

LAVOISIER AND THE CALORIC THEORY

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Introduction

PROFESSIONAL historians of science generally recognize the importance of Lavoisier's theory of heat. However, it commonly receives scant attention in the historical treatment of his chemical theories except perhaps as an example illustrating his conservatism and giving the impression that the caloric theory, although perhaps important in the development of ideas on the nature of heat, is independent of and bears little relationship to his general chemistry or is incidental to an understanding of that chemistry.¹ An examination of Lavoisier's writings suggests that the caloric theory is not merely a milestone in the development of physics; and rather than an omittable appendage, his concept of heat forms an integral part of his chemical system and plays a central, necessary role in his oxidation theory in particular. The purpose of this paper is to give a general description of Lavoisier's ideas on the nature and action of heat, the origin of these ideas, their development, and their relation to his general chemistry, pointing out his conservatism as well as his innovations.

Formative period, 1766-77

Lavoisier's detailed presentation of his theory of heat first came with the reading of the papers printed in the *Mémoires* of the French Academy of Sciences for 1777. Prior published references to a theory of heat are very limited. Indeed, there are only two which mention heat in some sense other than as an agent used in chemical manipulations, and the first only mentions the existence of a theory of heat without saying what it is. In 1772 in a very short paper in Rozier's journal,² he referred to a report made to the Academy of Sciences on some ideas of Joseph Black.³ Lavoisier cited the constant-temperature melting of ice, stated that he had had a similar experience the previous year (in September 1771), and closed by remarking that he could explain this phenomenon but his explanation was

¹ The following examples are illustrative. Heat theory is ignored in a discussion of Lavoisier's chemistry in A. Wolf, *A History of Science, Technology & Philosophy in the 18th Century* (2nd edn., 2 vols., New York: Harper, 1961), i, 366-75. It is all but ignored in this connexion in A. R. Hall, *The Scientific Revolution, 1500-1800* (Boston: Beacon, 1956), pp. 328, 336-67. As an example of Lavoisier's conservatism, see H. Butterfield, *The Origins of Modern Science, 1300-1800* (new edn., New York: Macmillan, 1960), p. 207. Certainly not all historians have ignored the chemical role of caloric; see J. R. Partington, *A History of Chemistry* (4 vols., London: Macmillan, 1961-70), iii, 421-2.

² 'Expérience sur le passage de l'eau en glace communiquée à l'Académie des Sciences', *Introduction aux Observations sur la Physique*, ii (1772), 510-11.

³ The report was made in August 1772 and subsequently published: 'Expériences du docteur Black sur la marche de la chaleur dans certaines circonstances', *Introduction aux Observations sur la Physique*, ii (1772), 428-31. For the report on Black to the Academy see H. Guerlac, *Lavoisier—The Crucial Year: The Background and Origin of his First Experiments on Combustion in 1772* (Ithaca, N.Y.: Cornell Univ. Press, 1961), pp. 68-9, 92-3.

related to a paper on the elements which was nearing completion (but which, as it happened, was never published).⁴

His other published reference to a theory of heat dating from before 1777 is also brief but more substantial. In a short passage in his *Opuscules* of 1774, he described his idea of the nature of fluid elasticity as being simply a state produced by the matter of fire⁵ combining with some other substance:

tout fluide élastique résulte de la combinaison d'un corps quelconque solide ou fluide, avec un principe inflammable, ou peut être même avec la matiere du feu pur, & que c'est de cette combinaison que dépend l'état d'élasticité . . .⁶

Fortunately three manuscripts from this period are extant which not only relate to the origins of Lavoisier's theory of heat but also show that, although not published in any detail until 1777-8, some of the main features of the theory were suggested as early as 1766, outlined by the middle of 1772, and firmly stated in April 1773.

In 1766 Lavoisier wrote a short paper on the nature of the chemical elements.⁷ Accepting the traditional four elements and the theory that each can exist in two forms, free and fixed, he speculated briefly on the nature of water vapour and of air.

⁴ This is the manuscript of July 1772 discussed below. Concerning its identity with that to which Lavoisier referred, see Guerlac, *op. cit.* (3), pp. 93-7.

⁵ Lavoisier used various terms to indicate heat matter. In manuscripts of 1773 and in his *Opuscules* he referred to this fluid as phlogiston or an inflammable principle; see René Fric, 'Contribution à l'étude de l'évolution des idées de Lavoisier sur la nature de l'air et sur la calcination des métaux', *Arch. Int. Hist. Sci.*, xii (1959), 149-50, and *Opuscules Physiques et Chimiques* (Paris, 1774), pp. 279-80. However, Lavoisier's later denial of the existence of phlogiston resulted in his subsequent use of different terminology. Except for this restriction, prior to the nomenclature revision of 1787 (L. B. Guyton de Morveau *et al.*, *Méthode de Nomenclature Chimique proposée par MM. de Morveau, Lavoisier, Berthollet, & de Fourcroy* [Paris, 1787], cited hereafter as *Nomenclature Chimique*), Lavoisier was indifferent to the terminology he used. He called heat the igneous fluid, fire matter, heat matter, the principle of heat, the matter of fire or light, the matter of fire, heat, and light, in addition to other similar phrases. In the manuscript preparation of his *Traité de Chimie* he proposed the terms 'thermogène' and 'principe échauffant' (quoted in M. Daumas, 'L'élaboration du *Traité de Chimie* de Lavoisier', *Arch. Int. Hist. Sci.*, iii [1950], 580, 584), although in the published *Traité* he used 'calorique', conforming to the new nomenclature (*Nomenclature Chimique*, p. 30). The term 'calorique' was probably Guyton's invention. The adjective 'calorifique' had seen widespread usage throughout the century. However, in 1785 Guyton had used it as a noun indicating the matter of heat or of fire; see Partington, *op. cit.* (1), iii, 421. Cf. the same usage in *Observations sur la Physique*, xxx (1787), 45-6, and see R. Fox, *The Caloric Theory of Gases from Lavoisier to Regnault* (Oxford: Clarendon Press, 1971), p. 6n. Another change in the new nomenclature was the listing of light as a distinct element; see *Nomenclature Chimique*, pp. 28-30. Lavoisier was indifferent to the problems of differentiating between heat and light and of specifying the chemical role of light: see, for example, *ibid.*, p. 293n., and *Traité Élémentaire de Chimie* (2 vols., Paris, 1789), i. 200-2; also H. Metzger, 'Newton: La théorie de l'émission de la lumière et la doctrine chimique au XVIIIème siècle', *Archeion*, xi (1929), 24-5. He did state in a few places that the state of oxygen gas is due to both caloric and light combined in it: for example, in *Nomenclature Chimique*, p. 296; *Traité*, i. 201; ii. 523; and *Mémoires de Chimie* (2 vols., Paris, 1803?), ii. 155. In the *Traité de Chimie*, ii. 523, he gave as a basis for this some work by Berthollet showing that 'obscure' heat cannot produce oxygen gas from oxide of mercury.

⁶ *Opuscules*, p. 280.

⁷ J. B. Gough, 'Lavoisier's early career in science: an examination of some new evidence', *Br. J. Hist. Sci.*, iv (1968-9), 52-7.

L'eau a un certain degre de chaleur entre en expansion. Elle se reduit en vapeur. Est-ce une dissolution qui se fait de l'eau dans l'air, ou bien est-ce dans le fluide igné? L'air ne seroit-il pas lui-meme un fluide en expansion.⁸

If water vapour and air are both fluids 'en expansion' and as water vapour is clearly a state produced by the matter of fire, then perhaps air itself is also merely a state produced by fire.

Although only a suggestion in 1766, this idea became a major and persistent feature in Lavoisier's theory of heat. Indeed, supporting his contention that air is simply a vapour is the central issue of a crucial manuscript of July 1772.⁹ Citing effervescences to illustrate his idea that air can exist in either a free or a fixed state, Lavoisier stated that fire matter behaves in a similar fashion. Both air and fire are combined, released, or stay the same in a chemical reaction depending upon the quantity of these elements contained in the product compared to the quantity present in the ingredients. Cooling indicates combining fire matter, and as cooling accompanies evaporation, all vapours are igneous compounds. He cited water as an example of the processes of vaporization (combining fire matter) and condensation (release of fire) and four times explicitly drew an analogy between water vapour and air. If our entire atmosphere were destroyed, he said, another atmosphere would form, analogous to the first but composed of water vapour. The direction of Lavoisier's argument is clear: vapours and air are analogous not only in their physical properties but also in the way they are formed.

He pointed out that many effervescences are accompanied by cooling. Having equated cooling with combining fire matter, in what substance is the fire combined if not in the released air?

Mais comment l'air existe-t-il dans les Corps Comment Ce fluide Susceptible d'une Si terrible expansion peut il Se fixer dans [les corps et y] un Solide et y occuper un espace six cent fois moindre qu'il n'occupoit dans l'atmosphere. Comment concevoir que le meme corps puisse exister dans deux etats Si differens.¹⁰

The explanation of vaporization in terms of combining fire matter provided the answer to this perplexing question, and Lavoisier's concluding 'theorie Singuliere' is that air is not a simple substance but a compound of fire matter and a particular fluid.

There is in both manuscripts a very close relationship between his ideas on air and on fire. In 1766 this association and his suggestion that air may be a vapour is given in a context of theoretical speculations on elements in general. By July 1772, however, Lavoisier's interests seem

⁸ Quoted in *ibid.*, 54.

⁹ For the probable date of composition, see Guerlac, *op. cit.* (3), pp. 100-1. The manuscript, originally published by Fric, in *op. cit.* (5), is reproduced in Guerlac, pp. 215-23.

¹⁰ Quoted in Fric, *op. cit.* (5), 145. The words in brackets are those crossed out in the manuscript.

largely focused on the chemical role of air. Indeed, it would seem from his line of reasoning in the later paper that his theory of heat had been devised for the single purpose of explaining how it is possible for air to be an expansible fluid and yet be fixed in a solid form with a six-hundred-fold reduction in volume. Aside from stating his theory more firmly in 1772, there are other differences between the two memoirs. In 1766 he explained vaporization as a process of dissolution in the igneous fluid; in 1772 he described this change as due to the chemical combination of the matter of fire.¹¹ Another difference between the two papers is that in 1772 there is a clear implication that the explanation of vaporization as being due to combining fire applies to fusion as well, although Lavoisier was not quite certain how.¹²

The third manuscript memoir, generically related to the other two, is dated April 1773.¹³ It opens with a discussion of the three states of matter. All substances without exception can exist as solids, liquids, or vapours depending on the quantity of fire combined with them. As in the memoir of the preceding July, Lavoisier cited water to illustrate the processes he was describing: vaporization in the July 1772 memoir, both vaporization and fusion in the paper of April 1773. Vapours are analogous in all physical properties to air; and air itself is a vapour, that is, a substance combined with fire. In the July memoir he had speculated on what would happen if our atmosphere were destroyed; in the 1773 paper he discussed the possible consequences for the atmosphere of moving the Earth closer to the Sun or farther away. His point in both memoirs is that the atmosphere is composed of vapours and that the nature of the vapours depends upon the temperature to which substances are exposed. Air is simply a volatile fluid which, given the conditions on Earth, is in the vaporous state. The latter half of the 1773 document is primarily devoted to pursuing the consequences of this idea and goes beyond the memoir of July 1772. If air is an igneous compound, fire should be absorbed when air is converted to its elastic state and fire should be released when air becomes fixed. He concluded that both phenomena occur as predicted.

The first half of the 1773 work is essentially a revised, expanded version of the paper of mid-1772. Their titles are the same ('*Essay sur la nature de l'air*') and their purpose is the same: to demonstrate that air is an igneous compound, a vapour, and that when this vapour condenses,

¹¹ Dissolution was considered to be a chemical process; see G. F. Venel, 'Menstrue & action menstruelle, ou dissolvant & dissolution', *Encyclopédie ou Dictionnaire Raisonné . . .*, ed. Diderot and d'Alembert, x (1765), 339, 340. As far as I can tell, however, prior to Lavoisier, of all changes of state only *evaporation* (not vaporization in general) was considered to be a dissolution in which *air* (not fire) acts as the menstruum; see [A. R. J. Turgot], 'Expansibilité', *Encyclopédie*, vi (1756), 282, and the corrections, p. 927.

¹² Cooling was the single phenomenon which indicated to Lavoisier a combination of fire had taken place; the only fusion phenomenon which he associated with his theory of combination of fire was the cooling of an ice-salt mixture. See Fric, *op. cit.* (5), 141-2.

¹³ *Ibid.*, 147-51.

as it must to become fixed, fire is released. Although his theory accounts for changes of state in general (implied in 1772, explicit in 1773), his major concern was with vaporization and he employed his theory of heat primarily for a single purpose: to explain the fixation and release of air and the other phenomena associated with these processes. His more general application of the theory seems incidental.¹⁴

These manuscripts provide the background for the short statement published in the *Opuscules* in 1774, where he stated his concept of air as a vapour. The same idea is repeated in a manuscript of 1775 where he explained that for combustion to occur, both the combustible and air must furnish their share of fire matter to the flame; combustibles do not burn in fixed air because the fire is too firmly attached to the latter.¹⁵

Formal presentation, 1777-81

Among the many papers presented to the Academy of Sciences in 1777¹⁶ were two which together comprise the first formal description of Lavoisier's oxidation theory. They also contain his first published detailed discussion of his theory of heat and they appear as revised, expanded versions of the earlier manuscripts. In the first paper Lavoisier presented his thesis concerning the role of fire matter in vaporization and developed his argument concerning the nature of elastic fluids as igneous compounds. He opened with a statement of his general assumption 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.¹⁷

In explaining the role of fire, Lavoisier again drew an analogy to water. As water may act as water of solution or may be combined in

¹⁴ Guerlac argues that the appearance of the July memoir as being devoted primarily to explain the fixation of air is because the memoir was never completed; see 'Lavoisier's draft memoir of July 1772', *Isis*, lx (1969), 381-2. Cf. R. J. Morris, 'Lavoisier on air and fire: the memoir of July 1772', *Isis*, lx (1969), 374-7.

¹⁵ 'De l'élasticité et de la formation des fluides élastiques', published by J. B. Gough, in 'Nouvelle contribution à l'étude de l'évolution des idées de Lavoisier sur la nature de l'air et sur la calcination des métaux', *Arch. Int. Hist. Sci.*, xxii (1969), 271-5.

¹⁶ See M. Daumas, *Lavoisier, Théoricien et Expérimentateur* (Paris: Presses Universitaires de France, 1955), pp. 38-41.

¹⁷ 'De la combinaison de la matière du feu avec les fluides évaporables, et de la formation des fluides élastiques aëriiformes' [1778], *Mémoires de l'Académie Royale des Sciences, 1777* (1780), p. 420. The date in brackets refers to the date the paper was first read. The date in parentheses is the publication date for the volume of *Mémoires*. Thus this paper, presented to the Academy in September 1777, was read in July 1778 (Daumas, op. cit. [16], pp. 40, 42), and published in 1780 in the *Mémoires* for 1777.

substances as the water of composition, so too with the igneous fluid. Fire may be free or fixed and the latter does not register on a thermometer. Echoing the memoir of July 1772, he explained that temperature changes in *any* chemical reaction indicate changes in the state of fire from free to combined (or reverse) which in turn depend upon the quantity of fire in the constituents before reaction compared with that contained in the products. From this assumption and well known observations that evaporation produces cooling¹⁸ which is proportional to the rate of evaporation, Lavoisier deduced that all vapours are the result of the combination of fire matter with some fluid. Then reasoning by analogy, he declared that it directly follows that 'les vapeurs, & en général, les substances aëriiformes, sont un composé d'un fluide quelconque, dissout & combiné avec la matière de feu.'¹⁹

This statement, essentially repeated from his earlier manuscripts and his *Opuscles*, is the bridge which connects his theory of heat to his general chemistry and to the oxidation theory in particular; and it gives his theory of heat a central position in the latter. There is no fundamental difference between vapours and the permanently elastic fluids. Airs are simply the vapours of substances having a boiling point below temperatures naturally encountered or perhaps artificially produced. Hence the explanation of the formation of vapours, which are patently the result of a change of state, applies to all aeriform substances.²⁰ The heat contained in these fluids is that heat which is responsible for their elastic state.

Although clearly his purpose was to show that air is itself a vapour, apart from his earlier declaration that all aeriform substances are igneous compounds, he had made no explicit attempt, even by analogy, to link air with other elastic fluids. Towards the end of the paper, however, he raised a question concerning effervescences. Implying that the processes of evaporation and effervescence are similar, he countered a possible objection to his theory based on the observation that so many effervescences are accompanied by increased rather than decreased temperatures. Heating merely shows that less fire is required in the new compounds than existed in the components prior to the reaction. The quantity of fire released is obviously greater than that required to vaporize the air, and

¹⁸ Lavoisier cited George Wilhelm Richman (1711-53), Jean Jacques Dortous de Mairan (1678-1771), William Cullen (1710-90), and Antoine Baumé (1728-1804) as having demonstrated evaporative cooling (*ibid.*, p. 424, and footnotes). He had cited Cullen and Baumé in the same context in 1775 (Gough, *op. cit.* [15], 271; see Gough's discussion).

¹⁹ *Mém. Acad. R. Sci.* 1777, p. 425. The concept of air as a state had been stated earlier by Turgot (*loc. cit.* [11]). For a brief discussion of the development of this concept, see M. P. Crosland, 'The development of the concept of the gaseous state as a third state of matter', *Actes du X^e Congrès International d'Histoire des Sciences; Ithaca, 1962* (1964), pp. 852-53. For the possible influence of Turgot on Lavoisier, see Gough, *op. cit.* (15), 269-70. Cf. Morris, *op. cit.* (14), 377n.

²⁰ Although a persistent theme since at least 1766, his only published reference to his idea prior to the *Mémoires* for 1777 was the short passage in the *Opuscles* quoted above. He may have mentioned the idea in May 1777; see Daumas, *op. cit.* (16), p. 38. A memoir in the *Oeuvres de Lavoisier* (6 vols., Paris, 1862-93; v. 271-81) purports to be a slightly modified version of the one read in May 1777. The original was not published.

the resulting increase in temperature masks the cooling due to some matter of fire being carried away combined with air. Lavoisier reasoned that if fire were combined in the vapour and removed as postulated, there should be an inverse relationship between the increase in temperature and the quantity of vapour formed. He then cited experimental evidence supporting this relationship and concluded that heating effervescences caused no problem for his theory.²¹

In the second article published in the *Mémoires* for 1777 Lavoisier proposed his new theory of combustion.²² He began by listing the phenomena always observed in combustion and which, he said, also occur in calcination and respiration. Admittedly Stahl's theory accounts for some of these phenomena. But 'l'hypothèse opposée'²³ does the same. Lavoisier's hypothesis is *opposée* to Stahl's because Lavoisier did not suppose the existence of fire in combustibles and metals. Yet where is the matter of fire prior to combustion? Not in solids, for substances combined with fire acquire new properties 'qui les rapprochent de celles de la matière du feu.'²⁴ Fire must be contained in elastic fluids.

Restating the conclusions reached in the first article, Lavoisier went on to examine the nature of dephlogisticated air. As an elastic fluid, it is an igneous compound in which the matter of fire or light forms what he called the dissolvent and another substance forms the base.²⁵ If the base unites with a substance for which it has a greater affinity than it has for fire matter, the dissolvent (fire) would be set free. This is what happens during combustion and calcination.

It is at this point that his theory of heat plays its crucial role. The phlogistonists are mistaken in their belief that fire is fixed in combustible substances. As the three states of matter depend only on the relative quantity of fire combined in them, it is plain that vapours contain the most fire and solids the least. Thus, if combustion is a process of condensation and combination of a vapour (air) with some solid or liquid, the heat of combustion must come from the vapour and not from the liquid or solid combustible. Indeed, solids should contain no fire at all, except perhaps

²¹ *Mém. Acad. R. Sci.* 1777, pp. 429-32.

²² 'Mémoire sur la combustion en général' [1777], *Mém. Acad. R. Sci.* 1777, pp. 592-600. The chronological difficulties with this paper are similar to the previous one; see n. 17 above. The paper was read in November 1777 and again in December 1779; see Daumas, *op. cit.* (16), pp. 40, 44. Although the first reading preceded that of the memoir on the formation of elastic fluids (see n. 17), it was published in the *Mémoires* following the latter and was clearly written with the latter in mind.

²³ *Mém. Acad. R. Sci.* 1777, p. 595.

²⁴ *Ibid.*

²⁵ In the *Opuscules* (p. 280) he had called the base of air 'la partie fixe' but he had used the terminology of the paper on combustion in preceding articles published in the *Mémoires* for 1777. He referred to the base of aeriform fluids in his 'Mémoire sur la combustion des chandelles dans l'air atmosphérique et dans l'air éminemment respirable' (*Mém. Acad. R. Sci.* 1777, p. 204), in 'Expériences sur la combinaison de l'alun avec les matières charbonneuses et sur les altérations qui arrivent à l'air dans lequel on fait brûler du pyrophore' (*Mém. Acad. R. Sci.* 1777, p. 371), and in his 'Mémoire sur la vitriolisation des pyrites martiales' (*Mém. Acad. R. Sci.* 1777, p. 399n.).

what is present in the form of free fire owing to the tendency of fire matter to equilibrium.²⁶

Lavoisier considered his new theory of combustion to be the reverse of the phlogiston theory not because he viewed combustion as a process of *combination* of a combustible with part of the air rather than as the *dissolution* of an essentially compound combustible, but because of his conception of the nature of the igneous compound which is the source of the fire released. The heat and flame of combustion come not from a solid, compact combustible, as Stahl believed. The source of fire is a fluid, elastic air.

The *sine qua non* of Lavoisier's theory of heat and its connexion with the oxidation theory hinges on the assumption of the basic identity in the process of formation of vapours and of gases. With or without phlogiston, there is still the problem of explaining the heat and flame of combustion. Lavoisier associated fire matter with dephlogisticated air; and prior to its release, fire is contained in this air in the form of the latent heat of vaporization.

The main outlines of Lavoisier's theory of heat, particularly the close, complementary relationship between this theory and his explanations of the chemical action of air, persist in his subsequent publications. Until 1781 his theory of heat is a coherent whole. His point of view is fairly uniform and there is a clear progression of ideas from the manuscripts of 1766 to the papers on elastic fluids and combustion of 1777-8. His attention was riveted to the process of vaporization almost to the complete exclusion of everything else. Although he said that all changes of state are caused by the combination and release of fire, specific discussions of fusion are conspicuously absent. His single-minded purpose was to demonstrate his theory that fluid elasticity is a state, that aeriform fluids are vapours, and that vaporization is a chemical process caused by the combination of the matter of fire influenced by external pressure of the atmosphere. Both experimental and theoretical work on heat until 1781 seem to have been restricted almost entirely to this end.²⁷

Throughout, the single phenomenon which clearly indicates change in

²⁶ *Mém. Acad. R. Sci.* 1777, pp. 595-8.

²⁷ From early spring of 1777 he was assisted in his experimental work by Laplace, and their collaboration is often cited in subsequent papers; see H. Guerlac, 'Laplace's collaboration with Lavoisier', *Actes du XII^e Congrès International d'Histoire des Sciences; Paris, 1968*, iii B., 31-36. In addition to the papers discussed, there are several others which stem from this period and express the same viewpoint. One is the manuscript mentioned in n. 20 above. Two others extend his theory of vapours to show that it is in accord with chemical phenomena of a variety of elastic fluids. The first is 'De quelques substances qui sont constamment dans l'état de fluides aëriiformes au degré de chaleur et de pression habituel de l'atmosphère'. Almost all the experiments cited were performed in February 1776. The paper was submitted to the Academy early in 1776 to be initialled, *déposé* in 1777 (Daumas, op. cit. [16], pp. 36-7, 41), and published in Lavoisier's posthumous *Mémoires de Chimie*, i, 348-85. The second is entitled 'Mémoire sur quelques fluides qu'on peut obtenir dans l'état aëriiforme à un degré de chaleur peu supérieur à la température moyenne de la terre' [1780], *Mém. Acad. R. Sci.* 1780 (1784), pp. 334-43. Daumas (op. cit. [16], p. 45) describes it as 'la suite naturelle' of the preceding paper.

the state of fire is change in temperature. The experimental evidence he cited showed such a change—evaporation, condensation, effervescence, combustion. He ignored vaporizations caused by the application of external heat. Indeed, in what was practically his only mention (unpublished) during this period of boiling over an external heat source, he said: 'il est impossible de S'appercevoir dans Cette occasion de labsorption de la matierre du feu'²⁸ for the simple reason that the external heat source furnishes more matter of fire than is absorbed during vaporization.

Ce nest donc point par la *vaporisation a chaud* qu'on peut prouver la verite de la proposition quon vient davancer mais il faut avoir recours a *levaporation a froid*.²⁹

Constant-temperature phenomena were not cited in any of his papers as evidence to support his theory. Yet Lavoisier had learned of Black's ideas in August 1772, and in October 1772 he even cited his own fusion experiment as a further example of what Black had observed. But neither this experiment nor any other constant-temperature phenomena play a part in Lavoisier's work up to 1781 except what may be read into his general idea that almost all substances can exist in three states and that all changes of state are due to the combination of the matter of fire.

Crawford and Magellan

Beginning in the middle of 1781, the character of the experiments on heat changes and Lavoisier's subsequent memoirs which relate to this work express a point of view different from that which characterizes the earlier period. For the first time he began to take a hard look at the phenomena on which Black based his concept of latent heat and heat capacity. At the same time, in his attempt to explain these phenomena, his theory of heat acquires a distinctly physical flavour lacking in the preceding work and perhaps due to the influence of Laplace or of Gaspard Monge.

In 1779, the year before Lavoisier's papers of 1777-8 were printed, the Irish physician and chemist Adair Crawford (1748-95) published a work on heat in which he anticipated (in print) some of Lavoisier's ideas.³⁰ Crawford believed that air is the source of the heat of animals, of combustions, and hence of calcinations; and, as the title of his book indicates, he attempted 'to resolve these phaenomena into a general law of nature'. His work, as he admitted, is based on Black's ideas and more specifically

²⁸ Fric, op. cit. (5), 152. The date of this manuscript is uncertain although it must have been written before 1781. Its content suggests a close relation with the memoirs of July 1772 and April 1773.

²⁹ Ibid., italics mine. Cf. a similar statement in the paper of July 1772, *ibid.*, 142.

³⁰ *Experiments and Observations on Animal Heat and the Inflammation of Combustible Bodies, being an Attempt to Resolve these Phaenomena into a General Law of Nature* (London, 1779). He published a considerably expanded second edition in 1788, also in London.

on those of a former student and collaborator of Black's, the Scottish chemist William Irvine (1743-87).³¹ Crawford's theory explains temperature changes accompanying chemical transformations as due to changes in the capacity for heat (specific heat) of the substances involved.³² The total quantity of heat contained in a substance at a given temperature is proportional to its capacity for heat (specific heat), for it takes a lesser quantity of heat to produce a given temperature in a substance with a lesser capacity for heat and a correspondingly greater quantity of heat to produce the same temperature in a substance with a greater capacity. If, for example, the capacity (specific heat) of a substance at a given temperature were to be reduced suddenly, the substance would now contain more heat than it requires (owing to its new capacity) to remain at the original temperature. The temperature thus would increase until the excess heat dissipates. Similarly if two substances react chemically with each other, heat will be evolved or absorbed depending upon how the capacities for heat of the substances before the reaction compare with their capacities after the reaction.

In respiration, combustion, and calcination, there is a transformation of atmospheric air into fixed and phlogisticated air. According to Crawford, the capacity for heat of atmospheric air compared with that of fixed air is in the ratio 67 to 1.³³ This ratio indicates that in the transformation of atmospheric air to fixed air, 66 parts of the fire matter out of the original 67 have become excess. During respiration, however, the formation of fixed and phlogisticated air from atmospheric or dephlogisticated air is accompanied by the transformation of venous to arterial blood. The capacity for heat of arterial blood is greater than that of venous blood,³⁴ and the fire which becomes excess due to a decrease in the capacity for heat of the air is absorbed by the blood owing to its increase in capacity. Similarly

³¹ Crawford acknowledged his indebtedness to these two men. For example, see *Animal Heat* (1779), pp. 2, 4, 12n., 17n., 49n. Irvine was professor of chemistry at Glasgow; see Andrew Kent, 'William Irvine, M.D.', in *An Eighteenth-Century Lectureship in Chemistry*, ed. Andrew Kent (Glasgow: Jackson, 1950), pp. 140-50. Crawford had gone to Scotland in 1776 where he attended Irvine's lectures. His experiments were begun in the summer of 1777 (*Animal Heat* [1779], p. 18). His theory was communicated to Irvine and others that autumn and explained to the faculty and students in Edinburgh during the 1777-8 session (*Animal Heat* [1788], p. 4). For a discussion of various aspects of Crawford's ideas see R. Fox, 'Dalton's caloric theory', in *John Dalton & the Progress of Science*, ed. D. S. L. Cardwell (Manchester: Manchester Univ. Press, 1968), pp. 190-2; J. R. Partington and D. McKie, 'Historical studies on the phlogiston theory. III: Light and heat in combustion', *Annals of Science*, iii (1938), 346-50; and E. Mendelsohn, *Heat and Life: The Development of the Theory of Animal Heat* (Cambridge, Mass.: Harvard Univ. Press, 1964), pp. 123-33, and *passim*.

³² Crawford (*Animal Heat* [1779], p. 16) defined capacity as the power of a given substance to collect and retain 'the element of fire', and it is determined by the change of temperature produced in the substance by a given quantity of fire compared to the change produced by the same quantity of fire in the temperature of some other substance (water) taken as a standard. He did not use the term 'specific heat'. This term was introduced by Magellan; see below.

³³ *Ibid.*, p. 51. Crawford was apparently the first person to determine the heat capacities of airs; see D. McKie and N. H. de V. Heathcote, *The Discovery of Specific and Latent Heats* (London, 1935), p. 43, n. 4.

³⁴ *Animal Heat* (1779), p. 58.

the change of tin, for example, into its calx is accompanied by an increase in capacity³⁵ indicating that a quantity of heat is *absorbed* by the calx.

These relationships suggested to Crawford that phlogiston must be something other than the matter of fire, and that air is the source of the heat released. He concluded that heat and phlogiston are largely mutually exclusive principles, that the loss of phlogiston causes an increase in heat capacity and an absorption of heat, and that the gain of phlogiston causes a decrease in capacity and a consequent release of heat.

From the above experiments we learn, that atmospherical air, contains much absolute heat; that when it is converted into fixed and phlogisticated air, the greater part of this heat is detached; and that the capacities of bodies for containing heat, are diminished by the addition of phlogiston, and increased by the separation of it. From 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 abound with phlogiston [*sic*], and contain little absolute heat; atmospherical air, on the contrary abounds with absolute heat, and contains little phlogiston.³⁶

Although he confined his experiments and explanations to the processes of respiration and calcination-combustion, Crawford clearly implied that the theory accounts for all changes of temperature which accompany changes in 'form', including changes of state. As he related, the theory makes it possible to determine 'with certainty and accuracy' the proportions in which fire is distributed in nature.³⁷ Irvine had applied the theory to a number of 'curious and important' phenomena, and Crawford mentioned his teacher's 'discoveries with regard to the cause of the phenomena of latent heat'. But as these discoveries 'have not been communicated to the world, I have not taken the liberty to point out their connection with this part of my subject'.³⁸

Such liberties were taken by John H. Magellan (1722-90),³⁹ who wrote a commentary on Crawford's book in 1780 which subsequently appeared in 1781 in two instalments (May and June) in the *Observations sur la Physique*.⁴⁰ Magellan's praise of Crawford was extravagant.

³⁵ *Ibid.*, p. 61.

³⁶ *Ibid.*, p. 76.

³⁷ *Ibid.*, p. 15n.

³⁸ *Ibid.*, p. 49n.

³⁹ Magellan played a central role in introducing British ideas of pneumatic chemistry into France in 1771-2 (Guerlac, *op. cit.* [3], chapter II, *passim.*) and possibly transmitted to Paris the brief article published in 1772 (cited in n. 3) concerning Black's work on heat (*ibid.*, pp. 68-9).

⁴⁰ J. H. Magellan, 'Essai sur la nouvelle théorie du feu élémentaire et de la chaleur des corps', in *Collection de Différens Traités sur des Instrumens d'Astronomie, Physique, etc.* (London, 1780); 'Essai sur la nouvelle théorie du feu élémentaire & de la chaleur des corps', *Observations sur la Physique*, xvii (1781), 375-86; and 'Suite du 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), 411-22. An announcement of the publication of Crawford's book and a brief summary of his theory appeared early in 1780; see 'Extrait d'une lettre de M. Magellan de la Société Royale de Londres sur les montres nouvelles qui n'ont pas besoin d'être montées, sur celles de M. Mudge, & sur l'ouvrage de M. Crawford', *Observations sur la Physique*, xvi (1780), 62-3. For a summary of Magellan's account see McKie and Heathcote, *op. cit.* (33), pp. 40-5.

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 moderne.⁴¹

Magellan added significant details to Crawford's discussion. He reviewed Black's concept of latent heat and then did what Crawford had refused; he explained the phenomena of latent heat in terms of changes in capacity, with the following modification. What Crawford (following Irvine and Black) had called capacity for heat, Magellan called 'chaleur spécifique'.⁴² The quantity of heat in a substance is proportional to its specific heat, and the difference between the specific heat of a fluid or vapour and the specific heat of the corresponding solid is called 'chaleur latente'.⁴³ Magellan included a table of specific heats, obtained from Richard Kirwan, expressing specific heats as decimal fractions with that of water taken as unity.⁴⁴

Here was a fairly complete theory which explained those phenomena which were Lavoisier's chief concern and arrived at the same conclusion regarding the source of heat in combustion, respiration, and calcination. In addition, the new theory specifically accounted for those constant-temperature changes which Lavoisier had virtually ignored and which he felt it was impossible to use as illustrations of the combination of the matter of fire. The new theory was more comprehensive than Lavoisier's, and it appeared to be well founded on quantitative, experimental data. It approached heat phenomena at a more fundamental level in attempting to measure the actual quantities of heat involved in changes of form as opposed to Lavoisier's concentration on relative, momentary temperature changes. Even if Magellan had known of Lavoisier's theory, he might well have continued to maintain that Crawford had indeed founded a new branch of physics.

Joint memoir on heat, 1781-3

Crawford's idea of changes in specific heat offered, in theory, a precise means of calculating from direct measurement the quantity of heat a substance contains. More important, from his theory Crawford had reached the same general conclusions as Lavoisier regarding the distribution of heat matter in substances; and Crawford's determination of various specific heats, if accurate, would lend considerable experimental support

⁴¹ *Observations sur la Physique*, xvii (1781), 375.

⁴² *Observations sur la Physique*, xvii (1781), 376. Its appearance in the 1780 edition of Magellan's paper (op. cit. [40], 167) is apparently the first published use of this term; see McKie and Heathcote, op. cit. (33), p. 42.

⁴³ *Observations sur la Physique*, xvii (1781), 381.

⁴⁴ *Ibid.*, 384. This is apparently the first published table of specific heats; see McKie and Heathcote, op. cit. (33), p. 43.

to Lavoisier's own views. This alone was sufficient reason to examine in detail the concept of changes in capacity.

Magellan's commentary was published in May and June 1781, and, according to the twenty-four-year-old recollections of Jean André Deluc, Crawford's theory created 'great agitation' among members of the French Academy of Sciences.⁴⁵ In November Lavoisier was experimenting on the latent heat of vaporization of ether.⁴⁶ In December he was calculating heats of fusion using the method of mixtures described in Magellan's articles.⁴⁷ Before the end of July 1782 he had given up the method of mixtures in favour of the ice-calorimeter.⁴⁸ Work, suspended during the late summer and early autumn, was resumed in November 1782 and continued through the winter. In June 1783 Laplace read the joint memoir on heat.⁴⁹

The 'Mémoire sur la chaleur' contains Lavoisier's first general statement regarding what the British were calling latent heat—a fixed quantity of heat which produces change of state without a change in temperature.⁵⁰ Indeed, the reasoning behind the ice-calorimeter presupposes his acceptance of this concept. The paper seems to have been in origin a response to and in substance largely a commentary on the concepts, data, terminology, and experimental and calculative techniques described in Magellan's articles. Although Magellan is never cited, references to the theory of changes in heat capacity are scattered throughout the memoir.⁵¹

Experimental tests of Crawford's theory were initially disappointing. Advance determination of the specific heats of reactants and their combinations did not enable the authors to predict the quantity of heat that would be evolved or absorbed in a given combination; and efforts to calculate absolute zero, based on the theory of changes in specific heat, were inconclusive. Although they admitted that the difference between calculated and observed data could have been due to their own experimental errors, they were inclined to the view that the specific heats of substances change with changes in temperature, which opposed Craw-

⁴⁵ J. A. Deluc, 'To the conductors of the Edinburgh Review', *The Edinburgh Review*, vi (1805), 511. In fact, Deluc stated that the Academy gave Monge and Vandermonde 'the special commission to examine and follow that new view [Crawford's].'

⁴⁶ Daumas, op. cit. (16), p. 45. The vaporization was produced by heated mercury and the temperature change of the latter was measured.

⁴⁷ *Ibid.*, p. 46.

⁴⁸ *Ibid.*, p. 47. The 'seconde séance' of experiments with the calorimeter is dated 27 July; the 'première séance' is mentioned but not dated.

⁴⁹ *Ibid.*, p. 48; Lavoisier and Laplace, 'Mémoire sur la chaleur' [1783], *Mém. Acad. R. Sci. 1780* (1784), pp. 355-408. Discussions of this paper are common in secondary literature; for example see Wolf, op. cit. (1), i. 183-8.

⁵⁰ Lavoisier and Laplace, op. cit. (49), p. 388. The term latent heat was not used. Magellan had rejected the term on the grounds that, strictly speaking, the effects of heat in this form are sensible not latent (*Observations sur la Physique*, xvii [1781], 381; cf. 385).

⁵¹ *Ibid.*, pp. 356, 383-4, 394. In addition to the terminology and explicit references to Crawford and his theory, the citation of Kirwan ('Kirven', pp. 385, 387, 390) is further indication of Magellan as their source of information.

ford's position that specific heats are constant at all temperatures as long as there is no change of form or state.⁵²

Yet they did not reject the concept entirely. They cited some of Crawford's work as supporting their own theory. Although not willing to accept without verification Crawford's high value for the specific heat of pure air, they admitted that 'si ces expériences [Crawford's] étoient exactes, il seroit aisé de faire voir que la chaleur libre existante dans l'air pur, est plus que suffisante pour produire tous les phénomènes de la chaleur', and this is what Lavoisier's theory was intended to demonstrate.⁵³ Furthermore, in explaining why the temperature of animals is about the same in all parts of their bodies in spite of the heat being absorbed in the lungs, they gave Crawford's explanation (without acknowledgment) which involves various changes in the specific heat of the blood during circulation.⁵⁴ As Crawford had expressed the concept, 'elle souffre des exceptions considérables'.⁵⁵ But the specific heat of water, for example, is greater than ice, and heat is absorbed during the conversion.

Lavoisier seemed to feel that the specific heat is related to the internal, physical constitution of a substance, that is, to the interplay between the forces of mutual attraction or affinity tending to pull the particles of a substance together and the contrary force of heat tending to separate them. He had apparently developed this idea during the early stages of his experimental work testing Crawford's hypothesis. During 1781 and 1782, along with the calorimeter experiments, he and Laplace had worked on the expansion of solids and liquids by heat.⁵⁶ In the joint memoir he suggested the possibility of 'rapports remarquables' between specific heats of substances and their respective changes in specific gravities (their expansibilities), and he proposed to publish a paper on the subject when the experiments were completed.⁵⁷ He also promised a memoir on affinity itself, for the equilibrium existing between the opposing forces of heat and

⁵² *Ibid.*, pp. 385-9. The calculations of absolute zero are further indications that Lavoisier and Laplace had read Magellan's articles. Although the calculational technique can be derived from Crawford's discussion and although, judging from William Irvine's posthumously published *Essays* (McKie and Heathcote, op. cit. [33], pp. 130-4), Crawford might well have learned the method during his stay in Glasgow, he made no mention of it and only referred in passing to the 'point of total privation' of heat (*Animal Heat*, p. 97n.). Magellan, on the other hand, discussed the theory and as an example calculated the total quantity of heat in ice at its melting point; see *Observations sur la Physique*, xvii (1781), 383-4. He stated further that he had obtained the method from Kirwan (*ibid.*, 384). For a discussion of the technique of calculation, see McKie and Heathcote, op. cit., pp. 130-7.

⁵³ *Mém. Acad. R. Sci.* 1780, p. 394. Although they described a method to determine the specific heat of airs (pp. 295-6), none were given. Such work was carried out during the winter of 1783-4 but not published until the *Mémoires de Chimie*.

⁵⁴ *Mém. Acad. R. Sci.* 1780, p. 406. The authors cited no experimental data to support this explanation; see Mendelsohn, op. cit. (31), pp. 150-1.

⁵⁵ *Mém. Acad. R. Sci.* 1780, p. 387.

⁵⁶ Daumas, op. cit. (16), pp. 45, 46. The account of this work was published in Lavoisier's *Mémoires de Chimie*, i. 246-80, 295-311.

⁵⁷ *Mém. Acad. R. Sci.* 1780, p. 374.

affinity offers, he said, a very precise means of determining the latter by measuring the former in certain reactions.⁵⁸

1785 and the memoir on phlogiston

The concept of an equilibrium of forces to which Lavoisier alluded in 1783 in the joint memoir received more extensive treatment in a paper read in March 1785 on the affinities of oxygen.⁵⁹ In his prefatory remarks he stated that the particles of substances are continually acted upon by two opposing forces, the igneous fluid tending to separate them and an opposing attraction or affinity tending to draw them together. Affinity depends upon the separation among particles; and the separation may be increased, and the affinity decreased, by introducing more matter of heat. Thus a table of affinities can be valid only at a given temperature.⁶⁰

The balance between the opposing forces of heat and affinity offers a precise means to determine the force of the latter, and hopefully a thorough knowledge of affinity would one day enable a mathematician in his study to calculate chemical phenomena in the same way he now calculates the movement of celestial bodies.

Les vues que M. de la Place a sur cet objet, & les expériences que nous avons projetées, d'après ses idées, pour exprimer par des nombres la force des affinités des différens corps, permettent déjà de ne pas regarder cette espérance absolument comme une chimère.⁶¹

It seems clear that the projected 'expériences' involved the measurement of heat. Lavoisier thus implied that both he and Laplace believed that this facet of their theory of heat offered the key to placing chemistry on a rigorous mathematical foundation and thereby to achieving for chemistry a status comparable to that of celestial mechanics.⁶²

The appearance of the concept of a balance of forces marks a definite change in Lavoisier's theory of heat. Beginning with the joint memoir of 1783, his point of view became increasingly physical as well as chemical, and his concern with interparticulate forces and explanations involving this concept are superimposed upon the older view of fire acting as a chemical constituent being combined and released. The new idea, alluded to in 1783 and outlined briefly in the memoir of March 1785, is a major

⁵⁸ *Ibid.*, pp. 391-2. Lavoisier and Laplace continued their experiments with the ice-calorimeter during the late autumn and winter of 1783-4 (Daumas, *op. cit.* [16], p. 51), but the results were published much later in the *Mémoires de Chimie*, i. 121-47.

⁵⁹ *Mémoire sur l'affinité du principe oxygène avec les différentes substances auxquelles il est susceptible de s'unir* [1785], *Mém. Acad. R. Sci. 1782* (1785), pp. 530-40. It was presented in December 1783 and read in 1785; see Daumas, *op. cit.* (16), pp. 51, 56.

⁶⁰ *Ibid.*, pp. 531-2. The forces of affinity and atmospheric pressure are opposed by that of heat matter, and the solid, liquid, and aeriform states depend upon whether the latter is weaker, equal to, or stronger than the former.

⁶¹ *Ibid.*, pp. 534-5.

⁶² For a general discussion of Lavoisier's ideas on affinity see M. Daumas, 'Les conceptions de Lavoisier sur les affinités chimique et la constitution de la matière', *Thalès*, vi (1949-50), 69-80. Daumas virtually ignores the role of caloric in this context.

feature of his famous memoir on phlogiston read to the Academy in June and July 1785.⁶³

As the title indicates, this memoir was intended as a sequel to his paper of 1777 on combustion and calcination. His opening paragraph illustrates the central role played by his theory of heat as well as the importance he attached to his concept of air as a vapour.

J'ai déduit toutes les explications d'un principe simple, c'est que l'air pur, l'air vital, est composé d'un principe particulier qui lui est propre, qui en forme la base, & que j'ai nommé *principe oxygine*, combiné avec la matière du feu & de la chaleur. Ce principe une fois admis, les principales difficultés de la Chimie ont paru s'évanouir & se dissiper, & tous les phénomènes se sont expliqués avec une étonnante simplicité.⁶⁴

The first half of the paper comprises a critique of various theories of phlogiston, and some of his criticisms relate directly to his theory of heat. For example, he stated that the matter of fire, which many equate to phlogiston, has no *sensible* weight and therefore chemists cannot use phlogiston to account for any weight change observed in chemical reactions.⁶⁵ Another problem for the partisans of the phlogiston theory is to reconcile the essential mobility and subtlety of the matter of fire with the fixity of many combustibles which presumably contain this fire as a necessary ingredient.⁶⁶ One criticism directly concerns his view that the distribution of fire in substances is related to their particular state. If a metal is compounded of a calx and the matter of fire, then any substance containing a large quantity of free fire should suffice to produce a metal from its calx. Water vapour is such a substance and thus should revivify metallic calces or, for that matter, convert sulphur into vitriolic acid; and yet nothing like this is observed.⁶⁷ Furthermore if metals are compounds of a calx and fire, then metals ought to contain more fire than their calces. However, he said, with an implied reference to the theory of heat capacity, 'les expériences de M. Crawford, celles de M. Wilke, celles de M. de la Place & les miennes, prouvent le contraire.'⁶⁸

In the second half of the memoir Lavoisier presented his own substitute for the phlogiston theory he had just demolished; and as he had introduced his 1777 memoir on combustion and calcination, to which this

⁶³ 'Réflexions sur le phlogistique pour servir de développement à la théorie de la combustion & de la calcination publiée en 1777' [1785], *Mém. Acad. R. Sci. 1783* (1786), pp. 505-38; Daumas, op. cit. (16), p. 58.

⁶⁴ *Mém. Acad. R. Sci. 1783*, p. 505.

⁶⁵ *Ibid.*, pp. 509, 517; see below for Lavoisier's ideas on the weight of heat fluid.

⁶⁶ *Ibid.*, p. 506; cf. 'Sur la combustion' [1777], *Mém. Acad. R. Sci. 1777*, pp. 595-6 for a similar argument (see above).

⁶⁷ *Mém. Acad. R. Sci. 1783*, pp. 509-10.

⁶⁸ *Ibid.*, p. 519. Johan Karl Wilcke (1732-96). Wilcke's work on specific heat was published in the memoirs of the Swedish Academy for 1781; see McKie and Heathcote, op. cit. (33), pp. 95-108. Lavoisier and Laplace had referred to this paper in the joint memoir stating they had seen it after reading their own in June 1783 (*Mém. Acad. R. Sci. 1780*, p. 373n.). Wilcke mentioned Black, Crawford, and Kirwan, deriving his information from Magellan (McKie and Heathcote, op. cit., p. 108).

was the sequel, with a preliminary paper discussing his theory of heat, so here too he prefaced his alternative to the phlogiston theory or theories with a discussion of the matter of fire and the most general heat phenomena. In contrast to his characterization of the current state of the phlogiston theory, Lavoisier devoted the remainder of his memoir to a consistent application of his comparatively well defined concept of heat to explain changes in temperature in a representative variety of chemical reactions from the relative quantities of heat released by various combustions and calcinations to the heat produced by mixing water and concentrated vitriolic acid and the cooling accompanying the solution of salt in water. Although his general explanations are unchanged from his earliest work, his discussion is more physical than chemical, in keeping with his comparatively newly developed interest in particulate interactions outlined earlier in the same year in his paper on the affinity of oxygen.

From the well known observation that objects expand when heated and contract when cooled, it follows, Lavoisier said, that the particles of an object do not touch and that the spaces among them are filled with heat matter.⁶⁹ Solidity of substances must be due to the force of attraction between particles, a force which 'est une loi générale de la Nature à laquelle toute la matière paroît être soumise.'⁷⁰ All particles are thus acted upon by two forces, the force of their mutual attraction, aided by atmospheric pressure, and the expansive force of the igneous fluid. The three states of matter depend upon the balance between these opposing forces.

Treating change of state as a physical rather than as a chemical transformation with fire acting as a mechanical agent to separate the particles, Lavoisier attacked two problems, several aspects of which had been discussed two years earlier in the joint memoir on heat. The first was to explain the relative specific heats (heat capacities) of substances. He believed specific heat to be related to the volume of empty space within a substance, that is, to the physical capacity of a substance to contain heat matter,⁷¹ coupled with the resistance to expansion offered by the mutual attraction among the particles of a substance. A liquid should contain more empty space than the corresponding solid; therefore it should require more heat than the solid to raise its temperature a given number of degrees since the greater separation among the particles of the liquid reduces their mutual attraction and also provides more space into which the heat fluid can move. Hence the specific heat of a substance in the liquid state will be greater than when it is solid, and when aeriform the specific heat will be still greater.⁷²

⁶⁹ The *Traité de Chimie* (i. 1-3) opens with a similar statement which is repeated in the *Mémoires de Chimie* (i. 3-4).

⁷⁰ *Mém. Acad. R. Sci.* 1783, p. 524. In his *Mémoires de Chimie* (i. 5) he identified the force as universal gravitation.

⁷¹ Indeed, *heat capacity* was the term most generally used.

⁷² *Mém. Acad. R. Sci.* 1783, pp. 527-8.

Concerning the second problem, that of predicting temperature changes in chemical reactions, Lavoisier remarked that as heat matter may affect the state of a substance by causing a change in the spaces among particles, a change in these spaces will affect the igneous fluid. This mutual relationship enabled him to predict in a general way whether heat will be released or absorbed in a given chemical reaction. A gas which solidifies in a reaction should lose part of its capacity to contain heat and thus heat fluid should be released. This is precisely what happens during combustion and calcination.⁷³ Temperature increase depends upon the quantity of air which undergoes the change and the rate of the reaction. In most calcinations the rate is slow, so that the matter of fire dissipates as it is released. Optimum conditions for maximum heating are three: both the combustible and vital air should be aeriform before the reaction, all the combustion products should be solids, and the reaction should be instantaneous.⁷⁴

The transformation of air into a liquid or a solid was for Lavoisier the 'cas très-simple' of combustion. What if the product of combustion were aeriform as occurs in the combustion of carbon? Lavoisier explained that the volume of the product is less than that of vital air.⁷⁵ The heat evolved is due both to this decrease in volume and to the presence of carbon in the combination since carbon particles occupy space which, in the absence of carbon, would have been filled with heat fluid. In addition, the previously explained relationship between pore-space and specific heat should provide a check, 'une expérience décisive', on the decrease in pore-space deduced from theory. If fixed air has less pore-space, it should have a lesser capacity for heat than vital air, and therefore it should have a lower specific heat. Experiment shows, said Lavoisier, that this is indeed the case.⁷⁶

Lavoisier summarized his argument on combustion by repeating in substance what he had said in his 1777 paper. 'Il est aisé de voir que cette doctrine est diamétralement opposée à celle de Stahl & de tous ses Disciples' because rather than placing the matter of heat in the combustible, experience and analogy show it is the air which furnishes 'la très-majeure partie' of the matter of heat released during combustion. He then went on to show how a consistent application of his theory could explain temperature changes in kinds of chemical reactions other than combustion. He

⁷³ *Ibid.*, pp. 529-30.

⁷⁴ *Ibid.*, pp. 532-3.

⁷⁵ This was mentioned in the joint memoir on heat (*Mém. Acad. R. Sci. 1780*, p. 401) and repeated in his 'Mémoire sur la formation de l'acide nommé air fixe ou acide crayeux', *Mém. Acad. R. Sci. 1781*, p. 454, where he stated that the change in volume is proportional to the change in density. According to modern theory, the volume should not change.

⁷⁶ *Mém. Acad. R. Sci. 1783*, pp. 530-2. His knowledge of the relative specific heats of the two airs probably came from Crawford. Apparently Lavoisier and Laplace only determined the specific heats of vital and atmospheric air (see n. 83).

used the concept of volume change, or more precisely change in internal pore-space, to account for the heating which is observed when water is mixed with various substances. In each example there is a reduction in volume.

. . . les interstices qui existoient entre leurs molécules sont nécessairement diminués; il reste donc moins d'espace pour loger la matière de la chaleur; elle est donc obligée de se répandre au dehors dans l'état de chaleur libre, & de se répartir dans les corps environnans.⁷⁷

In the specific case of mixing water with concentrated vitriolic acid, there is less heat released with each successive addition of acid, and correspondingly the reduction of volume is less with each addition until finally, when one observes no reduction in volume, there is no heating.

N'est-ce pas une nouvelle preuve que le fluide de la chaleur occupe les interstices des corps? Que toutes les fois que les interstices diminuent, il y a de la chaleur qui en est chassée & qui devient libre? Que toutes les fois qu'ils augmentent, il se forme en quelque sorte un vide qui se remplit aux dépens de la chaleur de tous les corps environnans?⁷⁸

Just as the formation of fixed air seemed at first glance to contradict the general premise, so too with the solution of salts in water. In this case, there is a reduction in volume accompanied by cooling rather than heating. Lavoisier explained that when a salt is dissolved in water it changes state from a solid to a liquid. Cooling indicates that more heat fluid is absorbed by the liquefaction of salt than is released by the decrease in volume; and the reappearance of this fluid of heat when the salt

⁷⁷ Ibid., pp. 535-6.

⁷⁸ Ibid., p. 536. Lavoisier added (p. 537) that the ideas relating absorption and release of heat to volumetric changes 'ne me sont point propres. Mrs. Vandermonde & Monge ont avancé la même chose dans un Mémoire lû à l'Académie.' I have not been able to locate this paper. Lavoisier stated that Monge, among others, considered all mixtures and combinations in which there is a release of the matter of heat as species of combustion, and the example given was the mixing of water with various substances causing a reduction in volume accompanied by a release of heat. Lavoisier again referred to the ideas of Monge and Vandermonde in his *Mémoires de Chimie* (i. 8). In discussing his idea that the capacity of a substance to contain heat fluid depends upon the internal pore-space within the substance, Lavoisier stated that the consequence 'qui se trouve confirmée par les expériences de MM. Wilk [*sic*], Vandermonde, Monge, de la Place, et par les miennes, ne me paroît pas moins exacte; c'est que si on rapproche, par une force égale quelconque, les molécules de plusieurs corps, la quantité de calorique qui en sortira, sera différente.' An incomplete manuscript by Monge describing a theory of heat has been published by R. Taton, 'A propos de l'oeuvre de Monge en physique', *Rev. Hist. Sci.*, iii (1950), 177-9. It was purportedly written around 1783 (ibid., 177) although use of the term 'calorique' suggests a later date. It expresses the same ideas and uses the same terminology as the first part of a 1790 paper published in the second volume (1816) of the *Dictionnaire de Physique* [*Encyclopédie Méthodique*] (4 vols., Paris, 1793-1822), pp. 170-1; discussed in R. Taton, *L'Oeuvre Scientifique de Monge* (Paris: Presses Universitaires de France, 1951), pp. 323-5. In it Monge explained heat phenomena entirely in terms of forces: the mutual attraction among the particles of a substance, the attraction between these particles and caloric, and external pressure. Any change in the first of these which causes the particles of a substance to come closer together will result in the extrusion of some of the interposed caloric (*Dictionnaire*, ii. 171-2). The origin of these ideas is not known; see n. 45 above, for Monge's possible knowledge of Crawford's theory.

recrystallizes shows that this change is no different from changes of state in general.⁷⁹

Crawford's influence is still apparent. Lavoisier deferred to Crawford in the matter of terminology.⁸⁰ He also accepted in principle Crawford's premise that specific heat reflects the relative quantity of free heat fluid in a substance and he used the idea to account for a wide variety of heat phenomena. For example, the major part of the heat released by mixing water with various substances comes from the water because it has a much greater specific heat than the substances mixed with it.⁸¹ That the specific heat of fixed air is less than vital air illustrates that a rearrangement of particles occurs in the formation of the former, and this rearrangement is the cause of part of the matter of heat released. He also cited his own, Crawford's, and Wilcke's experimental data that there is more igneous fluid in calces than in the corresponding metals to refute the claims of phlogistonists that the reverse should be the case.⁸²

But changes in specific heat cannot account for all heat phenomena, and it was doubtful that Crawford's theory, when quantitatively applied, could account for any. Attempts to calculate absolute zero or the precise quantities of heat transferred in chemical changes had proved fruitless, and since the joint memoir, Lavoisier and Laplace had determined (but published much later) a value for the specific heat of air which was vastly different from the figure Crawford had given.⁸³ This cast further doubt on Crawford's concept, and Lavoisier was even more firmly convinced that in some cases fire is chemically combined as well as free. The specific heat of air is indeed greater than most other substances (although considerably less than Crawford believed). Yet the quantity of free fire indicated by the specific heat is not enough to account for all the heat released; additional fire must be combined. This is what he meant when, in explaining how his theory is diametrically opposed to that of Stahl, he said that

l'air & le corps combustible y contribuent [fire released in combustion] chacun; 1.^o en raison de leur chaleur spécifique; 2.^o en raison de la portion de chaleur combinée qui devient libre; mais comme l'expérience & l'analogie prouvent également que la chaleur spécifique de l'air & celle

⁷⁹ *Mém. Acad. R. Sci. 1783*, pp. 537-8. In 1773 in Rozier's journal, he had published an account of temperature changes accompanying the crystallization and solution of salts ('Observations lues par M. Lavoisier à l'Académie Royale des Sciences sur quelques circonstances de la cristallisation des sels', *Observations sur la Physique*, 1 [1773], 10-13) probably based on experiments performed late in 1771 (Daumas, op. cit. [16], p. 27). There is no indication in this article nor in his reference to the phenomena in the manuscript memoir of July 1772 (Fric, op. cit. [5], 141-2) that he considered the solution of salt to be simply a change of state like fusion.

⁸⁰ *Mém. Acad. R. Sci. 1783*, pp. 527, 528.

⁸¹ *Ibid.*, p. 536.

⁸² See the discussion above.

⁸³ Although not published until the *Mémoires de Chimie* (i. 136-7), in February 1784 (Daumas, op. cit. [16], p. 51) a value of 0.65 was determined for the specific heat of vital air, a figure considerably less than the value Crawford had given and which Lavoisier had tentatively accepted in 1783.

[matter of heat] qui lui est combinée, est infiniment plus abondante que celle de quelque corps combustible que se soit, si ce n'est l'air inflammable, il en résulte que c'est l'air qui fournit la très-majeure partie de la matière de la chaleur qui se dégage pendant la combustion.⁸⁴

The paper on phlogiston marks Lavoisier's first frontal assault on Stahl's view. Half of that paper presents a theory of heat which, unlike the phlogiston theory, can simply, easily, and consistently explain all manner of heat phenomena. Indeed, the presentation of his alternative to the phlogiston theory is restricted almost entirely to a discussion of this theory of heat and its application. The particular view advanced in 1785 is a modification of an earlier theory, a change partly developed in the joint memoir on heat read in 1783 and one which probably originated during the latter half of 1781. The theory developed in the paper on phlogiston remained essentially unchanged in Lavoisier's subsequent publications.

Traité de Chimie, 1789

In the first part of his *Traité Élémentaire de Chimie*, published in 1789, he followed in general the sequence of ideas presented in his manuscript of April 1773, the memoirs of 1777 and 1778, and the latter half of the 1785 essay on phlogiston. He began by outlining the caloric theory and his concept of elastic fluids as being one of three states of matter (Chapter I) leading to the implications of this theory for ideas on the nature of the atmosphere (Chapter II). His concept of the nature of gases runs through the next two sections (Chapters III and IV), dealing with the atmosphere, which serve as the introduction to his explanation of combustion and the formation of acids in a section (Chapter V) significantly entitled 'De la décomposition du gaz oxygène. . .'.⁸⁵

Lavoisier's discussions are couched primarily in terms of the balance-of-forces concept developed in the memoir on phlogiston. Several ideas expressed earlier are further developed. One of these is his concept of the liquid state of matter. In the memoir on phlogiston, he had stated that a substance becomes liquid when the expansive force of heat equals the force of mutual attraction among particles. Thus the slightest increase in heat would be sufficient to cause vaporization were it not for atmospheric pressure which prevents the vaporization of water, for example, at 0°R rather than at the normal temperature of 80°R.⁸⁶ He repeated this

⁸⁴ *Mém. Acad. R. Sci. 1783*, p. 535; note that the heat in vital air is free heat (specific heat) and combined heat.

⁸⁵ *Traité*, i. 57. The discussion of heat is unchanged in the second edition (2 vols., Paris, 1793) and in the third (2 vols., Paris, an IX [1801]).

⁸⁶ *Mém. Acad. R. Sci. 1783*, pp. 524-5. This can be deduced from the role of air pressure discussed in the 1778 paper on the formation of elastic fluids (*Mém. Acad. R. Sci. 1777*, pp. 425, 429).

in the *Traité* and added that 'On voit donc que, sans la pression de l'atmosphère, nous n'aurions pas de liquide constant. . .'.⁸⁷

He also elaborated his discussion of fusion. The fusion of substances by caloric is precisely the same as the solution of salts in water.

Ni le dissolvant [water], ni le corps tenu en dissolution [salt] ne sont décomposés dans cette opération [solution]; aussi, dès l'instant que la cause qui tenoit les molécules écartées cesse, elles se réunissent, & la substance saline reparoit telle qu'elle étoit avant la solution.

On opère aussi de véritables solutions par le feu, c'est-à-dire, en introduisant & en accumulant entre les molécules d'un corps une grande quantité de calorique. Cette solution des corps par le feu se nomme *fusion*.⁸⁸

Indeed, caloric and dissolvents (such as water) not only act alike but they also act together. All solutions in water, and for the most part evaporations in air as well, should be viewed as mixed solutions in the dissolvent (water or air) and caloric as both substances are present and each reinforces the action of the other.⁸⁹

The *Traité* also illustrates the further development of Lavoisier's views concerning the distribution of combined caloric in substances. The purpose of the 1777 presentation of his theory of heat was to explain his idea on the nature of the so-called permanently elastic fluids. He thus focused his attention on vital air as the source of the matter of heat evolved in combustion and explicitly denied the probability that heat might be combined in solids, for example, combined as phlogiston in solid combustibles. However, his general argument relating quantity of heat to the state of a substance requires that all gases contain a relatively large quantity of heat. He later indicated that, other things being equal, more heat would be released during combustion if the combustible (for example inflammable air) were aeriform prior to the reaction and if the products were solid. An exception to this general rule is *l'acide nitreux*. As only a comparatively small quantity of the matter of fire is released in its forma-

⁸⁷ *Traité*, i. 8; cf. the somewhat stronger statement in the *Mémoires de Chimie* (i. 296-7): '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.'

⁸⁸ *Traité*, ii. 534. Cf. the statement by Guyton de Morveau: 'Le feu est exactement aux métaux 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 cristallisations métalliques', *Observations sur la Physique*, xiii [1779], 90). Lavoisier consistently referred to the action of the matter of fire as a dissolution process; and it is clear that he considered dissolution in caloric and combination with caloric to be equivalent (for example, see *Mémoires de Chimie*, i. 322). The novelty of the concept of *fire* as a dissolvent is suggested by the debate during the 1770s over whether crystals formed upon the solidification of molten metals are true crystals or whether that true crystals come only from aqueous solutions; C. S. Smith, 'The development of ideas on the structure of metals', *Critical Problems in the History of Science*, ed. M. Claggett (Madison: Univ. of Wisconsin Press, 1959), p. 488.

⁸⁹ *Traité*, ii. 422-8, 432-3, 437-9.

tion, this acid and consequently *le nitre* contain a relatively large quantity of combined fire. This, he said, accounts for the effects of detonations.⁹⁰

The *Traité de Chimie* contains a more extensive treatment of this subject which illustrates Lavoisier's use of quantitative data and how little his subsequent belief in the combination of heat matter in a variety of substances affected his commitment to the more fundamental principles concerning the nature of elastic fluids and the source of the heats of combustion and calcination. He assumed that of all possible combinations of a given quantity of oxygen with other substances, the greatest quantity of caloric is given off by the union of oxygen with phosphorus because the resulting compound is a solid.⁹¹ In the reaction, one *livre* of oxygen gas releases enough caloric to melt over sixty-six *livres* of ice. Using this as his standard, he computed the quantities of ice melted by the union of one *livre* of oxygen gas with a variety of substances, such as carbon and hydrogen gas, and concluded that a substantial quantity of caloric is retained by oxygen when it unites with these other substances.⁹²

Mémoires de Chimie

Lavoisier's discussion in the *Traité* represents a modification in detail of the general treatment in the essay on the phlogiston. The same is true of his most detailed and systematic discussion of the caloric theory, which is contained in his posthumously published *Mémoires de Chimie*.⁹³ This work, if completed, would have comprised about eight volumes; and, as Madame Lavoisier stated in the introduction, it would have presented in a way 'l'histoire de la chimie moderne.'⁹⁴

The first volume of the two that were published deals solely with a

⁹⁰ *Mém. Acad. R. Sci.* 1780, pp. 399-400.

⁹¹ In 1787 he had indicated that the combustion of inflammable gas evolves more heat than the combustion of phosphorus (*Nomenclature Chimique*, pp. 294-7).

⁹² *Traité*, i. 103-15. Similar calculations are given in the joint memoir on heat; however, their purpose was to give a quantitative demonstration of the general principle that when the product of combustion is a solid, more heat is released than when the product is a gas (*Mém. Acad. R. Sci.* 1780, pp. 398-9). Lavoisier returned to this subject in his *Mémoires de Chimie* (i. 137-41) where he repeated many of his earlier computations. In discussing the presence of caloric combined in solids, he admitted that oxygen in uniting even with phosphorus may not give up all its caloric; hence caloric is probably combined in phosphoric acid and perhaps even in carbon.

⁹³ Madame Lavoisier, in the brief introduction, said that work on this was begun in 1792 (i. p. iii). In one of the memoirs Lavoisier stated that he was writing in 1793 (i. 122). Although the date of publication is usually given as 1805, Partington has shown that the book was distributed in or before 1803 (op. cit. [1], iii. 372). For a discussion of the facts of publication and a résumé of the articles, see D. I. Duveen and H. S. Klickstein, *A Bibliography of the Works of Antoine Laurent Lavoisier, 1743-1794* (London: Dawson, 1954), pp. 199-214, and D. I. Duveen, *Supplement to a Bibliography of the Works of Antoine Laurent Lavoisier, 1743-1794* (London: Dawson, 1965), pp. 113-14. W. A. Smeaton in his review of the Duveen and Klickstein *Bibliography* argues that Lavoisier intended the title to be *Mémoires de Physique et de Chimie*; see *The Library*, xi (1956), 133.

⁹⁴ *Mémoires de Chimie*, i. p. iii.

discussion of heat theory.⁹⁵ As was the case in his earlier presentations, the volume was intended as the introduction to his theory of oxidation and the formation of acids; and the development of ideas, although more systematic and more detailed, follows the same general sequence. Indeed it covers in some four-hundred pages the same ground as the first two chapters of the *Traité de Chimie*.⁹⁶ Significantly, virtually all of the experimental data which is published here for the first time derives from the period prior to 1785, indeed most of it is prior to 1783. Thus, as might be expected, although modified in detail, the theory expressed is the same as that expounded in the essay on phlogiston and in the *Traité de Chimie*.

The most significant theoretical addition in the *Mémoires de Chimie* is Lavoisier's treatment of the states of caloric and the modifications it undergoes when it combines. Through all his writings, from the manuscript of 1772 to the *Mémoires de Chimie*, he had explained changes of state as due to the combination of the matter of heat with some other substance. Beginning in 1785 with the memoir on phlogiston this explanation was intertwined with explanations in terms of his concept of the balance of forces. In changes of state combined caloric retains its elasticity, or at least part of it, otherwise there would be no change in the degree of fluidity-elasticity in the substance with which it is combined; and the balance of forces concept is premised upon this assumption. Yet in the paper on phlogiston, he stated that in combination the matter of fire suffers a *loss* of its elasticity and the example he gave is the formation of *l'acide nitreux* which is, as he had explained earlier, the exception to the general rule that the quantity of combined heat in a substance is directly related to the degree of its fluidity or elasticity.⁹⁷ Thus, logically, there must be various states of combination of caloric although Lavoisier did not address himself publicly to this question.⁹⁸

In the *Mémoires de Chimie* he discussed in some detail the possible

⁹⁵ The volume ('Part I' of the *Mémoires*) is entitled 'Vues générales sur le calorique, ou principe de la chaleur, sur ses effets, sur leur mesure, et sur la formation des liquides et des fluides' (*ibid.*, p. 1). Part I is incomplete, ending on p. 416 in mid-sentence. However, considering the length of the volume and the development of ideas, it is likely that the missing part is comparatively insignificant. The second volume ('Part II' of the *Mémoires*) is entitled 'De la décomposition de l'air de l'atmosphère . . .' (*ibid.*, ii. 1). The purpose of the first few papers is the same as Chapter III of the *Traité*, to demonstrate that atmospheric air is not a simple substance but a mixture. Indeed, the opening sentences of the first paper in Part II indicates the purpose of Part I.

'Je n'ai présenté jusqu'ici [that is, in Part I] que des considérations générales sur la formation des fluides élastiques aëriiformes; j'ai cherché à établir qu'ils sont tous formés de la solution d'une substance quelconque, dans le calorique et la lumière.

Il est résulté des principes que j'ai posés, que notre atmosphère devoit être un mélange, un composé de toutes les substances susceptibles d'être tenues dans l'état aëriiforme aux degrés de chaleur et de pression que nous éprouvons' (*ibid.*, ii. 1-2).

⁹⁶ The increased length is due to the inclusion of four papers by an associate Armand Seguin (which comprise over a fourth of the entire volume) and of papers by Lavoisier, the contents of most of which had been only summarized or alluded to in his earlier works.

⁹⁷ *Mém. Acad. R. Sci.* 1783, p. 526; *Mém. Acad. R. Sci.* 1780, pp. 399-400.

⁹⁸ A major part of the manuscript of 1775 is devoted to a discussion of the different degrees of affinity that fire has for substances with which it is combined in forming the vaporous state; see Gough, *op. cit.* (15), 272-5.

relationships between particles of caloric and those of other substances. Modifying his earlier statements that caloric exists in two states, free and combined, he concluded that caloric can exist as either free, adherent, or combined 'molécule à molécule' with the elementary constituents of other substances. However, it is easily seen that caloric is always more or less adherent to substances,⁹⁹ and 'qu'il doit par conséquent exister des dégradations insensibles et une infinité d'intermédiaires entre l'état de calorique parfaitement libre et celui de calorique dans un état de combinaison.'¹⁰⁰ Combined and free thus mark the limits of a continuum of possible relationships.

Caloric in a state approaching the combined end of the continuum can be removed only by means of chemical decomposition; and it 'ne contribue en rien aux phénomènes qui accompagnent l'échauffement et le refroidissement des corps.'¹⁰¹ In this state it acts as any other chemical element according to the laws of elective affinity. In vapours such as water vapour, however, caloric approaches the free end of the continuum and can be removed by simply lowering the external temperature. In this state, the effects of its own elasticity are more apparent and the theory of changes in heat capacity most applicable. In fusion caloric occupies an intermediate position. It is not combined in the sense described above; yet the change in volume during fusion is insignificant compared with vaporization. Hence part of the elasticity of the caloric has been lost and thus the caloric partially combined.¹⁰²

In spite of the specific definitions, in describing the infinite number of relationships possible between caloric and the particles of other substances, Lavoisier used 'combination' in cases ranging from an almost total loss of elasticity when caloric is combined in *le nitre*, for example, to a patent retention of most of its elasticity in vapours.¹⁰³ Thus in combination there are degrees of blending of characteristics of the constituents in which caloric may completely lose its identifying features or retain them almost entirely. In the latter case, caloric physically separates the particles of substances, and its role can be described as

⁹⁹ In the 1785 essay on phlogiston, he had indicated that, strictly speaking, heat can never be absolutely free because of the mutual adherence between it and the particles of other substances (*Mém. Acad. R. Sci.* 1783, pp. 526-7).

¹⁰⁰ *Mémoires de Chimie*, i. 14.

¹⁰¹ *Ibid.*, i. 137.

¹⁰² *Ibid.*, i. 286-8.

¹⁰³ The same inconsistency occurs in Lavoisier's use of the term 'dissolution'. The dissolution of metals in acids is different from the dissolution of salts in water. In the former, the elementary constituents of both metal and acid are affected, whereas in the latter the individual particles of the salt are separated without affecting their original identity. In the *Traité de Chimie* (ii. 423-4), Lavoisier attempted to distinguish these two kinds of reactions by restricting the term 'dissolution' to apply to the former and using the term 'solution' for the latter. Unfortunately this distinction was not rigidly maintained either in the *Traité* or in his other works. Robert Kerr in his translation was more precise in his use of the terminology than was Lavoisier in the original: *Elements of Chemistry in a New Systematic Order Containing All the Modern Discoveries* (Edinburgh, 1790). Compare Kerr's translation (pp. 368-72, 375, 380) with the corresponding sections in the *Traité* (ii. 423-8, 432, 438).

chemical only in the sense that it acts at the level of ultimate particles.¹⁰⁴ Thus vaporization and to a lesser extent fusion are due to caloric acting as a mechanical agent rather than a chemical constituent. This position, the end result of the concept of a balance of forces, represents a considerable shift from his earlier views. Beginning with fire combined in vital air solely by virtue of its state, he concluded in the *Mémoires de Chimie* that a very substantial portion of the caloric in oxygen gas is combined in a form unrelated to state.

The *Mémoires de Chimie* contain papers which separately might be considered primarily physical rather than chemical in nature.¹⁰⁵ Appearances notwithstanding, Lavoisier was not interested in the physical aspects *per se* of his caloric theory, for he viewed these matters as inextricably associated with his general chemistry. With two exceptions, each of the memoirs contain explicit references to this view, which was the motivation for them all.

The two apparently exceptional papers are those on the expansion of solids and liquids.¹⁰⁶ The experiments described derive from the period 1781-2 when Lavoisier was actively engaged in testing Crawford's theory and in altering his own concept accordingly; and passing reference to this work in the joint memoir of 1783 indicates the reasons why Lavoisier and Laplace undertook the research. Following a short table listing the specific heats of twelve substances (including iron, glass, and mercury, the substances the later papers concentrate on), the authors stated that they proposed to continue their work so that the list could be expanded. Furthermore,

il seroit intéressant d'avoir dans un même Tableau, les pesanteurs spécifiques des corps, les variations qu'occasionne la chaleur dans ces pesanteurs, ou, ce qui revient au même, les dilatabilités respectives des corps, & leurs chaleurs spécifiques; la comparaison de ces quantités feroit peut-être découvrir entr'elles des rapports remarquables; nous avons fait, dans cette vue, un grand nombre d'expériences sur les dilatations, que nous nous proposons de publier, lorsqu'elles seront entièrement terminées.¹⁰⁷

He never stated precisely what these remarkable relationships might be. It is probable, however, that the idea he had in mind was the precise determination of chemical affinity, for in another passage he remarked that

L'équilibre entre la chaleur qui tend à écarter les molécules des corps [that is, to expand bodies], & leurs affinités réciproques qui tendent à les

¹⁰⁴ *Traité*, ii. 422-3.

¹⁰⁵ Duveen and Klickstein, *op. cit.* (93), p. 201, describe it as a 'monograph on physics'.

¹⁰⁶ *Mémoires de Chimie*, i. 246-80, 295-311.

¹⁰⁷ *Mém. Acad. R. Sci.* 1780, p. 374. In the opening paragraph of the memoir on the expansion of liquids, Lavoisier stated 'il sembleroit donc qu'il existe une sorte de relation entre l'augmentation de capacité de chaleur qui a lieu dans les changemens d'état, et l'augmentation de dilatabilité' (*Mémoires de Chimie*, i. 295).

réunir, peut fournir un moyen très-précis de comparer entr'elles ces affinités. . . .¹⁰⁸

Subsequent work did not confirm these early expectations. As Lavoisier remarked in his *Mémoires de Chimie*, the expansion of substances bears no relationship

ni avec l'adhérence et la ténacité de leurs parties [to which specific heat is directly related], ni avec aucune autre des propriétés que nous leur connoissons.¹⁰⁹

As there were no 'rapports remarquables' to report, these papers in the *Mémoires de Chimie* contain only descriptions of experiments performed and the apparatus used.

Influence of Black

The compatibility of the caloric theory and Black's concepts of heat raises the question of the possible influence of Black's theories on Lavoisier.¹¹⁰ The historical evidence indicates that the essential part of Lavoisier's theory, that part which relates to his ideas on the nature of air and the closely associated roles of air and fire when air combines with other substances, are his own and antedate his knowledge of Black's ideas on heat.¹¹¹

Lavoisier's manuscript of July 1772 on the nature of air clearly states his theory that fire matter can exist both free and combined, that vapours are igneous compounds, that air itself is a vapour, and that this explains how air can condense to become fixed in a solid form. There is no evidence to indicate that at the time this was written Lavoisier had any knowledge of Black's ideas on heat. Lavoisier did learn something of Black's heat experiments a short time later. Assuming the account of Black's theory published in September 1772 fairly represents the substance of Lavoisier's later knowledge of Black's ideas, we can perhaps determine the extent of Black's influence. The article describes Black's idea that heat becomes latent during fusion and vaporization. Although Black may have believed heat is combined in these changes, no hint of this idea

¹⁰⁸ *Mém. Acad. R. Sci.* 1780, p. 391.

¹⁰⁹ *Mémoires de Chimie*, i. 281. Seguin denied there is a direct relationship between heat capacity and expansion (*Annales de Chimie*, iii [1789], 154n.) and in 1790 claimed that he had discussed the matter several times with Lavoisier and had persuaded him to abandon the view that there is a correlation between the two effects; see 'Réponse de M. Seguin à la lettre de M. de Luc insérée dans le Journal de Physique du mois de mars 1790', *Observations sur la Physique*, xxxvi (1790), 420. However, influence of the idea is seen in the opening lines of the paper on the expansion of fluids (n. 107 above).

¹¹⁰ See Morris, op. cit. (14), 377-9; cf. Guerlac, op. cit. (14), 380-2.

¹¹¹ Partington (op. cit. [1], iii. 131) described Lavoisier's concept of air as a state as 'an extension of Black's theory of latent heat'. See similar statements in McKie's introduction to Lavoisier's *Elements of Chemistry* (op. cit. [103], pp. xxiii, xxviii) and in Duveen and Klickstein, op. cit. (93), pp. 52, 54.

appears in this article.¹¹² Lavoisier had already hit upon the idea of combining matter of heat in the formation of vapours and air, and furthermore he had derived it from observations of the cooling which accompanies evaporation and many effervescences, not from constant-temperature changes of state.¹¹³ Although in July 1772 he had said virtually nothing concerning fusion, he had started with some hesitation to explain the cooling of an ice-salt mixture. His explanation is incomplete, but the context indicates he was thinking in terms of fire matter being combined somehow in fusion as well as in vaporization. Although he had already noticed the constant-temperature melting of ice in an ice-water mixture (in September 1771), he had not associated this phenomenon with the heat theory when he wrote the July memoir.¹¹⁴

The difference between this memoir and Lavoisier's revision of it in April 1773 is one of tone and manner of expression as well as substance. As in the earlier paper, his discussion focuses on the process of vaporization to justify his ideas on the nature of air. However, his expression is more assured and he explicitly mentioned fusion as an example of combining fire and stated that the states of matter are due to this combination. The difference between the two manuscripts in the expression of heat theory was perhaps due in part to Lavoisier's knowledge of Black's ideas. Black's concepts of latent heat could provide more extensive underpinnings for a theory Lavoisier had obtained by another route, and the specific, explicit inclusion of fusion in the concept of combined fire served to broaden his theory to include firmly all changes of state and at the same time provide a more substantial observational foundation.

Yet in the light of his subsequent discussions of a theory of heat, it is doubtful that Lavoisier fully understood the import of Black's theory. Except in his brief paper of October 1772, in which he mentioned Black's

¹¹² Black explained changes of state in terms of combined fire in his *Lectures on the Elements of Chemistry*, ed. J. Robison (2 vols., Edinburgh, 1809), i. 49, 129, 157, 176, 192-5. Although there is some doubt as to whose ideas are stated in Black's *Lectures*, a statement of this particular version of Black's views appeared in the second edition of the *Encyclopaedia Britannica* (10 vols., Edinburgh, 1778-83; 'Congelation', iii [1778], 2189; 'Evaporation', iv [1779], 2847, 2848; 'Heat', v [1780], 3539). However, the article of 1772 (loc. cit. [3]) states only that heat is absorbed and becomes hidden during changes of state. The same idea is contained in Thomas Cochrane, *Notes from Doctor Black's Lectures on Chemistry*, 1767/8, ed. D. McKie (Cheshire: Imperial Chemical Industries Ltd., 1966), pp. 12, 13, 15, and in the anonymous account of Black's ideas published in 1770: *An Enquiry into the General Effects of Heat, with Observations on the Theories of Mixture* (London), pp. 40, 48.

¹¹³ Lavoisier was not alone in explaining changes of state in terms of the combination of fire matter. In 1772 Wilcke published his theory of the latent heat of fusion; see McKie and Heathcote, op. cit. (33), pp. 78-94. Wilcke and Black seem to have arrived at the concept of latent heat by consideration of times and quantities of heat required to melt ice and snow (ibid., pp. 16, 78). A conclusion similar to Lavoisier's and based on the same kinds of evidence that Lavoisier used was published in 1772 in Deluc, *Recherches sur les Modifications de l'Atmosphère* (2 vols., Geneva). Deluc cited evaporative cooling and the condensation of water vapour on a cold surface to demonstrate that vaporization is caused by a combination of the matter of fire with water (ibid., i. 178, 180, 182-3, 264-5; ii. 175).

¹¹⁴ See a discussion of this point in Morris, op. cit. (14), 378-9; cf. Guerlac, op. cit. (14), pp. 380-1.

work,¹¹⁵ he made no further reference to the phenomena summarized in Black's concept of latent heat until his laboratory notebooks of late 1781; nor did he utilize the British concept of latent heat in any way to bolster his own argument.

Considering his theoretical discussions between 1772 and 1781, Lavoisier probably saw Black's work as being of very limited significance. The 1772 account of Black's theory deals almost exclusively with fusion; and Lavoisier, thoroughly involved in developing a radical view of combustion and calcination, was not very interested in fusion. Indeed, up to 1781 Lavoisier virtually ignored fusion, apart from what is implied in his often repeated statement that the three states of matter are due to the quantity of fire combined therein.

He was, however, vitally interested in vaporization. The account of Black's work does mention that change of state at constant temperature occurs in vaporization as in fusion; however, it is given without evidence, in an off-hand manner, and might have been easily overlooked. In any case, if Lavoisier noticed it, he ignored it; his paper of October 1772 where he commented on Black's ideas contains no mention of vaporization. Although he stated in the manuscript of July 1772 that heat is combined during the vaporization of water placed over an external flame,¹¹⁶ he also remarked (in a manuscript dating from *c.* 1773) that under these conditions it is impossible to perceive the combination of fire matter, and thus such vaporizations cannot be used to prove the truth of his theory.¹¹⁷ Before 1781 change in temperature was the only clear demonstration of a change in the state of the matter of fire. Black's views notwithstanding, his own experimental evidence, different from Black's, and his own line of reasoning were in his own mind completely convincing of the truth of his theory.

In 1781 the situation was different. The initial impact of Magellan's article was probably due not so much to the ideas of specific heat or of change of state at constant temperature that it contains as to Crawford's conclusions that combustion, calcination, and respiration are fundamentally identical processes and that air is the source of the heat released. Crawford had preempted in print the core of Lavoisier's originality and thus Lavoisier felt compelled to examine the quantitative experimental bases of Crawford's theory, or rather Magellan's version of it. As it turned out, the phenomena upon which Black had based the concepts of latent heat and heat capacity could be easily incorporated into Lavoisier's theory.¹¹⁸

The knowledge of Black's ideas via Crawford and Magellan, which Lavoisier gained in 1781, served to broaden his theory of heat to include

¹¹⁵ Cited in n. 2 above.

¹¹⁶ Fric, *op. cit.* (5), 142.

¹¹⁷ *Ibid.*, 152.

¹¹⁸ The major point on which Lavoisier and Crawford disagreed was on whether fire is combined or not.

the concepts of specific heat and of change of state at constant temperature; and through the use of the latter notion it led to the development of the ice-calorimeter, which in turn resulted in the wealth of quantitative data he used to support his theory in his subsequent publications. This in itself had only an indirect effect on the basic theory for it did not touch his fundamental assumptions. Crawford's idea of heat capacity, however, had a far greater influence, for its physical implications suggested to Lavoisier the possibility of reducing the explanations of heat phenomena (and hence of chemical phenomena) to a consideration of interparticulate forces which, in theory, would be subject to mathematical treatment. The balance-of-forces concept which bulks so large in Lavoisier's discussions after 1783 is in part if not wholly due to his interpretation of the idea of heat capacity.¹¹⁹ Thus certain aspects of Black's theory as they were developed in the hands of William Irvine, then Crawford (and perhaps Kirwan), and finally Magellan had a far more profound impact on Lavoisier's thinking than did Black's original views. Lavoisier's *effective* knowledge of Black's theory and of the ideas based upon it came in 1781, and directly and indirectly resulted in a complete reorientation in the nature and technique of his and Laplace's experimental work in heat as well as a modification of some of the basic concepts of the caloric theory.

Tradition

Many aspects of the caloric theory represent a continuation of a tradition which had dominated scientific thinking throughout most of the eighteenth century. Indeed, historians commonly cite caloric as a prime example of Lavoisier's conservatism and of the incorporation of traditional concepts into the new chemistry. To a limited extent, this view is justified. Caloric itself and the language used to describe it are certainly in the eighteenth-century tradition of ascribing various phenomena to the effects of a variety of subtle fluids whose characteristics were tailored to fit the particular phenomena in question. And Lavoisier never faltered in his belief that the cause of sensible heat is a material substance. In his 1778 paper on the formation of elastic fluids he said he could dispense with proofs of the existence of heat fluid because opinion favouring its existence was held by the vast majority of physicists. Besides, its accord with all physical and chemical phenomena serves in itself as a demonstration of its existence.¹²⁰

Although in the 1783 joint memoir on heat the authors stated they would avoid a commitment to a particular theory of heat,¹²¹ subsequent explanations of specific phenomena reveal Lavoisier's commitment to the

¹¹⁹ Or Monge's interpretation?

¹²⁰ *Mém. Acad. R. Sci.* 1777, p. 420.

¹²¹ *Mém. Acad. R. Sci.* 1780, p. 358.

concept of heat as a material substance.¹²² However, he was never able to provide, to his own satisfaction, a positive demonstration of the existence of heat matter, and under pressure from his critics (and perhaps some supporters such as Laplace), he conceded in 1785 that this subtle fluid may be hypothetical. But he added,

c'est la seule [hypothèse] 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 du fluide igné est une hypothèse, elle est commune à leur système & au mien.¹²³

He even declared that the assumption that heat is a real substance is unnecessary; all that is needed is to assume that heat 'soit une cause répulsive quelconque qui écarte les molécules de la matière.'¹²⁴

These admissions notwithstanding, his discussions of specific phenomena take for granted the existence of heat matter as a fact of nature not requiring justification. Even in those papers where he admitted the hypothetical nature of heat fluid, his subsequent explanations are entirely in terms of a subtle heat substance. His true feelings regarding this 'single hypothesis' are indicated in his *Mémoires de Chimie*. Still unable to provide a positive demonstration of the existence of heat fluid, he wrote that when one considers how easily the concept explains the results of experiments, and that it is in accord with all the phenomena, 'cette hypothèse cessera d'en être une, et on pourra la regarder comme une vérité.'¹²⁵

Lavoisier's acceptance of traditional theories was not limited to his belief that heat is a material substance. The idea that heat matter can exist in two distinct states, free or combined, was used by his predecessors and contemporaries in explaining various phenomena of combustion and calcination.¹²⁶ Fire matter fixed as phlogiston still retains some of its identifying features. Hence its presence is recognizable from the characteristics such as softness, ductility, and malleability that it imparts to the compound. So too with caloric. Even when fixed, it retains with few exceptions part of its identity and its presence in the compound is recognizable through the effect of its own elasticity in causing increased fluidity-elasticity in the substances in which it is combined.¹²⁷

There is ample precedent also for many of Lavoisier's explanations of specific phenomena, particularly in his use of the balance-of-forces concept to explain changes of state. Earlier eighteenth-century material-

¹²² See for example his discussion of heat *combined* in various substances (*ibid.*, pp. 394, 399-400). If Lavoisier wavered in his view, he did so only in the first half of this memoir.

¹²³ 'Sur le phlogistique' [1785], *Mém. Acad. R. Sci.* 1783, p. 524.

¹²⁴ *Traité*, i. 6.

¹²⁵ *Mémoires de Chimie*, i. 2.

¹²⁶ Venel, 'Feu (Chimie)', *Encyclopédie*, vi. 609; Macquer, *Elémens de Chymie-théorique* (new edn., Paris, 1753), p. 16. For a discussion of Rouelle and his significance in this connexion, see R. Rappaport, 'Rouelle and Stahl: the phlogistic revolution in France,' *Chymia*, vii (1961), 76-7, 85-6.

¹²⁷ Indeed, Joseph Black attributed the qualities of softness, ductility, and malleability to latent heat (*Lectures*, i. 138-40).

heat theories universally accounted for these changes as due simply to the mechanical separation of particles by means of an interposition of igneous fluid.¹²⁸ Indeed, except for the use of the term 'combination', many of Lavoisier's discussions taken out of context are virtually indistinguishable from those which went before.

Innovation

Although many of Lavoisier's ideas plainly come from older chemical and physical theories, his theory of heat contains a great deal which is novel. For example, he made a definite attempt to break away from some of the older ideas associated with theories of subtle fluids, especially the view that these substances are a species apart, *sui generis*, obeying laws peculiar to themselves. Caloric is indeed a subtle fluid, but it is a form of matter nevertheless and as such should obey the laws common to matter in general. He described caloric and the electric and magnetic fluids as forming a more rarefied state to be included with the usual solids, liquids, and gases.¹²⁹ Caloric is so tenuous that it passes more or less freely through the pores of the most dense materials; but its materiality becomes manifest when it is produced in large quantities in a short period of time as illustrated in the explosion of gunpowder where caloric augments the effects produced by gases in propelling the cannon ball.¹³⁰

His general view that caloric is subsumed under the laws governing matter in general led him to examine the properties by which caloric is identified. Operationally speaking, caloric is imponderable and as such is of no direct use in accounting for the changes in weight observed in various reactions. However, as a form of matter, caloric must obey the law of universal gravitation. Its weight is simply too small to be detected:

. . . cet élément [matter of heat], ce fluide subtil obéit probablement, comme tous les autres, aux lois de l'attraction, mais sa pesanteur est si petite qu'il n'est pas possible de la rendre sensible dans aucune expérience physique.¹³¹

Caloric has 'une pesanteur si petite, qu'elle échappe à tous les instrumens qui ont été employés jusqu'ici pour la déterminer . . .'¹³²

¹²⁸ For example, the idea of opposing forces was stated by Boerhaave (*A New Method of Chemistry*, trans. P. Shaw [3rd edn., 2 vols., London, 1753], i. 246-7) and Turgot (op. cit. [11], p. 282). The latter (p. 277) described changes of state as nuances of the general expansive action of heat.

¹²⁹ *Mémoires de Chimie*, i. 404-11. These fluids differ from gases in that they have varying abilities to penetrate the pores of different substances such as glass and metals. Caloric is more subtle than the electric and magnetic fluids.

¹³⁰ *Traité*, ii. 526-7.

¹³¹ 'Sur le phlogistique' [1785], *Mém. Acad. R. Sci. 1783*, p. 509. As Seguin remarked, 'notre idée se refuse à l'existence d'un corps dont la pesanteur est absolument nulle' (*Annales de Chimie*, iii [1789], 185; cf. a similar statement by him in Lavoisier's *Mémoires de Chimie*, i. 158-9, note).

¹³² *Mémoires de Chimie*, i. 408. Cf. similar statements in '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 décomposition & de récomposition, *Mém. Acad. R. Sci. 1781*, p. 473; 'Nouvelles réflexions sur l'augmentation de poids qu'acquière en brûlant le soufre & le phosphore, & sur la cause à laquelle on doit l'attribuer', *Mém. Acad. R. Sci. 1783*, pp. 419-21; 'Sur la pesanteur de la matière de la chaleur', *Oeuvres*, v. 293.

A more difficult property of caloric in this respect is its great elasticity. The apparent self-repulsive property of particles of heat was for most chemists of the eighteenth century as fundamental a force in nature as gravity. For them, including Lavoisier, all fluidity and more especially fluid elasticity is explained by resorting to this feature of the matter of fire.¹³³ However, as Lavoisier admitted, to explain elasticity by simply resorting to another, prior elasticity is a regressive argument which still leaves the basic property unexplained. Caloric obviously does communicate an effective repulsive force. But as caloric should not possess an anomalous characteristic, this effective force must be ultimately caused by some kind of attraction or combination of different attractions as exemplified by the expansion of a dry sponge when penetrated by water.¹³⁴ He also drew an analogy to the action of water on salt during solution. Water separates the particles of salt, yet one does not usually say that water imparts a self-repulsive force to these particles. He admitted, however, that difficult problems arise from the denial of a self-repulsive force among the particles of caloric and concluded that repulsion is an effect, the cause of which is as yet unknown.¹³⁵

The view that caloric must obey the laws common to matter in general also probably led him to reject an almost universal feature of the theories of his predecessors that the particles of fire are endowed with a continual, inherent motion which is only to a limited extent arrested when fire combines with other constituents.¹³⁶ However, a motion unique to fire matter would be inadmissible. Except for a single reference to heat fluid as 'un fluide Stagnant',¹³⁷ Lavoisier simply ignored this supposed motion.¹³⁸

Lavoisier's innovations extended beyond the physical characteristics of heat matter to include new ideas on its activity in relation to other substances. At first glance the correspondence between caloric and phlogiston would seem to be another example illustrating the traditional line in Lavoisier's theories. For most of Stahl's followers, phlogiston is the

¹³³ Macquer had remarked that without heat all matter would be 'une seule masse immense, homogène, & d'une dureté absolue' (*Dictionnaire de Chimie* [2 vols., Paris, 1766], i. 498).

¹³⁴ *Traité*, i. 24-7. Regarding repulsion as being in reality an effect of attraction, see Seguin's views in Lavoisier's *Mémoires de Chimie*, i. 158-9, note.

¹³⁵ *Mémoires de Chimie*, i. 6-7, 19-25.

¹³⁶ For example see Boerhaave, *Method of Chemistry*, i. 359-64; and Macquer, *Dictionnaire* (1766), i. 498; ii. 203. This feature gave Lavoisier's predecessors greater latitude in accounting for heat phenomena, for temperature could be related to either the quantity of fire matter or the degree of its own internal motion.

¹³⁷ Fric, *op. cit.* (5), 142.

¹³⁸ The motion feature was absent in most material theories of heat discussed during the last quarter of the century. This resulted in a weakness in the explanations of mechanical production of heat, a weakness not present in the earlier material heat theories and one which Count Rumford exploited in his unsuccessful attempt to revive a vibratory theory in 1798. Most writers simply ignored the question of the motion of fire matter. The few who argued against it did so on the grounds that fire, being matter, should not possess a property which is not characteristic of matter in general; see 'Fire', *Encyclopaedia Britannica* (2nd edn.), iv (1779), 3003; and Jean Baptiste Pierre Antoine de Monet de Lamarck, *Recherches sur les Causes des Principaux Faits Physiques* . . . (2 vols., Paris, an II [1794]), i. 51, 66-7.

matter of fire which has become fixed in combustibles and metals; caloric is simply the new name given to this material substance; and in both theories, fire is released during combustion and calcination. However, what the phlogistonists attributed to the combustible substance, chemists of the new school transferred to oxygen gas. Using the definition of a combustible as the substance containing the heat fluid prior to its release, the new theory would have to say, as Lavoisier himself remarked, that pure air 'est donc dans cette opinion le véritable corps combustible, & peut-être le seul de la Nature.'¹³⁹

Lavoisier's innovation is more profound than simply shifting the location of caloric from the combustible to oxygen gas, for associated with this shift was the elevation to a pre-eminent position of a class of phenomena virtually ignored by earlier chemists—changes of state. Lavoisier treated caloric as behaving like any other elementary substance capable of entering into and being released from chemical combination according to the laws of elective affinity; and the reactions in which caloric becomes combined or released are almost always accompanied by a corresponding change of state.¹⁴⁰ Indeed, in his early thought, change of state is practically the only process in which caloric acts as a chemical constituent. Heat is absorbed in evaporation, effervescence, the solution of salts in water, and the reduction of metals; and in each case there is a concomitant change of state. As he explained in 1773, phlogiston (fire matter) and calx do react to produce a metal. However, phlogiston does not unite with the calx itself but rather with the air fixed in it to vaporize this air which then leaves the metal behind.¹⁴¹

Every change in the degree of cohesion among particles should also produce a corresponding change in the state of caloric, and conversely. From this point of view, the quantity of caloric combined in a substance is directly related to the degree of fluidity-elasticity of the substance and not necessarily related to its degree of combustibility or metallicity. In fact one would expect metals to contain little or no caloric simply because most are solids. For Lavoisier, changes of state were not to be viewed as a separate class of phenomena perhaps associated with but fundamentally independent of chemical transformations *per se*; they assumed a position as part of the chemical process itself and an essential necessary part in every reaction where there is a change of temperature. This was the most striking innovation in Lavoisier's theory of heat.

Summary and conclusions

In broad outline, Lavoisier's theory of heat forms a reasonable, easily

¹³⁹ 'Sur la combustion' [1777], *Mém. Acad. R. Sci.* 1777, p. 598.

¹⁴⁰ According to Macquer (*Éléments de Chimie-théorique* [1753], p. 16), fire can be fixed only in the form of phlogiston which does not change the state of either solids or fluids; see also n. 128.

¹⁴¹ Fric, op. cit. (5), 149-50. Cf. the same argument in the *Opuscles*, p. 280.

visualized, coherent whole. A single theoretical framework accounts for a vast array of heat phenomena including expansion and contraction, changes of state or form, the role of heat as an agent in promoting new chemical combinations, and temperature changes in chemical reactions, especially combustion and respiration. Although the general features of Lavoisier's theory of heat persist virtually unchanged through almost the entire period of his chemical writing, there was a sequence of conceptual development.

Beginning with a discussion of caloric in almost purely chemical terms, Lavoisier from 1783 on made extensive use of the physical approach of the balance-of-forces concept in explaining a great variety of heat phenomena and in analysing the particulate interactions suggested by the theory of combination or dissolution itself. The balance-of-forces concept qualitatively accounts for an astonishing number of interrelated phenomena associated with change of state such as change of volume, change in specific heat, latent heat, and the effects of external pressure. And it even suggested a very precise means to determine chemical affinity. This physical view also accounts for the matter of heat retaining in almost all its actions its essential feature of fluidity-elasticity. Indeed, caloric rarely loses this identifying characteristic; it is, after all, the principle of fluidity and elasticity. Although the balance-of-forces and the associated physical explanations of heat phenomena came to comprise a major feature of his theory of heat, Lavoisier continued to discuss change of state in terms of the chemical combination of caloric. From 1783 both explanations are intertwined; and he made little explicit attempt to reconcile them.

His use of the term combination and his associated treatment of caloric as a chemical constituent is also a persistent theme which runs through all his writings. At a superficial level, the balance-of-forces concept appears as an explanation of the chemical activity of caloric from a different yet compatible point of view. The inconsistencies between the two are largely submerged within his general discussion, and his contemporaries, looking no deeper than his general treatment, almost universally accepted as Lavoisier's view the idea that caloric behaves as a chemical constituent modified in some instances by physical considerations of changes in pore-space.

In spite of the number of topics touched upon and the number of experimental investigations he undertook, Lavoisier's interests in heat were largely confined to explaining the relationship between caloric and gases, especially oxygen gas. Once his investigations indicated that the consequences and implications of his theory were in general accord with the experimental data or once it became clear that certain striking relationships suggested by theory would not be realized, his interest in these peripheral areas ceased. None of his writings contains a systematic,

general treatment of all heat phenomena.¹⁴² His main purpose was to show that gases in general and oxygen gas in particular contain a great quantity of caloric in them primarily because of their state. The only difference between gases and vapours, which are patently the result of a change of state, is the temperature and pressure at which they vaporize. He rarely missed an opportunity to express this idea. His chief concern was to account for the heat released during combustion and more generally to argue the proportionality between changes in various states of expansion or cohesion and the caloric evolved or absorbed. His discussion of heat theory is confined almost entirely to this argument. Indeed, the general impression imparted is that his interests in caloric were limited to explaining its relations with airs, and his ventures into areas involving a more general application of heat theory were motivated by this prior concern. Considering his work as a whole, the discussion of heat in a more general sense seems incidental.

An essential feature of Lavoisier's theory of heat is the very close textual association between it and his ideas of combustion and calcination.¹⁴³ One is rarely discussed without reference to the other. Indeed his heat theory not only complements the other but Lavoisier presents it as the logical foundation upon which the general theory of oxidation is based. In 1786, Sir James Hall related that Lavoisier told him that 'the whole [oxidation theory] is founded on the theory of Latent heat', and that 'latent Heat and fix[ed] air are two of its foundation stones'.¹⁴⁴ Although this statement may have been an attempt to curry favour with Black's associates in Edinburgh, there are indications in Lavoisier's own work which show Hall's remarks accurately reflect Lavoisier's feelings.

The close connexion between the two related theories is evident at the very beginning of Lavoisier's thoughts on the subject. From the manuscript of 1776 on, his discussion of heat is caught up in a larger discussion of air, its nature, and its chemical role, so much so that one might conclude that his theory of heat had been devised for the sole purpose of accounting for the role of air in chemical reactions. In a paper

¹⁴² The first volume of *Mémoires de Chimie* comes closest to conforming to this description and these papers together contain a discussion of virtually all Lavoisier had to say on the subject. Yet in spite of the breadth indicated by the titles of the various memoirs, the treatment in many is very restricted.

¹⁴³ The association was also chemical. Lavoisier's treatment of the heat phenomena of chemical reactions most commonly occurs in a context discussing the reactions of oxygen gas. In part as a result of this, he gives the impression that he believed caloric and oxygen to have a unique relationship which is maintained even when both are combined with other components. In this context, caloric is never treated as simply one of several chemical constituents united in a given compound. Caloric in these compounds is that retained by oxygen when the latter combines, and it is by virtue of its prior union with oxygen that caloric is carried over and becomes a constituent in other combinations: vital air 'retient plus ou moins de calorique, suivant la nature des substances avec lesquelles il se combine' (*Mémoires de Chimie*, i. 140).

¹⁴⁴ 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, 169-70.

in the Academy's *Mémoires* for 1777, prior to the formal presentation of his new theories, Lavoisier concluded an argument against Priestley's explanation of combustion by stating that he wished to offer an alternative explanation; however,

les preuves que je pourrois apporter de ces assertions, supposent des connoissances que mes Lecteurs ne peuvent avoir encore, & je suis obligé de suspendre le developpement de cette théorie, jusqu'à ce que j'aie prouvé d'une part l'existence de la matière du feu dans tous les fluides aëriiformes. . . .¹⁴⁵

He could not develop his alternative theory without first demonstrating the validity of his ideas on the nature of aeriform fluids, and this demonstration is premised on his theory of heat.

Lavoisier's 'proofs' concerning the nature of air appeared in the first of the two articles in the *Mémoires* for 1777 which comprise the formal presentation of his oxidation theory and the first detailed discussion of his theory of heat that he had published. He followed almost identically the order presented in the manuscript of April 1773 beginning with a discussion of heat matter leading to the nature of air as a vapour and ending with the explanation of combustion and calcination. The same sequence of ideas appears in subsequent writings. It occurs in a manuscript of about 1778 containing a proposed plan for a second volume of his *Opuscules*,¹⁴⁶ and is followed again in the 1785 essay on phlogiston. He used his 1787 report to the French Academy of Sciences on the new chemical symbols which accompany the revised nomenclature to justify the theory upon which the symbols are based; and his argument begins with a discussion of change of state and proceeds in the same fashion to the explanation of combustion.¹⁴⁷ The next year he quoted this section of his report in his refutation of Kirwan's phlogiston theory.¹⁴⁸ The same sequence also appears in his *Traité de Chimie* and in the *Mémoires de Chimie* as well.

The constant repetition of the same sequential development of ideas covering a span of over twenty years indicates the importance Lavoisier attached to his theory of heat. It also indicates his view of the relation of the oxidation theory to the older theory of phlogiston. The most obvious phenomenon which the phlogiston theory so handily explains is the release of fire during combustion. Lavoisier might ban phlogiston from chemistry,

¹⁴⁵ 'Sur la combustion des chandelles', *Mém. Acad. R. Sci.* 1777, p. 204; cf. a similar statement, *ibid.*, p. 399 n.

¹⁴⁶ 'Introduction et plan d'un deuxième volume des Opuscules Physiques et Chimiques', *Oeuvres*, v. 268.

¹⁴⁷ *Nomenclature Chimique*, pp. 292-7.

¹⁴⁸ Richard Kirwan, *An Essay on Phlogiston and the Constitution of Acids* [1784] . . . *To which are added Notes Exhibiting and Defending the Antiphlogistic Theory and Annexed to the French Edition of this Work* [1788] . . . *With Additional Remarks by the Author*, trans. W. Nicholson (London, 1789 [London: Cass, 1968]), pp. 11-22; cf. similar arguments by Lavoisier, pp. 45-52.

but to provide a viable alternative, he had to account for this central observation. The caloric theory could do this. That it also enabled him to explain *how* (not merely state the fact *that*) oxygen becomes combined in the process made the concept all the more compelling. The caloric theory was indeed the foundation stone upon which Lavoisier erected the new chemistry.