object depends upon the balance between these two opposing forces of gravity and heat expansion.[72] Temperature represents the intensity of heat, not the quantity; and this intensity can be changed in two ways, either by a change in volume, caused by an external force, or by a change in the quantity of heat matter without a change of state.[73]

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[66] Ibid., p. 497. [67] Ibid., p. 496. [68] Ibid., pp. 238-241.
[69] Ibid., p. 257. [70] Ibid., pp. 404-405. [71] Ibid., p. 434.
[72] Ibid., p. 448. [73] Ibid., p. 441.

Hutton said that within a solid substance, there are two distinct forces tending to unite the particles. One of these is gravity, the force of which is proportional to the distance among the particles. The other force is the "power of concretion."[74] The concreting power prevents movement of particles with respect to each other. It operates only at very close distances among particles. Once the particles are separated by this minute distance, the concreting force ceases to act.[75] Then gravity alone tends to unite the particles, and the particles are free to move with respect to each other. During liquefaction, the latent heat of fusion is used to overcome this concreting power; and because the concreting force acts over such a small distance, the expansion necessary to remove particles from the sphere of activity of this force is imperceptible.

Hutton stated that it is only with respect to the force of concretion that phlogiston, combined light, may act to some extent like sensible heat. Although not causing increased temperature, phlogiston does tend to decrease the concreting force to some degree. This results in the observed ductility and malleability of some phlogisticated substances.[76]

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[74] Ibid., pp. 470, 649.

[75] Ibid., p. 631. A similar idea had been stated by Isaac Newton: "I had rather infer from this Cohesion [among the particles of a substance], that their Particles attract one another by some Force, which in immediate Contact is exceedingly strong, at small distances performs the chymical Operations above mention'd and reaches not far from the Particles with any sensible Effect"; Opticks, or a Treatise of the Reflections, Refractions, Inflections, and Colours of Light (2d ed.; enlarged; London, 1718), p. 364.

[76] Hutton, Dissertations, p. 548.

Hutton considered that the latent heat of vaporization is used to overcome the remaining uniting force within the substance, that is, gravity.[77] The absorption of this heat without a temperature increase is due to the dramatic volume change which occurs.[78] The reason that more heat is absorbed during vaporization than during fusion is that with expansion, the force of heat repulsion decreases faster than that of gravity. Hence more heat matter is required to produce the same effect when the particles of a substance are more separated.[79] Since volume and hence the state of a substance depend upon the balance between heat repulsion and the uniting powers, external pressure will affect this balance with respect to the quantity of heat necessary to overcome the uniting forces.[80]

Hutton stated that the matter of light is uncombined when it acts in the form of heat, that is when causing expansion and changes of state, and his descriptions of this matter when it is in the form of heat are entirely in terms of mechanical action rather than chemical combination. In the form of heat, this matter acts as a agent rather than as a constituent. Phlogiston, on the other hand, is the combined matter of light; and its actions are entirely different from light when it is in the form of heat.

Hutton's attack upon the caloric theory is based upon a demonstration that the production of heat during combustion cannot be explained in terms of light matter in the form of heat. His argument was

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[77] Ibid., pp. 636-637.

[78] Ibid., pp. 451-452.

[79] Ibid., p. 478.

[80] Ibid., pp. 659-660.

that the antiphlogistonists had erroneously attempted to apply the theory of latent heat to explain the heat of combustion. He had no argument with the theory of latent heat. In fact, in the preface to his Dissertations of 1792 he was extravagant in his praise of Black and the concept of latent heat. In that preface Hutton described latent heat as "a Law of Nature most important in the constitution of this World, -- and a Physical Cause, which, like Gravitation, although clearly evinced by science, is far above the common apprehension of mankind."[81] The trouble with the French chemists was that they had failed to understand this law. He concluded that

> As much as the theory of latent heat has done honour to science, that of calorique has disgraced it, in being plainly inconsistent with the only principle on which it is founded, which is that of latent heat.[82]

In his 1794 Dissertation on Light, Heat, and Fire, Hutton followed the theoretical foundations expressed in his Dissertations of 1792.[83] He repeated his explanations of melting and vaporization,[84] and his argument that the heat of combustion does not derive from the latent heat of vital air.[85] He said that he could not deny that the condensation of vital air will produce heat; but he did deny that heat produced in this manner is sufficient to account for all the heat of

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[81] Ibid., p. [i].

[82] Ibid., p. 638, note.

[83] James Hutton, A Dissertation Upon the Philosophy of Light, Heat, and Fire, in Seven Parts (Edinburgh, 1794), abstracted in James Hutton, "Dissertation on the Philosophy of Light, Heat, and Fire [1794]," Transactions of the Royal Society of Edinburgh, IV (1798), History of the Society, pp. 7-16.

[84] Hutton, Dissertation on Light, Heat and Fire, p. 142.

[85] Ibid., pp. xvii, 146-147.

combustion.[86] The latent heat of vital air which is released by condensation is but "a small thing compared with the quantity of heat which is constantly abstracted by the atmosphere in contact with the burning body. . . ."[87]

The chief difference between this work of 1794 and the earlier one is in Hutton's discussion of radiant heat phenomena and in his repeated emphasis that the matter of light is the basic substance of both heat and phlogiston. This discussion of radiant heat was inspired by the experiments of Horace Bénédict de Saussure (1740-1799) and Marc Auguste Pictet (1752-1825).[88] Hutton's primary objection to de Saussure was the latter's explanation of radiant heat as being the matter of heat itself rather than the matter of light, as Hutton maintained:[89]

> We know heat only as a quality of bodies, and as acting either in expanding them, when it is called sensible heat, or in giving them fluidity, when it is termed latent heat. We never perceive it as existing in any other shape, and therefore, to suppose it capable of moving through space, independently of body, and of being reflected from a polished surface, is to ascribe to heat properties not predicable of it, and quite inconsistent with its nature, so far as we have information concerning it.[90]

To assume that heat can move without a substance and act like light is an "idea that would disgrace science."[91]

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[86] Ibid., p. 157.

[87] Ibid., pp. 157-158, note.

[88] Ibid., pp. [i], iii, 24-25. For a brief discussion of Saussure's and Pictet's experiments, see E. S. Cornell, "Early Studies in Radiant Heat," Annals of Science, I (1936), 222-224.

[89] Hutton, Dissertation on Light, Heat, and Fire, pp. 24-25, 29, 34.

[90] Hutton, Transactions of the Royal Society of Edinburgh, IV (1798), 8.

[91] Hutton, Dissertation on Light, Heat, and Fire, p. 34.

The experimentum crucis had already been performed by Pictet; but he had completely missed the point. Pictet had shown that the smoked bulb of a thermometer placed in the focus of a concave mirror heats more quickly and the temperature rises higher than if an unsmoked bulb is used. Hutton considered that this demonstrates that radiant heat is really the transmission of light matter rather than a peculiar matter of heat; soot is well known as a poor conductor of heat, whereas it is an excellent absorber of light.[92]

Hutton assumed that radiant heat is a species of light, which he called invisible light, or "obscure light."[93] There is an infinite gradation in species of light with respect to their heating properties as well as their visibilities.[94] Light matter ceases to be light and is transformed into heat when it becomes attached to another substance.[95] It becomes phlogiston when it combines with the other chemical elements of the substance.[96]

Pictet believed that there is no radiation among substances which are at a common temperature. A cold substance disturbs the equilibrium, and only then does radiation occur from warmer objects to the cold one. Hutton said that there is no reason why a cold substance should have any effect on the radiation from a warmer one. He concluded that all substances radiate invisible light, regardless of their temperature.[97] The quantity of radiation varies with the temperature of

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[92] Ibid., pp. 51-52.

[93] Ibid., pp. 44, 58.

[94] Ibid., pp. 37, 59.

[95] Ibid., p. 60.

[95] Ibid., p. 148.

[96] Ibid., pp. 73-76.

the substance; and the temperature change of the substance is determined by the ratio between the radiation received and that given off.[98] This theory of mutual irradiation had been proposed in 1791 by Pierre Prevost, although Hutton was probably not aware of it.[99]

Based upon his theoretical arguments, Hutton said that the use of the word "calorique" would "vitiate the science or philosophy in which it were employed."[100] Others opposed the word for various reasons. Jean André Deluc complained that "il ne fut jamais de mot plus inutile que celui de calorique. ..."[101] The word is equivocal, and besides "feu" means the same thing.[102] Stephen Dickson felt the same way about it.[103] George Pearson (1751-1828), a pupil of Black's and a Fellow of the Royal Society, disliked "caloric" for in Latin the word indicates the sensation as well as the cause. He thought "calorific" was better.[104]

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[98] Ibid., p. 86.

[99] Pierre Prevost, "Mémoire sur l'équilibre du feu," Observations sur la physique, XXXVIII (1791), 314-323; see pp. 59-60, Chapter II, above; Cornell, Annals of Science, I (1936), 224-225.

[100] Hutton, Dissertation on Heat, Light, and Fire, p. 126.

[101] Jean André Deluc, "Troisième lettre de m. de Luc à m. Fourcroy sur la nouvelle chimie," Observations sur la physique, XXXIX (1791), 127.

[102] Ibid., pp. 126-130.

[103] Stephen Dickson, An Essay on Chemical Nomenclature (London, 1796), p. 77.

[104] Louis Bernard Guyton de Morveau, et al., A Translation of the Table of Chemical Nomenclature Proposed by de Guyton, Formerly de Morveau, Lavoisier, Bertholet, and de Fourcroy, with Explanations, Additions, and Alterations, to Which Are Subjoined Tables of Single Elective Attraction, Tables of Chemical Symbols, Tables of the Precise Forces of Chemical Attractions, and Schemes and Explanations of Cases of Single and Double Elective Attractions, trans. and ed. George Pearson (2d ed.,

Some Frenchmen objected on the grounds that the word was not fitting to genius of the French language. Balthazar Georges Sage (1740-1824), director of the Ecole des Mines, described the new nomenclature as barbarous, insignificant, and without etymology.[105] Christophe Opoix (1745-1840), an apothecary, described the new nomenclature as being barbarous and mysterious. As for the word "calorique," he said that it is an isolated word insufficient, inexact, improper, and without connection with the French language.[106] And Jean Louis Antoine Reynier (1762-1824), a holder of numerous governmental positions, sarcastically claimed that proponents of the new doctrine had banned words like "feu" because they are "trop clairs & trop faciles à pronouncer."[107]

In support of their thesis that combustibles contribute some of the heat of combustion, both Lamétherie and Hutton argued that if vital air were the sole source of heat, then the quantity of heat should be proportional to the quantity of vital air which combines with the combustible substance. However, this proportionality, they said, does not exist.[108]

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enlarged; London, 1799), pp. 27-28. Guyton had proposed this term in 1787; see note 67, p. 124 , Chapter IV, above.

[105]Balthazar Georges Sage, "Lettre de m. Sage à m. de la Métherie sur la nouvelle nomenclature," Observations sur la physique, XXXIII (1788), 479. Cf. Sage's views, p. 231 and n. 51, above.

[106]Christophe Opoix, "Lettre de m. Opoix, maître en pharmacie à Provins & membre de plusieurs académies, à m. de la Métherie sur la nouvelle théorie," Observations sur la physique, XXXIV (1789), 77-78.

[107]Jean Louis Antoine Reynier, "Lettre de m. Reynier à m. de la Métherie sur la nature du feu," Observations sur la physique, XXXVI (1790), 94.

[108]See pp. 224-225, 226, 233-234, above. Lavoisier recognized

The same objection was raised by Leopold Vacca Berlinghieri. Berlinghieri was arguing for his own phlogiston theory in which the heat of combustion is due to fire matter combined within the combustible substance. Phlogiston is different from fire; but it is phlogiston which enables fire to be fixed in substances. When phlogiston is removed by its affinity for vital air, the fire becomes free also.[109] In proposing this theory, Berlinghieri argued that if the new chemistry were correct, then the heat should always be proportional to the quantity of air used, and this is not true. One livre and eight ounces of vital air melts about 100 livres of ice when the air combines with phosphorous. But five livres and ten ounces of vital air melt only about 300 livres of ice when combining with inflammable air. If the same ratio were maintained, then in the last reaction, about 500 livres of ice should have been melted.[110]

Robert Kerr (1755-1813), Edinburgh physicial and translator of Lavoisier's Elements of Chemistry, discussed the problem regarding the various quantities of heat released in combinations of oxygen.[111]

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this and explained that not all the heat is released when vital air combines with substances, see pp. 127-128, Chapter IV, above.

[109]Leopold Vacca Berlinghieri, "Mémoire sur la nature du feu et du phlogistique," Observations sur la physique, XXXV (1789), 435-436. Cf. his arguments, discussed pp. 215-217, above.

[110]Ibid., p. 434.

[111]Antoine Laurent Lavoisier, Elements of Chemistry in a New Systematic Order, Containing All the Modern Discoveries, Illustrated by Thirteen Copperplates, trans. Robert Kerr (3rd ed., enlarged; Edinburgh, 1796). Kerr's discussion appears verbatim in the fourth edition (Edinburgh, 1799), p. 153, note, and in the fifth edition (2 vols.; Edinburgh, 1802), I, 153, note. Kerr's note is absent in the first edition (Edinburgh, 1790).

Referring to the combination of oxygen and hydrogen, Kerr said that as hydrogen is thirteen times more rare than oxygen then it should contain thirteen times as much caloric.[112] Thus the caloric released when these gases unite should melt over a thousand pounds of ice instead of the twelve pounds observed; but this is absurd.

> This shews the fallacy of all reasonings drawn from the supposable quantities of caloric in bodies; and that we are hitherto very far from possessing any accurate knowledge of that part of chemistry in which caloric is concerned.[113]

"P. F." thought that the release of caloric during the explosion of cannon powder to be the irreducible phenomenon which invalidates the new chemistry.[114] Lavoisier had explained that azotic acid retains a large part of the caloric it had in the gaseous state when it becomes fixed in potash. However, P. F. continued, gun powder is a solid substance; and according to the theory, the change from a solid to a gas should absorb all the caloric lost during solidification. Furthermore, as azotic acid is reduced to its elements during the explosion, it should absorb even more caloric.[115]

Luigi Valentino Brugnatelli (1761-1818), professor of chemistry at Pavia, also made an attempt to account for the different quantities of caloric released when oxygen combines with substances. Brugnatelli

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[112] See pp. 233-234, above, for a similar argument by Hutton.

[113] Lavoisier, Elements of Chemistry (Edinburgh, 1796), p. 153, note.

[114] P. F., "Mémoire sur un nouveau principe de la théorie du calorique," Journal de physique, IV [XLVII] (An VI [1798]), 103-106. Lamétherie referred to him as "P. F., Portugais" in "Discours préliminaire," Journal de physique, XLVIII (An VII (1799)), 12.

[115] P. F., Journal de physique, IV [XLVII] (An VI 1798), 104.

thought that the caloric contained in oxygen gas exists there in two distinct states. The calorique fondant, as he called it, is caloric which gives the substance its aeriform state. In its other state, caloric is chemically united to the oxygen. Thus the base of oxygen gas is really a compound of oxygen and caloric, rather than simple oxygen. He called this base "thermoxigène."[116] Thermoxygen can enter into combination with other substances when it loses its "calorique rayonnant fondant." However, some substances can combine with oxygen alone. Thus either pure oxygen or thermoxygen can unite with other substances, and whether oxygen or thermoxygen unites is determined by the quantity of caloric released.[117] Later he changed the name of "calorique fondant" to "calorique rayonnant ou élastifiant," but he mantained the existence of thermoxygen as an explanation of the retention of caloric by oxygen gas when it unites with other substances.[118]

For those who considered phlogiston itself to be a cause of heat, the heat theory associated with the new chemistry was more of a source of conflict than for those who considered phlogiston to be a substance sui generis. For the former, as epitomized by Lamétherie and Hutton, the caloric theory became the cornerstone of the new chemistry,

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[116]Luigi Valentino Brugnatelli, "Réflexions sur la différence qui existe entre l'oxigène et le thermoxigène," Annales de chimie, XXIX (An VII [1798]), 182.

[117]Ibid., p. 183.

[118]Luigi Valentino Brugnatelli, "Réflexion sur les différences qui se trouvent entre l'oxygène et le thermoxygène," Journal de physique, LIII (An IX (1801)), 354-357; James R. Partington and Douglas McKie, "Historical Studies on the Phlogiston Theory: III. Light and Heat in Combustion," Annals of Science, III (1938), 340-342.

the single pillar upon which the entire structure of the oxidation theory rested, which, if it could be destroyed, would bring about the collapse of the whole system.

Lavoisier probably would have agreed with them. Having banished phlogiston from the realm of existence, he was left with the task of accounting for the heat and flame of combustion. As attention was now focused upon vital air, by whose union with other substances the process of combustion was now uniquely defined, the source of this heat must be found in the composition of that permanently elastic fluid. And what nicer way to explain the presence of heat matter in oxygen gas than to turn to the doctrine of latent heat. Lavoisier's chief concern with heat seems to have been to substantiating this reasoning; and his heat theory is crucial to the explanation of his theory of gases. Thus in Lavoisier's mind, the caloric theory was probably the keystone in his explanation of combustion; and he implied as much in his conversations with Sir James Hall.

Hutton and Lamétherie, however, did not see as clearly as Lavoisier the analogy between the condensation of oxygen gas and the condensation of steam. And their arguments were devastating. If the formation of the permanently elastic fluids is analogous to the formation of steam, why then does heat and flame issue uniquely from oxygen gas when it condenses and not from the other gases when they condense. According to general latent heat theory, and the caloric theory as well, the conversion of a solid into a gas should result in the absorption of heat. Whence the heat and flame of gunpowder?

Some of Lavoisier's followers apparently recognized the difficulty, and there was an increasing tendency among some of them to abandon the analogy between vapors and permanently elastic fluids. Oxygen gas is indeed the source of the heat of combustion, but the nature of the existence of heat matter in this gas is nothing like the existence of heat in steam. Hutton agreed that the analogy is invalid and claimed this vitiated the caloric theory. Lamétherie disagreed saying that the analogy was valid; but he also claimed that the caloric theory was without foundation. Such is the latitude of explanation which can accommodate a given set of phenomena and still allow two men to assume opposite hypotheses and reach the same conclusions.

CONCLUSION

The concept of the existence of a material heat substance dominated the eighteenth century. The competing idea that heat is a quality, some kind of motion of the constituent particles of an object, had few adherents, even though there was scarcely a decade that some form of it was not offered as an explanation of heat phenomena. The vibratory theory received its strongest support from the mechanical production of heat, and it was by means of mechanically produced heat that Count Rumford, at the close of the century, attempted to give life to the motion concept.

However, arguments against this view of heat were strong and compelling. The chief was the restricted nature of most explanations based upon motion. A single, detailed, coherent theory involving motion, a motion theory which could encompass all the known heat phenomena, never appeared. It could not compete in either breadth or detail with the theory of heat as a material substance. As Rumford remarked,

> I am very far from pretending to know how, or by what means, or mechanical contrivance, that particular kind of motion in bodies, which has been supposed to sonstitute heat, is excited, continued, and propagated, and I shall not presume to trouble the Society with mere conjectures; particularly on a subject which, during so many thousand years, the most enlightened philosophers have endeavoured, but in vain, to comprehend.
>
> But, although the mechanism of heat should, in fact, be one of those mysteries of nature which are beyond the reach of human

> intelligence, this ought by no means discourage us, or even lessen our ardour, in our attempts to investigate the laws of its operation.[1]

Where the motion theory was lacking, the material theory provided an acceptable explanation. In this respect, the concept of latent heat, which was maintained by proponents of both schools of thought, was particularly compelling. What kind of motion is it which transforms a substance from a solid to a liquid and yet does not register on a thermometer? To this question, the vibrationists had no convincing answer. But in addition to indirect arguments based upon a lack of comprehensiveness in the vibratory theory, there were objections which attacked the motion concept directly. Chief among these was the claim that if heat were indeed a mode of motion, then it should follow the known laws of motion, and experience shows that it does not. This objection was voiced almost from the beginning of the eighteenth century to the last. Herman Boerhaave, who placed such emphasis upon the role of motion in explaining heat phenomena, argued that motion alone is not sufficient to account for all the appearances. Black stated that "We are not at liberty to feign laws of motion . . .," and heat phenomena do not conform to these laws. It is for this reason, he said, that the vibratory theory is "totally inconsistent with the phenomena. I do not see how this objection can be evaded."[2]

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[1] Benjamin Thompson, Count Rumford, "An Inquiry Concerning the Source of the Heat Which Is Excited by Friction," Philosophical Transactions of the Royal Society of London, LXXXVIII (1798), 99-100.

[2] Joseph Black, Lectures on the Elements of Chemistry Delivered in the University of Edinburgh, ed. with notes by John Robison (2 vols.; Edinburgh, 1803), I, 83.

The vibrations of the constituent particles of substances do not conform to the known laws of motion, but neither do the vibrations of the particles of fire. As fire is a kind of matter, it should obey the general laws which govern matter. Thus the inherent motion of the particles of elementary fire is inconsistent with the properties of matter in general, and during the 1770's, Lavoisier's quiescent fire substance replaced the dynamic, active fire of Boerhaave. This, however, was not the only change which the material theory underwent during the eighteenth century.

It is possible for fire matter to play two different rules in heat phenomena. It may act as an instrument in chemical operations, as an agent which separates the particles of substances, decreasing the cohesion among these particles to separate some constituents or to promote the combination of others. Fire may also be a constituent itself and combine or be separated from other principles as any other elementary substance. In the course of the eighteenth century, there was a progressive reduction in the role of fire as an agent or instrument with a concomitant expansion of the role of fire as a constituent or principle which could enter into the composition of <u>mixtes</u> or compounds.

For Boerhaave, the chief exponent of the material theory which dominated the first half of the century, fire matter was indeed an element, but he regarded it as an element apart. It could separate the particles of substances and it could be trapped within the pores of these substances; but it never became a constituent part of them. It was an omnipresent, vibrating fluid, penetrating all other matter, filling its pores. It could be concentrated and even hidden within objects so as to be imperceptible; but even when confined, fire never lost its

characteristics properties. It was always moving to expand objects, and when confined, it was always waiting for the opportunity to makes its presence known.

For Rouelle, however, whose chief spokesman was Macquer, the motion of fire could be largely arrested. It could enter substances as a constituent principle and combine with other principles. Fire never lost its tendency for motion, but motion itself ceased to a great extent when fire matter combined. When playing its new role as an elementary constituent of objects, the matter of fire was given a new name, phlogiston. Phlogiston was combined fire, not the vibrating fire particles encased within objects, but fire with its motion restrained, chemically united to the other elementary particles of which the object was composed. The fundamental characteristic of fire became not motion itself, but the tendency to motion, a tendency which was realized whenever fire matter became free. However, this transformation of fire was not complete, for the motion of fire when combined was not completely eliminated. To the small movement which remained was attributed the malleability and ductility of some phlogisticated substances.

The third step in the reduction of the role of instrumental fire occurred when the concept of latent heat was created. Heat matter was latent because it had become combined. The agent, free fire, was now restricted to explain the single phenomenon of expansion. Free heat, however, was not totally free. Lavoirier described all heat matter as being more or less adherent, and Black suggested that the heat which causes expansion was somehow united to the object expanded.[3] The transformation

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[3] Ibid., pp. 176, 192.

seemed complete. Virtually all heat phenomena were explicable in terms of combined heat matter. As fire had become combined and thus hidden in the formation of inflammables and metals, it was now combined and hidden in liquids and airs as well. However, just as the fixed fire of the phlogiston theory had provided a ready-made explanation of the concept of latent heat, the concept of latent heat was turned by Lavoisier to explain the heats of combustion and calcination. In his theory, the entire spectrum of heat phenomena, with the exception of expansion, was explained in terms of the concept of latent, that is, combined heat matter.

The explanation of changes of state in terms of fire matter acting as a constituent rather than as an agent and hence combining with substances to bring about this change was one innovation in Lavoisier's caloric theory. Lavoisier, however, was not the only one who had arrived at his particular explanation of fluidity and fluid elasticity, and several authors suggested similar ideas during the 1770's. Although Joseph Black never published his theory of latent heat, an account of these views appeared anonymously in 1770.[4] In 1772, a short article appeared in the Introduction aux observations sur la physique describing Black's theory that heat is absorbed and becomes hidden during fusion and vaporization and that this heat is the cause of fluidity and vaporous elasticity.[5] In the same volume of this journal, Lavoisier cited Black and

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[4] An Enquiry into the General Effects of Heat, with Observations on the Theories of Mixture (London, 1770), cited and discussed briefly in Douglas McKie and Niels H. de V. Heathcote, The Discovery of Specific and Latent Heats (London, 1935), p. 51.

[5] Joseph Black, "Expériences du docteur Black sur la marche de la chaleur dans certaines circonstances," Introduction aux observations sur la physique, II (1772), 428-431.

the constant temperature of melting ice and said that he could explain the phenomenon.[6]

In the same year, Johan Karl Wilcke published in the proceedings of the Swedish Academy of Science his theory of the latent heat of fusion,[7] and Jean André Deluc, in his Recherches sur l'atmosphère, described vaporization as being caused by a combination of fire with the particles of water.[8] To demonstrate his conclusion, Deluc cited the condensation of atmospheric vapor on the sides of a cold container and the cooling which accompanies evaporation.[9]

In 1774, Lavoisier published his Opuscules phisiques et chimiques in which he attributed the aeriform state in general to a combination of various substances with fire matter.[10] He said virtually the same thing again in a paper read to the French Academy of Sciences in 1777, although not published until 1780, and he extended this idea to liquids and the fusion process in another paper presented and published with the first paper.[11] Some of Black's views were repeated between 1778 and 1780 in

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[6]Antoine Laurent Lavoisier, "Expérience sur le passage de l'eau en glace, communiquée à l'Académie des Sciences," Introduction aux observations sur la physique, II (1772), 510-511. Lavoisier's explanation is supposedly contained in the MS discussed in n. 10, Chapter IV, p. 104, above.

[7]Johan Karl Wilcke, "Om Snöns kyla vid Smältningen," Konglia Svenska Vetenskaps Akademiens Handlingar, XXXIII (1772), 97 ff., cited and discussed in McKie and Heathcote, Latent Heats, pp. 78-94.

[8]Jean André Deluc, Recherches sur les modifications de l'atmosphère, contenant l'historie critique du baromètre et du thermomètre, un traité sur la construction de ces instrumens, des expériences relatives à leurs usages et principalement à la mesure des hauteurs & à la correction des réfractions moyennes, avec figures, dédiées à m. m. de l'Académie Royale des Sciences de Paris (2 vols.; Genève, 1772), I, 178, 180, 264-265; II, 175.

[9]Ibid., I, 182-183. [10]See n. 12, Chapter IV, pp. 104-105, above.

[11]See pp. 102-107, Chapter IV, above.

several articles published in the second edition of the Encyclopaedia Britannica,[12] in Crawford's book on animal heat, published in 1779,[13] as well as in Magellan's 1780 commentary on Crawford.[14]

These dates show that the ideas of latent heat and the combination of heat in changes of state were becoming widely spread during the 1770's. It is probable that Deluc, Wilcke, and Lavoisier, as well as Black, arrived at their views independently. However, Crawford and Lavoisier were the most effective in disseminating the concept of latent heat, in making it fundamental in heat theory, an idea taken for granted in subsequent explanations of heat phenomena. Crawford's work is highly quantitative, but Lavoisier was unaware of the quantitative aspect of Black's work and his own early explanations contain only a very qualitative theory that fire matter combines to bring about changes of state. His quantitative researches in the field were carried out after the appearance of Crawford's theory.

Although priority for the creation of the concept of latent heat belongs to Black, his own explanation of this concept seems to have remained virtually unknown outside the immediate circle of his students and associates. According to the Britannica, Black considered heat to

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[12] "Congelation," Encyclopaedia Britannica (2d ed., enlarged; 10 vols.; Edinburgh, 1778-1783), III (1778), 2188; "Evaporation," IV (1779), 2846-2848; "Fluidity," IV (1779), 3048; "Heat," V (1780), 3539, 3540-3541.

[13] Adair Crawford, Experiments and Observations on Animal Heat and the Inflammation of Combustible Bodies, Being an Attempt to Resolve These Phenomena into a General Law of Nature (London, 1779), cited in McKie and Heathcote, Latent Heats, p. 38.

[14] John Hyacinth Magellan, Essai sur la nouvelle théorie du feu élémentaire et de la chaleur des corps (London, 1780), cited in McKie and Heathcote, Latent Heats, p. 40.

be a substance, and he explained that heat becomes latent when it is "taken into the inmost essence or composition of the body, so as to become an essential part of itself."[15] This version of Black's ideas was repeated in John Robison's edition of Black's chemistry lectures.[16]

Black, Lavoisier, and many of their followers explained latent heat in terms of combined heat matter. But combined heat was not the only way to explain the absorption of heat during changes of state. Contemporary knowledge of Black derived mainly from Crawford; and Crawford and his supporters explained latent heat entirely in terms of changes in heat capacity, and they completely denied that heat matter combines with substances to bring about changes of state. And Lavoisier himself frequently used physical explanations of these changes, explanations which if examined alone can scarcely be distinguished from those of Boerhaave.

Nevertheless, latent heat theory was the basis of Lavoisier's concept of gases which in turn formed the basis for his oxidation theory of combustion. In this sense, latent heat theory was the foundation of the new chemistry, and many of Lavoisier's critics considered it as such as did some of his supporters. For example, Black said that the new theory "is founded on the doctrine of latent heat, and is, indeed, an extension of it."[17] To apply latent heat theory to explain the heat of

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[15] "Congelation," Encyclopaedia Britannica (2d ed.), III (1778), 2189; see also "Evaporation," IV (1779), 2847, 2848; "Heat," V (1780), 3539. The 1772 article in the Introduction aux observations sur la physique states only that heat is absorbed and becomes hidden in changes of state; ibid., II (1772), 428-431.

[16] Black, Lectures on Chemistry, I, 49, 129, 131, 133, 157, 161, 165, 176, 192-195.

[17] Ibid., p. 239.

combustion, Lavoisier had ranked vapors and airs or gases together as being identical in that they were formed by the same process. But the heat combined in vapors forms such a feeble union that a mere decrease in external temperature is sufficient to destroy it, whereas the union of heat in airs is so strong as to require a third substance to overcome it; and there are many other phenomena of gases which have no analogy with those of vapors. This was the basis for the devastating criticisms of Hutton and Lamétherie.

There is a considerable correspondence between caloric and phlogiston, that is, phlogiston as it was usually described. To men like Priestley and Crawford, who considered phlogiston to be a substance sui generis and different from the matter of heat, there was little correspondence. But most of these variant theories of phlogiston were later developments, created in response to criticisms from the proponents of the new chemistry. For most of Stahl's followers, however, phlogiston was the matter of fire which had become fixed in substances; and caloric was the new name given to this matter, the material cause of heat. In this sense, caloric was Boerhaave's fire matter deprived of its motion; it was also Stahl's phlogiston, at least phlogiston as Rouelle described it, combined in oxygen gas rather than in the combustible substance. Just as Macquer had attributed the qualities of softness, ductility, and malleability to the phlogiston combined within substances, so Black attributed these same properties to latent heat.[18]

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[18] Ibid., pp. 138-140.

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