THE STUDY OF THE THERMAL PROPERTIES OF GASES IN RELATION TO PHYSICAL THEORY, FROM HOUTHOLFER TO MAIRAULT

by

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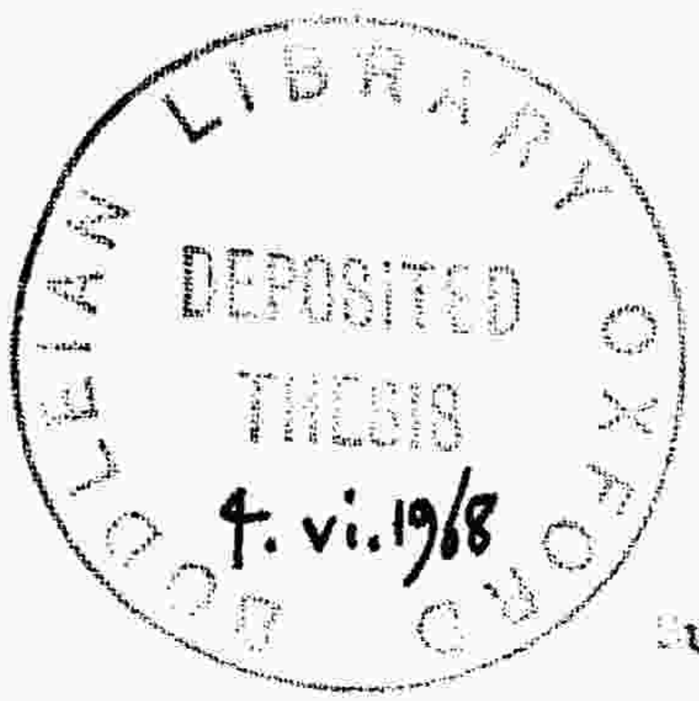

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ABBREVIATIONS

Ann. Chim.	Annales de Chimie, Paris.
Ann. Chim. Phys.	Annales de Chimie et de Physique, Paris.
Ann. Phil.	Annals of Philosophy, London.
Ann. Sci.	Annals of Science, London.
Bib. Univ.	Bibliothèque Universelle des Sciences, Belles-Lettres, et Arts. Sciences et Arts, Geneva and Paris.
Bull. de Férussac	Bulletin des Sciences Mathématiques, (Astronomiques), Physiques et Chimiques. Première section du Bulletin Universel des Sciences...de M. le Baron de Férussac, Paris.
Bull. Soc. Phil.	(Nouveau) Bulletin des Sciences par la Société Philomathique de Paris, Paris.
Comptes Rendus	Comptes Rendus hebdomadaires des Séances de l'Académie des Sciences, Paris.
D. N. B.	Dictionary of National Biography, London, 1906-9.
Edinburgh Essays	Essays and Observations, Physical and Literary. Read before a Society in Edinburgh, and published by them, Edinburgh.
Edin. New Phil. J.	The Edinburgh New Philosophical Journal, Edinburgh.
Edin. Trans.	Transactions of the Royal Society of Edinburgh, Edinburgh.
Enc. Brit.	The Encyclopaedia Britannica, various editions, Edinburgh.
Enc. Méth. (Chimie)	Encyclopédie Méthodique. Chimie, (Pharmacie) et Métallurgie, Paris and Liège.
Enc. Méth. (Physique)	Encyclopédie Méthodique. Physique, Paris and Liège.
Gilb. Ann.	Annalen der Physik, ed. L. W. Gilbert, Halle.

Giornale di Fisica	Giornale di Fisica, Chimica e Storia Naturale, Pavia.
Hist. Acad. Sci. Berlin	Histoire de l'Académie Royale des Sciences et Belles-Lettres, Berlin.
Intr. aux Obs. sur la Physique	Introduction aux Observations sur la Physique, sur l'Histoire Naturelle et sur les Arts, ed. Rozier, Paris.
Jahres-Bericht	Jahres-Bericht über die Fortschritte der physischen Wissenschaften von Jacob Berzelius, Tübingen.
J. éc. polytech.	Journal de l'École (Royale) Polytechnique, Paris.
J. Mines	Journal des Mines, Paris.
J. Phys.	Journal de Physique, de Chimie, d'Histoire Naturelle et des Arts, Paris.
K. Svensk. Akad. H. Abhand.	Der Königl. Schwedischen Akademie der Wissenschaften neue Abhandlungen, Leipzig.
Manchester Memoirs	Memoirs of the Literary and Philosophical Society of Manchester, London.
Mém. Acad. Sci.	(to 1788) Mémoires de Mathématique et de Physique, tirés des Registres de l'Academie des Sciences, Paris. (from 1816) Mémoires de l'Académie Royale des Sciences de l'Institut de France, Paris.
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino, Turin.
Mém. Inst. Fr.	Mémoires de la Classe des Sciences Mathématiques et Physiques de l'Institut (National, Imperial) de France, Paris.
Mém. Soc. Arcueil	Mémoires de Physique et de Chimie de la Société d'Arcueil, Paris.
Mem. Soc. Ital.	Memorie di Matematica e di Fisica della Società Italiana delle Scienze residente in Modena, Modena.
Mém. de Trévoux	Mémoires pour l'Histoire des Sciences / des Beaux Arts, Trevoux.

N. B. G.	Nouvelle Biographie Générale, depuis les temps les plus reculés jusqu'à nos jours, Paris, 1855-66.
Nicholson's Journal	A Journal of Natural Philosophy, Chemistry, and the Arts, ed. J. Nicholson, London.
Obs. sur la Physique	Observations sur la Physique, sur l'Histoire Naturelle et sur les Arts, ed. Rozier, Paris.
Phil. Trans.	Philosophical Transactions of the Royal Society of London, London.
Pogg. Ann.	Annalen der Physik und Chemie, ed. J. C. Poggendorf, Leipzig.
Proc. Roy. Soc.	Proceedings of the Royal Society of London, London.
Proc. Verb.	Académie des Sciences. Procès-Verbaux des Séances de l'Académie tenues depuis la fondation de l'Institut jusqu'au mois d'août 1835, Mendaye, 1910-1922.
Quart. J. Sci.	The Quarterly Journal of Science, Literature, and Art, London.
Rev. Deux Mondes	Revue des Deux Mondes, Paris.
Rev. Hist. Sci.	Revue d'Histoire des Sciences et de leurs Applications, Paris.
Taylor's Scientific Memoirs	Scientific Memoirs, selected from the transactions of foreign academies of science and learned societies, and from foreign journals, ed. R. Taylor, London.
Trans. R. Irish Acad.	The Transactions of the Royal Irish Academy, Dublin.

A note on terminology and dates

It has generally been thought unnecessary to define or explain the elementary scientific terms used in this work, although it should be noted that the quantity specific heat is taken throughout to indicate the heat required to raise the temperature of unit mass of a substance through one degree. It is represented by the symbol c_p (for the case in which the pressure remains constant during heating) or by c_v (for the case in which the volume is kept constant). Where volume specific heat is referred to, this is stated explicitly and the quantity is designated $c_p(v)$ or $c_v(v)$.

The terms 'capacity' or 'thermal capacity' indicate the heat required to raise the temperature of a body through one degree. In certain contexts they can be used interchangeably with specific heat, although it should be observed that in such cases the mass of the body is not necessarily unity.

The use of the adjective 'adiabatic' to describe conditions other than those in which there is no heat exchange at all between a gas and its surroundings has been thought unavoidable. In this work the term is frequently introduced in connection with experiments in which conditions were far from being truly adiabatic but in which thermal insulation was sufficient to allow temperature changes to occur when gases were rapidly compressed or expanded.

In most French primary sources of the period 1793-1809 dates are given according to the revolutionary calendar which was in use at that time in France, but these have normally been converted to the corresponding dates on the more familiar Gregorian calendar wherever possible. In a few cases in which it seemed particularly instructive to retain the original form of the date the conversion has not been made.

Introduction

One of the most important events in nineteenth-century physical science was the emergence, about the middle of the century, of a well founded and acceptable kinetic theory of gases. According to this theory gases were thought to be composed of particles which moved about rapidly, colliding frequently with the walls of the containing vessel and so giving rise to the phenomenon of pressure. Since this is basically the view which we still accept today, it is not surprising that its origins and early development have provided a popular and profitable subject for historical research. Attempts to understand what it was that the kinetic theory replaced, on the other hand, have been far less numerous and all too often the earlier, erroneous opinions on gas structure have been dismissed in a brief introductory paragraph. We are told that before the advent of kinetic theory the particles of gases were thought to be stationary and that repulsive forces between them were postulated in order to account for pressure and for the characteristic property which all gases possess of expanding to fill completely any vessel in which they are placed. Such an account is essentially correct but it contributes little to our understanding of the true achievements of the early kineticists. It does not tell us, for example, whether the 'static' theory which they rejected had developed over the years and attained some real degree of sophistication or whether it had never progressed beyond the status of a vague and arbitrary guess. Was it a fruitful theory which had been at the centre of scientific debate, throwing up important

theoretical issues, or had it rather been an inhibiting factor? From one point of view the work which follows can be seen as an attempt to answer such questions as these by examining a research tradition to which the almost universal acceptance which was accorded the 'static' theory in the first half of the nineteenth century is obviously and specially relevant.

In another important respect, however, the work represents a contribution to the study of the physics of imponderable fluids, for in the period covered, roughly from the 1780s to the 1850s, the belief that heat was a weightless fluid called caloric[1] whose particles repelled one another but were attracted by ordinary ponderable matter was almost as widely held as the 'static' theory already mentioned. In fact, the two beliefs were most intimately related, for it was the presence of the fluid of heat, either round or between the particles of gases, which was usually supposed to be the cause of the inter-particle repulsion.

While it will be one important function of the thesis to follow the development of the views on gas structure and heat held in our period and in particular to point to a noticeable decline in the fortunes of caloric after 1820, it would be wrong to lose sight of the unifying theme provided by the general acceptance of both the 'static' theory of gases and the caloric theory of heat. It is partly in order to emphasize this unity (and partly because the research tradition whose history we are tracing became

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1. The term 'calorique' was introduced for the first time in 1787 in L. B. Guyton de Morveau, A. L. Lavoisier, C. L. Berthollet and A. F. de Fourcroy, Méthode de Nomenclature Chimique (Paris, 1787), p.31.

one of special interest about them) that the narrative opens in the early 1780s. At this time it would be difficult indeed to select any one figure whose contribution to the study of the thermal properties of gases was outstandingly significant, for the work was usually no more than a minor concern of men whose chief interests lay in such varied fields as hygrometry, altitude measurement, animal heat and the correction of volumes in chemistry. The choice of the Montgolfier brothers' first public demonstration of their hot air balloon in June 1783 as an approximate starting point reflects this fact. So far as is known, the Montgolfiers themselves performed no experiments of the type which will concern us here, but the ascent of their balloon and the subsequent manned flights at least gave spectacular expression to a growing contemporary interest in gases and heat and in the relation between them.

This interest lasted with varying degrees of intensity until the middle of the nineteenth century, when Victor Regnault at last gave definitive answers to so many of the questions which had been asked in the previous seventy years. Of course, the study of the thermal properties of gases has continued since then, but Regnault's great experiments mark a fitting conclusion to our story, since it was roughly in the middle of his working life that the views on heat and the structure of gases underlying the earlier work were decisively abandoned.

There can be no denying that what follows is essentially a history of the type which has been termed 'intellectualist'.[1] It is largely concerned

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1. D. S. L. Cardwell, 'Science and technology in the eighteenth century', History of Science, i (1962), 30.

with the purely internal factors which governed the development of a research tradition and in particular with the influence of experimental knowledge on a number of related theoretical issues. However, this should not be taken as indicating any disregard of the need, which is now so generally recognized, for historians of science to place their work in a broad context, one which will take full account of general social, economic and cultural circumstances, whose relevance to the course of science may not be immediately obvious. Such 'externalist' factors are given due consideration wherever they appear to have a genuine bearing on the events described. Indeed, it may well be that the most interesting of all the many subjects for future study which have been suggested by this work will prove to be one such factor, namely the apparent overall decline in the quality of French physical science during the second quarter of the nineteenth century. How small is the contribution made here to the understanding of this problem will be only too obvious to anyone who examines Chapters 6 and 7 but, if something approaching the ideal of 'history in depth'[1] is to be achieved, such formidable, general issues can surely not be avoided. They are as much a part of science and its history as experiments and academic discussions.

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1. On this see I. B. Cohen, 'History in depth, the early Victorian period', History of Science, iii (1964), 20-36.

CHAPTER 1

The Growth of Interest, 1783-1800

Gases and Heat before 1783

The growth of interest in the thermal properties of gases after 1780 was the natural sequel to three of the most important developments in physical science during the eighteenth century. The first of these was the discovery of methods for the preparation and identification of gases which were recognized to be of a quite different nature from ordinary atmospheric air. Although Robert Boyle had unwittingly prepared both hydrogen and nitric oxide as early as 1659,[1] it was not until Stephen Hales described his greatly improved methods for the collection and handling of gases in 1727[2] that the techniques necessary for the science of pneumatic chemistry became available. Hales, however, was not concerned to identify the different types of gas collected in his experiments and another quarter of a century elapsed before Joseph Black prepared the first of what he termed the 'factitious airs'. The gas was carbon dioxide. In his doctoral dissertation Magnesia Alba, presented in 1754,[3] and in the enlarged version of it

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1. R. Boyle, New Experiments Physico-Mechanicall... (Oxford, 1660), pp. 176-179.

2. S. Hales, Vegetable Staticks (London, 1727). Especially important was the apparatus for the collection of gases depicted on the plate facing p.262.

3. J. Black, Dissertatio medica inauguralis, de...magnesia alba (Edinburgh, 1754).

which appeared in English shortly afterwards,[1] Black described how 'fixed air', as he called the new gas, had been liberated when he heated magnesia alba (basic magnesium carbonate). The identification of virtually all the common permanent gases followed quickly as a result of the work of Henry Cavendish,[2] Joseph Priestley[3] and the Swedish chemist Carl Wilhelm Scheele[4] and a period of intense activity on the part of all these men culminated in the discovery of oxygen, made independently by Scheele in 1773[5] and Priestley in 1774.[6] The discovery, quickly and brilliantly applied by Antoine Lavoisier, led to an entirely new theory of combustion which by 1783, when our story begins, had already reached a high stage of development and was beginning to replace the rival phlogiston theory. It is well known that the victory was not easily won. P. J. Macquer and Priestley were two who remained phlogistonists until their deaths, in 1784 and 1804 respectively, and such influential chemists as Claude Louis Berthollet,

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1. J. Black, 'Experiments upon magnesia alba', Edinburgh Essays, ii (1756), 157-225.

2. H. Cavendish, 'Experiments on factitious air', Phil.Trans., lvi (1766), 141-184.

3. J. Priestley, 'Observations on different kinds of air', Phil. Trans., lxii (1772), 147-264; see also the 3 volumes of Expts. and Obs. on Different Kinds of Air (London, 1774-1777) and the 3 volumes of Expts. and Obs. relating to...Natural Philosophy (London, 1779; Birmingham, 1781 & 1786).

4. C. W. Scheele, Abhandlung von der Luft und dem Feuer (Uppsala & Leipzig, 1777), conveniently translated in The Collected Papers of Carl Wilhelm Scheele, tr.L.Dobbin (London, 1931), pp.86-178.

5. Scheele, Collected Papers, pp.105-106.

6. Priestley, Phil. Trans., lxv (1775), 387-389 and 392; also Expts. and Obs...on Air (1775), ii. 29-103.

Antoine François de Fourcroy and Louis Bernard Guyton de Morveau were converted only in the mid-1780s.[1] In Britain Lavoisier's doctrines were not taught publicly until the winter of 1787, when Thomas Charles Hope first expounded them at Edinburgh.[2] But the debate was going very much Lavoisier's way and gases, which played such a prominent part in his system, were the subject of ever increasing attention.

That this attention extended to the study of their thermal properties was largely the result of two other developments. The first was the discovery of the concept of specific heat by Black about 1760.[3] Certainly the newly discovered gases possessed other thermal properties which deserved investigation, the extent to which they expanded when heated, for example, or the temperature changes which accompanied their rapid expansion or compression; but, as we shall see, the theoretical problems associated with the determination of specific heats were of a particularly fundamental nature. Moreover, the whole new science of calorimetry, which owed so much to Black's clear understanding of the concept of quantity of heat, had grown from his discovery of specific heat and that of latent heat which he made soon afterwards. Here was another research interest which rivalled the study of gases in its importance for scientists in the years preceding 1783. Although none of his own writings on the subject appeared in his

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1. See, for example, P. E. M. Berthelot, La Révolution Chimique - Lavoisier (Blanchard reprint: Paris, 1964), pp.135-143.

2. T. S. Traill, Edin. Trans., xvi (1849), 420.

3. For a full account see D. McKie and N. H. de V. Heathcote, The Discovery of Specific and Latent Heats (London, 1935).

lifetime, Black's influence extended far beyond his immediate contacts and important early experiments on specific heat were conducted by Richard Kirwan in Ireland[1] and by Johann Carl Wilcke[2] and Johan Gadolin[3] in Scandinavia. While noting this work as evidence of a widespread interest in calorimetry, we shall not examine it in detail since it was not concerned with matter in the gaseous state.

It was natural that the increasing familiarity of the concept of quantity of heat should tend to promote the material theory. The principles of calorimetry were so much easier to grasp when heat was considered to be an elastic fluid rather than a vibration of the particles of ordinary matter that implied support for the material theory was all too easily read into contemporary accounts. In fact in 1783 the vibrationalists' cause was by no means lost, but its position was weakening. It was soon to lose two of its most influential supporters, Macquer[4] by his death in 1784 and Fourcroy, Macquer's pupil, by his conversion to the material theory about 1786,[5] and the cause as a whole became increasingly marked by a shortage of

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1. J. H. de Magellan, Essai sur la Nouvelle Théorie du Feu Élémentaire (London, 1780), pp.176-179.

2. J. C. Wilcke, 'Über die specifische Menge des Feuers...', K. Schwed. Akad. N. Abhand., ii (1781), 48-79.

3. J. Gadolin, 'Über der Körper absolute Wärme', Ibid., v (1784), 222-239. See also his De theoria caloris corporum specifici (Abo, 1784), pp.13-16.

4. P. J. Macquer, Dictionnaire de Chymie (2nd edn., Paris, 1778), ii. 168-192.

5. Cf. Fourcroy's opinion in his Élémens d'Histoire Naturelle (2nd edn., Paris, 1786), i. 117 [written in 1784 according to W. A. Smeaton, Fourcroy, Chemist and Revolutionary (Cambridge, 1962), p.102] with that in the 'Discours Préliminaire' (Ibid., p.xxiv), dating presumably from 1786. See also Op. cit. (3rd edn., Paris, 1789), i. 127 and [P. A. Adet,] Supplément à la 2e édition d'Histoire Naturelle (Paris, 1789), pp.11-14.

new ideas. The vibrationalists seemed unable to relate the wealth of new discoveries in heat to their own theory, while their opponents rose far more impressively to the challenge.

This growing dominance of the material theory of heat is the third important development in eighteenth-century science which we should bear in mind when assessing the work described in this chapter. Despite all that his discoveries did to promote the theory, Black himself is reputed to have had positivist leanings.[1] John Robison, who later succeeded Black as lecturer in chemistry at Glasgow and who, in 1774, as the new Professor of Natural Philosophy, became his colleague in Edinburgh,[2] gives the following recollection of their first meeting in 1758:

> Gently and gracefully checking my disposition to form theories, he [Black] warned me to suspect all theories whatever, pressed on me the necessity of improving in mathematical knowledge, and gave me Newton's Optics to read, advising me to make that book the model of all my studies, and to reject, even without examination, every hypothetical explanation, as a mere waste of time and ingenuity.[3]

From the posthumously published Lectures, edited by Robison from Black's own lecture notes and from notes taken by a student and corrected by Black himself, we obtain the same impression of caution, but there are hints of a slight preference for the material theory of heat. Of a version of this theory proposed by William Cleghorn[4] Black said: '...such

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1. McKie and Heathcote, Specific and Latent Heats, pp.27-30.

2. J. Black, Lectures on the Elements of Chemistry (Edinburgh, 1803), i. pp.viii-ix.

3. Ibid., p. vii. For a similar view of Black see A. Ferguson, 'Life of Black', Edin. Trans., v (1805), part 3, lii.

4. See pp.14-15.

an idea of the nature of heat is...the most probable of any that I know', although he added: 'It is, however, altogether a supposition;'.[1]

The view that heat was a substance received further support from Black's other major discovery, that of latent heat. In forming the new concept Black may well have been assisted by his earlier work, for there was an obvious analogy between the fixed air which Black supposed to exist in magnesia alba before its release by heating and the heat which entered a solid or liquid to effect liquefaction or vaporization and which thereupon lost all its normal properties. Did not both fixed air and the heat which had been latent regain their original properties when they were released? Black's own comments, as we should expect, throw little light on the matter, but in his Lectures he firmly dissociated himself from a view which had been widely adopted by the time he revised his notes, in the late 1790s.[2] This was that changes of state occurred because the fluid of heat entered into some sort of chemical combination with ordinary matter, thereby becoming imperceptible to the thermometer, or 'latent'.

> This [Black said] will please the imagination, but does not advance our knowledge. I therefore avoid such speculations, as taking up time which may be better employed in learning more of the general laws of chemical operations. I content myself with saying, that in liquefaction and vaporisation, water absorbs a great quantity of heat, because this expression immediately raises the notion of a sudden, and somewhat copious, accumulation of heat.[3]

It would seem that Black's contemporaries were not satisfied with this

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1. Black, Op. cit., 34.
2. Ibid., p. x.
3. Ibid., 193.

cautious attitude to the processes of liquefaction and vaporization and his position became characterized by a number of writers[1] as one of support for the very opinion which he had explicitly rejected in the above passage. In this way the sharp distinction between the version of the material theory supposed to be adopted by Black and that of his former pupil William Irvine became established, despite the claims of both men that their views were essentially identical.[2] Irvine had first come into contact with Black as a medical student at Glasgow University and had assisted him in many early experiments, notably some important ones on the latent heat of steam in 1764.[3] His explanation of the emission and absorption of heat during changes of state must also date from about this time, since Black records that it originated almost immediately after his own discovery of latent heat.[4] Unfortunately Irvine, like Black, published nothing in his own lifetime, but it is not difficult to reconstruct his views from contemporary comments and from the collection of essays published by his son nearly twenty years after his death.[5] He supposed that heat was absorbed by a body during

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1. e.g. T. Thomson, A System of Chemistry (1st edn., Edinburgh, 1802), i. 323-324 and in Enc. Brit. (3rd edn., Edinburgh, 1801), supplement, i. 269; M. Irvine in Essays...by the late William Irvine... (London, 1805), p.50; R. Heron, Elements of Chemistry (London, 1800), pp.76-77; M. Landriani, J. Phys., xxvi (1785), 94; A. Seguin, Ann. Chim., iii (1789), 179.

2. Irvine, Op. cit., pp.51 and 54, and Black, Op. cit., 195.

3. Black, Op. cit., pp.xliv-xlv and 171-173.

4. Ibid., 194.

5. See note 1 above.

melting or vaporization simply because at the melting and boiling points sudden changes took place in the ability of the body to contain heat. Although this did not explain why the change of state occurred in the first place, as Black pointed out,[1] it won wide acceptance and was to influence even vibrationalists.[2] It was fundamental to Irvine's treatment that the relative quantities of heat contained in equal weights of different substances at any given temperature, their 'absolute heats',[3] were proportional to their 'capacities' at that temperature. 'Capacity', we should note, was used by both Black and Irvine to indicate specific heat, 'chaleur spécifique' being introduced by J. H. de Magellan only in 1780. As a convinced supporter of Irvine's theory, Magellan naturally saw the specific heats which he gave in that year as indicating far more than the relative quantities of heat required to raise the temperature of equal masses of the various substances by the same amount. They were, as he put it, the 'Raports de la Chaleur Spécifique, ou Feu Élémentaire, contenu en différentes Substances'.[4]

The Irvinist ideas are best illustrated by the analogy of a cylinder of uniform cross section filled with a liquid, the liquid in the cylinder representing the heat in a body (see Plate 1). The level of the liquid would then indicate the temperature of the body in degrees above the absolute

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1. Black, Op. cit., 194-195.

2. See pp.121-123 and 126.

3. A term introduced by Irvine (see A. Crawford, Experiments and Observations on Animal Heat (London, 1779), p.2).

4. Magellan, Essai, p.177.

zero of temperature. The typical procedure is well illustrated in this example, which is a corrected version of one given by Irvine's son in 1805.[1] The latent heat of a given mass of ice was taken as that quantity of heat which would raise the temperature of the same mass of water by 140 deg F and the values for the specific heats of ice and water (Kirwan's) were 0.9 and 1.0 respectively. Where the melting point was x deg F above the absolute zero it followed from Irvine's assumptions that the total quantities of heat in the ice before melting and in the water at 32°F after the change of state were proportional to 0.9x and 1.0x respectively and hence, on the assumption that heat had been conserved, that

$$x = 0.9x + 140$$

$$\text{and } x = 1400.$$

The zero in this calculation would therefore be at -1368°F. Irvine himself placed it at about -900°F,[2] which suggests that, if he had the same figure for the latent heat, he must have taken the specific heat of ice as 0.85.[3] It is instructive to note here how very considerable variations in the absolute zero could result from small changes in specific heat.[4] The calculation could of course be made equally well from data relating to

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1. Irvine, Essays, p.122.

2. Ibid., p.127

3. Not 0.87, as McKie and Heathcote, following an error by Irvine (Jnr.), suppose in Specific and Latent Heats, p.134. For correctly performed calculations see Magellan, Essai, p.176 and Crawford, Animal Heat (2nd edn., London, 1788), pp.453-454.

4. ee p.19.

vaporization or to a chemical reaction and Irvine apparently confirmed his figure from observations of the heat evolved during the mixing of sulphuric acid with water.[1] We have no details of how he measured either the heat evolved or any changes in capacity accompanying the mixing.

Irvine was probably not concerned to elucidate the nature and properties of the fluid, or vibration, which caused the sensation of heat. His son emphasized that Irvine's views did not imply belief in any particular theory[2] and the English physician Adair Crawford, who developed these views so successfully in the two editions of his Animal Heat in 1779 and 1788, expressed only tentative support for the material theory.[3] Yet, despite this show of agnosticism, there can have been few who did not agree with Crawford that such a concept as latent heat was more readily explained in terms of a fluid than of a vibration and many must have seen this in itself as strong evidence for the materiality of heat. Magellan[4] and Tiberius Cavallo[5] were typical in this respect, but neither gave such detailed support as William Cleghorn. In his doctoral dissertation De Igne, presented at Edinburgh University in 1779,[6] Cleghorn outlined a theory of heat

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1. Irvine, Essays, p.127.

2. Ibid., p.71.

3. Crawford, Animal Heat (1st edn.), p.115; (2nd edn.), pp.435-436.

4. Magellan, Essai, p.167.

5. T. Cavallo, A Treatise on the Nature and Properties of Air (London, 1781), pp.20-21.

6. W. Cleghorn, Disputatio physica inauguralis, theoriam ignis complectens (Edinburgh, 1779). See also pp.40-41.

which bore the strongest resemblance to what some years later was to become known as the true caloric theory.[1] He considered that the matter of heat was made up of 'fire particles' (ignis particulae or igneae particulae) which were mutually repulsive but which were attracted by ponderable matter with a strength determined by the nature of the substance. The amount of 'fire' in any body depended therefore on the relative magnitudes of these attractive and repulsive forces. Despite Black's qualified approval[2] Cleghorn's work attracted little attention. A doctoral dissertation was all too easily overlooked unless it was followed by other writings and Cleghorn published nothing more. He died in 1783, after some extensive continental travels and a period of teaching in Dublin had served to isolate him from the Scottish school of chemistry, and so played disappointingly little part in the development of the theory of heat.

The work of Black, Irvine and Crawford quickly became known in France. As early as 1772 an account of Black's views on latent heat, written by an unnamed Edinburgh student, had appeared there[3] and the first edition of Crawford's Animal Heat aroused considerable interest some years later. For this Magellan's Essai sur le Feu, published in London in 1780 as a

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1. As described, for example, in A. L. Lavoisier, Traité Élémentaire de Chimie (Paris, 1789), i. 17-27. Lavoisier himself had serious reservations, expressing particular doubts whether the 'molécules' of caloric were mutually repulsive (Ibid., 25-26). B. Higgins, A Syllabus of the Discourses and Experiments... (n.d., 1775?), p.56, suggests that views similar to Cleghorn's were being expounded by 1775.

2. See pp.9-10.

3. The paper, dated Sep. 1772, was reprinted in Rozier's Intr. aux Obs. sur la Physique, ii (1777), 426-431.

commentary on the Animal Heat but incorporating details of Irvine's work which Crawford had not mentioned, was no doubt largely responsible, especially after its republication in France in 1781.[1] The intensity of French interest is brought out well in an account by Jean André De Luc of a visit to Paris which he made in 1781. Referring to his meetings with Laplace, Lavoisier, Monge and Vandermonde during the visit, he recalled:

> Dr. Crawford's theory on the phenomena of heat observed when substances undergo certain changes in their nature, was then in great agitation among these philosophers, and the two last had, from the Academy, the special commission to examine and follow that new view.[2]

By 1781 Lavoisier was probably already committed to some form of material theory. Four years earlier he had expressed the view that gases resulted from the combination of 'matter of fire' (la matière du feu) with a 'base', which could be either a liquid or a volatile solid.[3] The mechanism of this combination, as he explained in a second paper written in the same year, resembled that of a normal chemical union.[4] Heat was liberated in combustion, for example, simply because the base of 'air vital' (oxygen) had a greater affinity for the inflammable substance than for the matter of fire and so combined with it, allowing the fire to escape. Lavoisier's conception of the 'matter of fire' was nevertheless vague at this

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1. Obs. sur la Physique, xvii (1781), 375-386 and 411-422.

2. J. A. De Luc, Edinburgh Review, vi (1805), 511.

3. A. L. Lavoisier, 'De la combinaison de la matière du feu avec les fluides évaporables...', Mém. Acad. Sci., (1777), 420-432.

4. A. L. Lavoisier, 'Mémoire sur la combustion en general', Ibid., 595.

time. Although he was in no doubt that its liberation accounted for the appearance of both heat and light, he gave few details of its nature, referring to it merely as:

> ...un fluide très-subtil, très-rare, très-élastique, qui environne de toutes parts la Planète que nous habitons, qui penetre avec plus ou moins de facilité les corps qui la composent, & qui tend, lorsqu'il est libre, à se mettre en equilibre dans tous.[1]

Lavoisier wrote nothing more on heat until he and Laplace presented their celebrated 'Mémoire sur la Chaleur' to the Académie des Sciences in June 1783.[2] The paper is particularly notable for the fine experiments on calorimetry which are described in it and we shall return to examine these in due course. For the moment, however, it is its bearing on the theoretical study of heat which concerns us.

The tone of the paper was cautious. After describing both the vibrational theory and a material theory similar to that which Lavoisier had already described in 1777, they continued:

> Nous ne déciderons pas entre les deux hypothèses précédentes; plusieurs phénomènes paroissent favourables à la derniere, tel est, par exemple, celui de la chaleur que produit le frottement de deux corps solides; mais il en est d'autres qui s'expliquent plus simplement dans la premiere; peut-être ont-elles lieu toutes deux à la fois.[3]

Despite this non-committal statement a tradition has grown up that Lavoisier was the champion of the material theory while Laplace was a vibrationalist.

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1. Ibid.

2. A. L. Lavoisier and P. S. Laplace, 'Mémoire sur la chaleur', Mém. Acad. Sci., (1780), 355-408.

3. Lavoisier and Laplace, Op. cit., 358.

It appears to have originated with E. M. Lémeray[1] and has been accepted somewhat uncritically by several more recent writers.[2] In fact, since Lavoisier was still inclined to support the material theory in 1789,[3] it seems reasonable to suppose that he held similar views six years earlier. The position of Laplace, however, is far less clear. It may well be that, like Macquer and Fourcroy, he did accept the vibrational theory at this time, but there is no conclusive evidence and it must at least be born in mind that Laplace had become a convinced caloriat when he next wrote on the subject about 1803.[4]

Among the other members of Lavoisier's circle Gaspard Monge stands out as a particularly vigorous advocate of the material theory and he was a man of no small stature in the discussions of the early 1760s. The following account is taken from the anonymous article 'Calorique' which appeared in the Encyclopédie Méthodique (Physique) in 1816. After describing Monge's increasingly close contact with Parisian scientists after his election to the Académie des Sciences in 1780, the writer continued:

> Admis dans la société de l'illustre Lavoisier, qui réunissoit chez lui, tous les lundis, les savans les plus distingués de la capitale; admis également avec plusieurs académiciens les

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1. E. M. Lemeray, L'Ether actuel et ses Precurseurs (Paris, 1922), pp.65-69.

2. See, for example, G. Bachelard, Etude sur l'Evolution d'un Probleme de Physique (Paris, 1928), 23n; C. C. Gillispie, The Edge of Objectivity (London, 1960), p.239; J. R. Partington, A History of Chemistry (London, 1962), iii. 428; Smeaton, Fourcroy, p.102.

3. Lavoisier, Traité, i. 4-5.

4. See pp.133-135.

mercredis & les vendredis, après l'académie, chez un ami de cet homme célèbre, Monge crut devoir soumettre aux hommes instruits qu'il y trouvoit reunis, la marche progressive de ses idées sur la theorie du calorique. Ses opinions étoient écoutées avec l'attention que le génie commande; quelquefois elles étoient discutées avec cette franchise & cette cordialité que mettent entr'eux les hommes qui ne s'occupent que de la recherche de la vérité: de-là sortirent ces idées belles & grandes que l'on a publiées de toutes parts sur le calorique, & dont personne n'a réclamé la découverte.[1]

Whether Monge took the opportunity of expounding his caloric theory to a wider audience when he began teaching at the École Polytechnique in 1794 is not known, but it is interesting that it was he who in 1809 contributed the article on caloric to a short work by Hachette intended for the use of students at the École.[2]

Their agnosticism did not prevent Lavoisier and Laplace from commenting on Irvine's views concerning the state of heat in bodies. Incorporating many of their own results for the specific and latent heats and for heats of reaction in Irvine's argument, they made five different determinations of the absolute zero.[3] Although the five figures showed no semblance of agreement and even included one which was above the melting point of ice, Lavoisier and Laplace were careful to emphasize, quite rightly,[4] that small errors in the specific heats could seriously affect the calculation. Yet they clearly had little sympathy for such basic Irvinist assump-

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1. Enc. Méth. (Physique), (Paris, 1816), ii. 170.

2. J. N. P. Hachette, Programmes d'un Cours de Physique (Paris, 1809), pp.54-72.

3. Lavoisier and Laplace, Op. cit., 382-386.

4. See p.13.

tions as the proportionality between the capacities of various bodies at a given temperature and the quantities of heat which they contained. This assumption, they said, was '...au moins très-précaire, & ne doit être admise qu'après un grand nombre d'expériences.'[1]

Strangely enough they made no mention of Black, but their cautious assertion that in a change of state some heat was absorbed which thereupon became imperceptible to the thermometer was one of which Black would surely have approved. There was, we note, no mention of a combination between heat and ponderable matter. But in one important respect they went beyond Black, for they suggested that the absorption of heat was necessary in order to effect not only melting and vaporization but also expansion.[2] Thus, when a body was heated, some heat would go to raise its temperature and some to increase its volume. The idea, skilfully developed by Laplace, became a most important one during the first quarter of the nineteenth century, but it provoked little immediate reaction and so need not detain us here.

The 'Mémoire sur la Chaleur' provided the first intimation of the inevitable weakness of Irvine's theory in the face of reliable data for specific heats. The attack was taken up by Armand Seguin, Lavoisier's partner in some important early work on respiration, in 1790[3] and Gadolin,

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1. Lavoisier and Laplace, Op. cit., 381.

2. Ibid., 388.

3. A. Seguin, 'Second mémoire sur le calorique', Ann. Chim., v (1790), 231-257.

arguing in a similar fashion in 1792,[1] was another who applied the results of new experiments (his own) to the rejection of Irvinist doctrines, although only eight years earlier he had upheld them and had determined the absolute zero in a perfectly conventional manner.[2] However, data of the extreme accuracy required to disprove the theory beyond all doubt were not easily obtained and the survival of its influence until well into the nineteenth century owes as much to experimental deficiencies as to the merits of the theory itself. When our story begins the Irvinist cause was far from lost. Indeed, of its two greatest exponents, Crawford was only beginning to exert his full influence and John Dalton, a schoolmaster in Kendal, was still quite unknown.

Specific Heats of Gases

The first determination of the specific heat of a gas was made by Crawford in the summer of 1777. His main concern in this as in his later work was to derive an explanation for the heat evolved in the bodies of warm blooded animals and the experiments were described, appropriately enough, in the two editions of his Animal Heat.[3] Although he was educated at St. George's Hospital and spent most of his life in London, Crawford visited Scotland in 1776[4] and it was presumably during this visit that he

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1. J. Gadolin, 'De theoria caloris corporum specifici', Nova Acta Regiae Societatis Scientarum Upsaliensis, v (1792), 1-49.

2. See p.8, n.3 for references.

3. Crawford, Animal Heat (1st edn.), pp.34-43; (2nd edn.), pp.177-253.

4. D. N. B., art. Crawford.

heard the lectures of William Irvine.[1] His adoption of Irvinist doctrines throughout his work is sufficient evidence that he was impressed, but he appears to have been particularly interested by Irvine's suggestion that the absolute heats of atmospheric and fixed air were different.[2] According to Irvine's theory of heat all that was required to test this was a determination of the specific heats of the two gases and Crawford duly set about the experiments in the following summer. The theory of animal heat which he expounded in 1779 was based on this work and in particular on two results. First he showed that the absolute heats of atmospheric and fixed air were in the ratio 67 to 1, while that of phlogisticated air (nitrogen), although not precisely measurable, was extremely small. Since fixed and phlogisticated airs were known to be the major constituents of exhaled air, it followed that a large amount of heat must be released during the process of respiration, in which inhaled atmospheric air yielded these two products. The second result was that the absolute heats of the blood which entered the lungs and that which left them were as 10 to 11½. Thus, Crawford argued, the effect of passage through the lungs was to increase the blood's ability to contain heat, so that without any increase in temperature it could absorb the heat liberated by the conversion of atmospheric air to fixed and phlogisticated airs. Uniform distribution of this heat throughout the body was then effected through the gradual absorption of phlogiston by the blood during circulation and the

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1. Crawford, Op. cit. (1st edn.), p.17n.

2. Ibid.

consequent decrease in its absolute heat.

Crawford's method of determining the specific heats of the gases was crude. The principle was essentially to heat them in bladders and then to compare the rises in temperature which occurred when these were immersed in water, but the smallness of the quantities of gas which were used made his thermometer readings quite meaningless. In fact precise determinations were hardly important and it was enough to have shown, as Crawford was convinced he had done, that atmospheric air contained a greater quantity of heat than an equal mass of exhaled air. That it contained only about one fifth as much as dephlogisticated air was nevertheless interesting confirmatory evidence for his theory, since it accorded well with Priestley's recent discovery that dephlogisticated air was five times as effective as ordinary atmospheric air in supporting life.[1]

Crawford's work attracted widespread attention, as we have already seen, but all the comments were by no means as favourable as Magellan's, for example. In 1781 the actuary William Morgan severely criticized the way in which the experiments had been conducted[2] and on repeating them, with a number of modifications, he could detect no difference between the absolute heats of the various gases examined by Crawford.[3] It followed, Morgan concluded, either that equal weights of all gases contained the

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1. Ibid., p.53; Priestley, Expts. and Obs...on Air, ii. 48.

2. W. Morgan, An Examination of Dr. Crawford's Theory of Heat... (London, 1781), pp.6-27.

3. Ibid., pp.31-37.

same quantity of heat or that the experiments conducted hitherto were too insensitive to reveal any differences which did exist. In either case Crawford's theory remained unproved, an opinion maintained by one reviewer of Morgan's work.[1]

De Luc, by contrast, appears to have made his criticisms personally and at Crawford's own request.[2] He particularly emphasized the smallness of the temperature changes during the mixing process and in 1786 he wrote that Crawford had acknowledged the defects in his earlier work and was now engaged on new experiments.[3] It seems that the experiments of Lavoisier and Laplace, as well as some conducted by Kirwan, about which we know nothing more than is contained in De Luc's passing reference to them,[4] had been largely responsible for this admission.

The work of Lavoisier and Laplace deserves special mention, not merely for its relevance to the debate on Crawford's theory but also for the new standards which it set in the science of calorimetry. Chiefly responsible for this was their ice-calorimeter,[5] an instrument which measured quantities of heat by the weight of ice melted. The 'Mémoire sur la Chaleur' contained

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1. 'C', Critical Review, li (1781), 212-216.

2. J. A. De Luc, Idées sur la Météorologie (London, 1786), i. 145 and Introduction à la Physique Terrestre (Paris & Milan, 1803), i. 230-231.

3. De Luc, Météorologie, i. 145.

4. De Luc, Physique Terrestre, i. 233.

5. Described in Lavoisier, Traité, ii. 387-402 and Mém. Acad. Sci., (1780), 369-373.

a full description of their experiments and results relating to the specific heats of solids and liquids, and also on heats of reaction, but it seems unlikely that they had yet performed any successful experiments on gases. Lavoisier's laboratory note-books, as described by Berthelot,[1] contain only two references to determinations of the specific heats of gases, dated 9 and 10 February 1784 (for atmospheric air) and 20 February 1784 (oxygen). Yet the fact that their description of the relevant apparatus appeared in the 1783 paper suggests that they had done some preliminary work in the previous winter. The gas under examination was heated and then passed through a spiral tube inside the ice-calorimeter. Its temperature was measured both before and after its passage through the apparatus so that, by measuring also the weight of ice melted, the heat lost by any mass of a gas could be easily determined and its specific heat calculated. How successful this method was we cannot know, but Lavoisier and Laplace seem to have retained it in their experiments during the winter of 1783-1784 and also in subsequent years.[2] Although Lavoisier wrote in 1789 that they still allowed no winter to pass without doing some work with the ice-calorimeter,[3] the experiments were seriously interrupted and it was not until 1793 that he described this later work.[4] By then his fate at the

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1. Berthelot, La Révolution chimique, p.295.

2. . L. Lavoisier, Mémoires de Chimie (Paris, 1805), i. 122.

3. Lavoisier, Traité, ii. 402.

4. . L. Lavoisier and P. S. Laplace, '3e mémoire...contenant les expériences faites sur la chaleur, pendant l'hiver de 1783 a 1784', in Lavoisier, Mémoires, i. 121-147. On the authorship see Ibid., 144.

hands of the Revolutionary Tribunal was only too imminent and another twelve years elapsed before the paper appeared, as a joint memoir with Laplace. For gases only two specific heats were given, 0.65 for oxygen and 0.33031 for atmospheric air, where that of water was unity.[1] Both results were of course quite different from those given by Crawford. But although Lavoisier and Laplace applied these and some other data on heats of combustion to re-affirm their belief that part of the caloric in bodies existed in a combined and therefore latent state,[2] they fully recognised that their experiments could not yet be considered definitive.

When Crawford described his own new experiments in the second edition of the Animal Heat in 1788 he knew nothing of this work, but all earlier criticisms of the Irvinist doctrines would have been perfectly familiar. Crawford's confidence in his theory of animal heat was nevertheless undiminished. Moreover, although he readily admitted to serious errors in his original experiments,[3] the principle of his method remained unchanged. Two identical brass cylinders now replaced the bladders used in 1777 and numerous precautions were taken, principally to reduce heat losses. The cylinders, each containing a different gas, were heated to the temperature of boiling water and then rapidly immersed in separate vessels containing cold water. Accurate measurement of the resulting rise in temperature

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1. Ibid., 134-137.

2. Ibid., 138-147.

3. Crawford, Animal Heat (2nd edn.), 'Advertisement' pp.3-4 and pp.225-226.

enabled the relative specific heats of the gases to be determined, at least in principle. In fact the heat capacity of the enclosed gas was always so small by comparison with that of the cylinder that errors were large. In one typical experiment[1] only 0.274 deg F of a total temperature rise of 2.2 deg F could be attributed to the cooling of the gas alone.

Nevertheless, the experimental results were an improvement on those of 1777. The differences between the specific heats of dephlogisticated, atmospheric and fixed airs were found to be much smaller than in his earlier experiments, although of the three that of dephlogisticated air was still the greatest and that of fixed air the smallest, so that his theory was not disproved. Indeed, an interesting calculation, of the specific heat of water vapour,[2] gave it considerable additional support. Assuming that the absolute zero of temperature was 1650 deg F below the boiling point of water, Crawford argued that the absolute heat of water compared with that of steam must be as 1650 to (1650 + 914), or 1 to 1.55, since enough latent heat was absorbed in vaporization to raise the temperature of an equal mass of water by 914 deg F (Watt's figure). The result confirmed his theory on two counts. In the first place, since water vapour was known to be a product of respiration, it was to be expected that its capacity should be less than that of atmospheric air (given now as 1.79). Secondly, the fact that the specific heat was greater than that of water agreed with Irvine's explanation of the phenomenon of latent heat. Another

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1. Ibid., pp.234-235.

2. Ibid., pp.269-270.

result which could be applied to good effect, in accounting for the large amount of heat liberated during the explosion of hydrogen with oxygen, was that hydrogen had a specific heat which, although considerably smaller than he had thought from some earlier experiments[1] was still far greater than that of any other gas.[2]

Crawford's later experiments were the first in which any attention had been paid to the distinction between the specific heats measured at constant pressure (c_p) and at constant volume (c_v). His awareness of the need for such a distinction almost certainly arose from his familiarity with the heating and cooling effects which accompany, respectively, the rapid compression and expansion of all gases. Although he nowhere offered an explicit explanation of these temperature changes, Crawford certainly believed that any variation in the volume of a gas would cause a change in capacity.[3] Thus, if a gas were allowed to expand while it was being heated, its capacity would increase and it would have to absorb more heat than would be required under constant-volume conditions. Such considerations were irrelevant to his own experiments, in which the gases were contained in closed brass cylinders, but Crawford undertook to demonstrate that the difference would have been negligible even if the gases had expanded during the heating process.[4] He had observed, and no existing ex-

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1. T. O. Bergman, Opuscula Physica et Chemica (Upsala, 1783), iii. 436. Kirwan was apparently the source of Bergman's information. The work on hydrogen is not mentioned in the 1st edn. of the Animal Heat.

2. Crawford, Op. cit., pp.221 and 247-249.

3. Crawford, Animal Heat (2nd edn.), pp.249-250.

4. Ibid., pp.250-253.

periments on the subject suggested that he was far wrong, that a fall in temperature of about 5 deg F accompanied the rapid evacuation of the receiver of an air pump, the cooling being approximately the same whether atmospheric, dephlogisticated or phlogisticated air was extracted. Using William Roy's results on the expansion of air by heat in conjunction with some very suspect results obtained by Priestley,[1] Crawford argued that a rise in temperature of 110 deg F would increase the volume of dephlogisticated air by half. Now he also concluded, from his experiments with the evacuated receiver, that such an expansion would cause a cooling of 3 deg F if the gas were thermally insulated. Thus, if dephlogisticated air were allowed to expand while being heated through 110 deg F, it followed that 113 units of heat would be required to effect the temperature change, compared with 110 units when the volume did not vary. Such a difference would have been quite undetectable in his experiments, as Crawford showed, since even with his improved apparatus a fall in the temperature of dephlogisticated air of about 110 deg F caused a heating of only 0.4 deg F in the water surrounding the brass cylinder so that an increase in the amount of heat communicated to the water of less than 3% would affect this by roughly $\frac{1}{100}$ deg F, 'a quantity so inconsiderable that it could not have been distinguished by the thermometer'.[2] Crawford's serious, if forgivable, underestimate of the magnitude of the difference was unfortunate and it must be seen as at

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1. See p.64. Crawford's debt to Priestley is obvious, though unacknowledged.

2. Crawford, Op. cit., p.253.

least one factor in accounting for the neglect of the distinction between c_p and c_v over the next twenty years.

Not surprisingly, the second edition of the Animal Heat aroused less interest than the first. Crawford's ideas had now been widely discussed for nearly ten years and the new edition raised no essentially new issues. Above all his experiments were still far too unreliable to allow the debate between the supporters of the rival versions of caloric theory to be taken further. Only Armand Seguin was moved to offer a detailed criticism. In two papers published in the Annales de Chimie in 1789 and 1790[1] he vigorously attacked both the experiments and the theory of heat adopted by Crawford, maintaining Lavoisier and Laplace's distinction between 'calorique interposé', which affected the thermometer, and 'calorique combiné', which did not contribute to temperature and which combined with a solid or liquid in bringing about a change of state. Seguin's views were not original, but his thorough re-examination of the evidence, especially that relating to the determination of the absolute zero, was an important contribution.

But by 1790 it must have been clear that, for the moment, there was little more that could usefully be said on the subject of specific heats. The need for new and greatly improved experiments, especially on gases, was only too evident and yet the practical problems were daunting. Fortunately the new century was to bring with it a renewed interest in gases and new hope for solving the outstanding problems, so that after ten years

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1. A. Seguin, 'Observations générales sur le calorique', Ann. Chim., iii (1789), 229-242 and v (1790), 191-271.

of comparative neglect the debate was to be re-opened.

Adiabatic Heating

It is well known that a rise in temperature occurs whenever a gas is compressed in conditions such that it loses little or no heat to its surroundings. The effect, now known as adiabatic heating,[1] is readily explained by the principle of the conservation of energy. The work done in compression has been converted to heat energy in the gas and, for a given amount of work, the same quantity of heat will always appear. It is natural and proper, therefore, that adiabatic heating, and the reverse effect, in which cooling results from the expansion of a gas against external pressure, should now be generally associated with this celebrated principle and with the closely related dynamical theory of heat. The association, in fact, goes back well into the nineteenth century. Carnot, Mayer, Joule and a number of others who have a claim to be considered discoverers of energy conservation saw adiabatic phenomena as decisive qualitative evidence and some used them quantitatively to calculate the mechanical equivalent of heat, the constant of proportionality relating work done and heat produced.[2] It might seem from this that adiabatic phenomena were in some important respect irreconcilable with caloric theory, but in fact the thermal effects associated with the compression and expansion of

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1. The term 'adiabatic' appears first in W. J. Macquorn Rankine, Phil. Trans., cxlix (1859), 180.

2. For a stimulating preliminary account see T. S. Kuhn, 'The caloric theory of adiabatic compression', Isis, xlix (1958), 132-133.

a gas had been known for nearly a century before they became indissolubly linked with energy conservation in the 1840s. In this period they had been explained almost exclusively in terms of material theories of heat and, as we shall see, had even appeared as strong evidence in favour of such theories.

This earlier history of adiabatic heating and cooling falls into three main periods. In the first, which lasted from 1755 until 1779, the effects were observed exclusively during the evacuation and re-filling of the receivers of air pumps. So little were they understood at this time that only one observer appears to have drawn the all important conclusion that a mere change in the volume of a gas could give rise to variations in temperature. In the second period, from 1779 to 1800, the effects were still normally observed during work with the air pump and the explanations offered were coloured accordingly. However, it was now recognized that genuine temperature changes did occur both in the air-pump experiments and when the volume of a gas was altered rapidly, although serious departures from true adiabatic conditions meant that the magnitude of the changes was seriously underestimated. A peculiar characteristic of the first two periods is that interest in the effect was almost entirely limited to those who had had contact with one of two schools, either that of the Scottish chemists and physicians, headed by Cullen and Black, or that in which the Swiss scientists Saussure and Pictet were the leading members and in which the main interest was meteorology. Of the best known early authorities only the German J. H. Lambert worked outside these schools, but his views, written in German, untranslated and, if only for

this reason, less accessible to the British and French, exerted such an influence on the Swiss that he can be conveniently grouped with them. The most surprising conclusion which emerges is that, until about 1800, adiabatic phenomena were virtually unknown in the French school of chemistry, although by 1783 Lavoisier and Laplace had devised a theory of heat which could have accommodated them in a most convincing and elegant way. The history of the phenomena in France is thus almost entirely restricted to our third period, which we shall examine in Chapter 2.

We return now to the first period. The discovery is usually and rightly attributed to William Cullen, Professor of Medicine at Glasgow University at the time, who mentioned it briefly in a paper on evaporation read to the Edinburgh Philosophical Society in May 1755.[1] Although he was almost certainly the first man to recognize that the movement of the liquid in a thermometer suspended in the receiver of an air pump did indicate that temperature changes had occurred, he was not the first man to observe it. In his History of Cold Robert Boyle described this experiment which he had performed on 20 November 1662:

> ...we took a weather-glass fill'd to a convenient height with well rectifi'd spirit of wine, and Hermetically seal'd, this we inclos'd in a glass Receiver of a Cylindrical form, of about two inches Diameter, and about a foot and a half high, and having cemented on the Receiver, we let it alone for some hours, that it might perfectly cool. Then drawing out the Air, and watching it narrowly, we observ'd, that the liquor in the weather-glass descended a little, though but a very little upon the first Exuction of the Air, and a little, though it seem'd somewhat less, upon the second, but afterwards we did not find it sensibly to

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1. W. Cullen, 'Of the cold produced by evaporating fluids...', Edinburgh Essays, ii (1756), 145-156.

descend. This subsidence of the liquor in all amounting to about the length of a Barley corn, we attributed to the stretching of the glass by the spring of the included Air, when the ambient was withdrawn, and accordingly upon our allowing a Regress to the excluded Air, we saw the spirit in the Thermometer, rise about half a Barley-corn's length to the place whence it began to subside. Afterwards we suck'd out, and let in the Air of the Receiver, as before, with like success, as to the descent and remounting of the liquor.[1]

As late as 1783 the Swedish chemist Torbern Olof Bergman independently attributed the apparent fall in temperature which accompanied the rapid evacuation of an air pump receiver to deformation of the thermometer bulb.[2] Since he did not enlarge on the subject, we can only assume that he would have accounted for the rise in the thermometer reading after the sudden re-introduction of air in exactly the same way. Boyle was thus not alone in treating his observation as a purely mechanical effect and it seems likely that in the late eighteenth century there were others besides Bergman who shared his view. Although only one later writer referred to the passage in Boyle,[3] both Erasmus Darwin and John Dalton[4] conducted experiments to show that no appreciable deformation of the thermometer bulb occurred during the evacuation and re-filling of the receiver. Neither Darwin nor Dalton mentioned any authorities for the view which they were

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1. R. Boyle, New Experiments and Observations touching Cold (London, 1665), pp.470-471.

2. Bergman, Opuscula, iii. 425. The section of the 'De attractionibus electivis' in which the reference appeared was added in the Opuscula and was not in the original version of the essay in Nova Acta Regiae Societatis Scientarum Upsaliensis, ii (1775), 159-248.

3. Wiegborn, De Igne, p.20.

4. See pp.56 and 95; also Biot, J. Phys., lv (1802), 176.

here attempting to disprove, but the very fact that they felt such experiments to be necessary indicates that it was more widely held than the published literature suggests. Such opinions, however, are unlikely to have originated with Boyle's single passing reference.

An obvious first task in this study was to ascertain whether any other observation similar to Boyle's had been made before Cullen's announcement, but a detailed search has revealed no other account. This delay in making the discovery and the slowness with which knowledge of it spread after 1755 deserves special comment in view of the extraordinary interest which had been taken in all branches of pneumatics since the middle of the seventeenth century. With the air pump and its accessories an established and important part of the 'philosophical apparatus' in any European laboratory, how had the discovery been missed. The answer is simply that the range of experiments which would yield true adiabatic phenomena by chance was extremely limited and that those which were observed could all too easily be misinterpreted. Consider, for example, the heating which must have long been familiar to anyone who tried to compress air with a condensing syringe. This instrument, widely used for attaining high pressures in the laboratory and as an essential component of the air gun, provided the simplest example of air being heated by compression, yet never once was the rise in temperature associated with a decrease in the volume of the gas. If we are to believe one comment dating from 1799,[1] the heating was widely attributed to friction between the piston of the

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1. See p.95.

syringe and the cylinder walls. With the air pump itself the smallness of the temperature changes obtained was probably the important obstacle, for, although it must have been an everyday practice to allow air to rush into an evacuated receiver, heat losses through the walls were nevertheless so great that temperature changes of the order of only 2 or 3 deg F would occur. Since the rapid evacuation of the receiver would give rise to a cooling which was equally small, it can be seen that the presence of a thermometer inside the receiver would be essential if any effect were to be noticed. It is significant therefore that the passage quoted from Boyle should contain the only reference that has been found to an experiment in which a thermometer was used in conjunction with the air pump before 1755. The typical experiments of the late seventeenth and early eighteenth centuries[1] concerned such problems as respiration under reduced or increased pressure, the failure of a vacuum to transmit sound and the striking mechanical effects of air pressure, as demonstrated by the Magdeburg hemispheres. None bore any relation to the study of heat. There was perhaps just one observation with the air pump which might have indicated that temperature changes were taking place. This was the appearance of mist during the rapid exhaustion of a receiver. The mist was particularly dense in a moist atmosphere and we know that it was familiar

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1. As described, for example, in F. Hauksbee, Physico-Mechanical Experiments (London, 1709); J. T. Desaguliers, A Course of Experimental Philosophy (London, 1744), ii. 375-411; J. A. Nollet, Leçons de Physique Expérimentale (Amsterdam, 1746), iii. 185-291 and Mém. Acad. Sci., (1740), 385-432 & 567-585 and Ibid., (1741), 338-362; P. van Musschenbroek, Introductio ad Philosophiam Naturalem (Leiden, 1762), ii. 823-905.

in any eighteenth-century laboratory.[1] Yet not until 1787[2] was it explicitly associated with the cooling of the air undergoing expansion.

Once the thermometer and the air pump were used together, as in Cullen's experiments, the discovery was inevitable. It did not result in the rather haphazard way which Professor Kuhn has suggested, namely from 'the increasingly routine deployment of...the thermometer',[3] but from one specific and carefully planned investigation which required both a measurement of temperature and the existence of a vacuum. We are not, after all, dealing with a discovery made independently by a number of different observers, as Kuhn appears to think, but with a single discovery which only gradually became well known.

Cullen's interest began with an observation by a pupil[4] who noticed that the reading on a thermometer fell immediately after having its bulb moistened in alcohol. This led Cullen to suspect that the process of evaporation produced cold, but he might well have conducted his investigation of cooling in the normal manner, without the aid of the pump, had he not wished to examine one particular point, namely whether the cooling could occur in the absence of the surrounding air or whether it arose from the mixture of the liquid with the air (after the fashion of the well known freezing mixtures in which the act of mixing substances lowered the tempera-

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1. See, for example, J. A. Nollet, Mém. Acad. Sci., (1740), 243-253.

2. E. Darwin, Phil. Trans., lxxviii (1788), 45.

3. Kuhn, Isis, xlix (1958), 133.

4. Identified in Black, Lectures, i. 162 as 'the late Dr. Dobson', presumably Matthew Dobson, M.D., F.R.S., of Liverpool (see H. Smithers, Liverpool (Liverpool, 1825), pp.417-418).

ture). It was while conducting his experiments on evaporation *in vacuo* that he observed a fall in temperature of 2 or 3 deg F whenever the receiver was evacuated, even when the bulb was unmoistened, and a similar rise in temperature when air was re-admitted. Cullen made only passing reference to the observation and offered no explanation. He related it in no way to evaporation, referring to it as merely one of 'a number of new and to me curious phenomena' which had occurred. Yet the fact that it was described together with the evaporation experiments and immediately before some observations on the cooling of a moistened thermometer *in vacuo* appears to have created the misconception, shared by several subsequent writers,[1] that Cullen viewed it as a case of evaporation. Horace Bénédict de Saussure went so far as to specify that Cullen's explanation might have been based on the evaporation of a thin layer of liquid from the surface of the thermometer bulb.[2] How Cullen was thought to explain the rise in temperature in this way is unclear, but no such difficulty really exists, for he neither gave nor implied any explanation. It seems unlikely, if he suspected evaporation to be the cause, that he would have omitted such striking evidence that evaporation in the void gave rise to cooling, a view which he was anxious to substantiate.

Saussure was not the first to misinterpret Cullen's views, however. In 1759, in his inaugural dissertation as Professor of Physics at the

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1. Including Kuhn, *Op. cit.*, 134.

2. H. B. de Saussure, *Essais sur l'Hygrométrie* (Neuchâtel, 1783), p.232.

University of Erlangen,[1] Johann Christian Arnold described his own, and Cullen's, work on the effects accompanying the evacuation and re-filling of air pump receivers. While he was convinced that Cullen had in some vague way associated the cooling with evaporation, he would commit himself no further than to comment:

> Quae omnia nexum aliquem inter frigus et exhalationem hisce in experimentis intercedere innuunt.[2]

Aware that evaporation could account for cooling alone, Arnold offered a novel explanation of the heating effect, attributing it to friction between the inrushing air and the sides of the entrance channel and of the receiver. It can be seen that Arnold's views shared one important characteristic with those of all the other writers of the first period in that he sought explanations in terms of familiar everyday phenomena such as friction and evaporation. This of course was exactly what Boyle and Bergman had done when they invoked the mechanical deformation of the thermometer bulb.

The contrast with the period after 1779 is striking. From that year all writers, with the single exception of Bergman, recognized that a completely new type of effect had been discovered. Whether they associated it with the entry of air into a vacuum or, more fundamentally, with a change in its volume, they were now in no doubt that the effect was truly thermal and of such significance as to justify any appropriate modification

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1. J. C. Arnold, De thermometri sub campana antliae pneumaticae suspensi variationibus (Erlangen, 1759).

2. Ibid., p.17.

in the theory of heat.

Between 1779 and 1800 a clear distinction can be drawn between the work of the Scottish and German-Swiss schools. An important representative of the former was William Cleghorn, who related the effect to the material theory of heat in his De Igne (1779). One strength of his account was that he used the same basic principle to explain both the heating and cooling. His view was as follows:

> ...quoniam ignis per corpora distribuitur, ut eorum attractio directe, et repulsio inter ignis particulas inverse, si in aliquo corpore prior minuitur, aut posterior augetur, ignis ex eo corpore fluet, donec aequilibrium rursus reductaur; et tunc calor dicitur generari. E contrario, si attractio cuiusdam corporis augeatur, aut repulsio inter ignis particulas minuatur, plus ignis in illud corpus fluet, et frigus generari dicitur.[1]

On this basis Cullen's experiments were easily explained:

> ...aëre, qui reliquus erat, rariore facto, repulsio inter ignis particulas minuebatur, eoque ignis e thermometro fluebat. At, aequilibrio cum aëre externo reddito, idem huius temperiem acquirebat; dein, aëre externo immisso, in recipulo contentus rarus, et temperie externo aequalis, subito comprimebatur; repulsione igitur ignis particularum aucta, ignis ex eo fluebat et thermometrum ingressus hunc erigebat.[2]

Although Cleghorn had understandably misconstrued the obscure evacuated receiver experiment, this passage is an important one since it contains the first recognition by any writer that the compression and rarefaction of air were the sole cause of the temperature changes. Of course his failure to appreciate that the compression is not experienced solely by

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1. Cleghorn, De Igne, p.20.
2. Ibid., p.21.

the small amount of air remaining but that air rushing into a vacuum continually compresses that which enters before it made his argument somewhat implausible. How, for example, could the compression of such a small quantity of air as remained give rise to so much heat? As Gay-Lussac later pointed out in his criticisms of a similar explanation given by John Leslie,[1] the heating effect was not known to diminish, even in the best available vacua.

Cleghorn's treatment, like Arnold's, was little known, the only subsequent reference to it being made by Black in his Lectures.[2] This is unfortunate, since it had as much to recommend it as the far more influential explanation proposed in the same year in Johann Heinrich Lambert's Pyrometrie.[3] By 1779 Lambert had known of the effect for some time, having been shown the experiments with the air pump by Arnold in 1761. At the time of their meeting Lambert had not seen Arnold's dissertation and he independently devised a quite different explanation, attributing the cooling to the fact that fire particles were abstracted from the receiver together with the air. If the density of the air were reduced by half, for example, the density of the fire particles, and hence also the temperature, which was proportional to this density, would be diminished by the same factor. In his references to temperature Lambert clearly had in mind absolute temperature, but there was no question of attaining the absolute

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1. See pp.111-112 and 139.
2. Black, Lectures, i. 196.
3. J. H. Lambert, Pyrometrie (Berlin, 1779), pp.266-269.

zero by the mere evacuation of air, since fire particles from the walls of the receiver and the base of the pump would quickly replace those abstracted.[1] Indeed, cooling could only occur if the rate at which the particles were abstracted exceeded that at which they were replaced. Conversely, if a gas were compressed to half its original volume without heat loss, its (absolute) temperature would be doubled and this, added to the effect of an isothermal decrease in volume, would cause the pressure of the gas to be increased four-fold. Again heat exchange with the surroundings would ensure that these ideal conditions were never actually attained. How Lambert explained the rise in temperature accompanying the entry of air into a vacuum is not mentioned, but M. A. Pictet, writing in 1790, gives the following passage which purports to be a translation of Lambert's own words:

> The heat that is carried by the mass of air which enters the receiver, joins that which existed already in the same receiver, unattached to any substance, and the rise of temperature is produced by this accumulation of the two quantities of heat in the same space.[2]

Unfortunately no further details have come to light but, since Lambert certainly considered that a vacuum could contain fire particles, to the point of maintaining that temperature changes would occur if the volume of the Torricellian vacuum in a simple barometer were altered rapidly,[3]

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1. Cf. Lambert's views on the zero of humidity in his 'Essai d'hygrométrie...', Hist. Acad. Sci. Berlin, (1769), p.101.

2. M. A. Pictet, Essay on Fire, tr.'W.B.' (London, 1791), p.29.

3. Lambert, Pyrometrie, pp.268-269.

there seems little reason to doubt that his explanation would have been essentially as Pictet described it.

It was through Lambert's work that adiabatic heating came to the notice of Saussure. Saussure's interest in hygrometry ensured his knowledge of Lambert's writings, among which he had been particularly impressed by the Pyrometrie.[1] It is appropriate to note here how closely the effect was linked with meteorological studies and particularly with hygrometry from Cullen to John Dalton. Nearly all the most influential eighteenth-century authorities, Lambert, Saussure, De Luc and Pictet, for example, as well as Cullen and Dalton, worked on hygrometry or were concerned with the study of vapours in some way. Having become fortuitously connected with this subject through Cullen, the effect, before 1800, was almost always reported and discussed in literature relevant to it. In view of this association with a particular type of literature and in view also of the specific and unusual conditions which were necessary for an independent discovery, it is hardly surprising that knowledge of the effect spread remarkably slowly to other research traditions. One fruitful analogy, which was widely adopted only after 1800, would have been with the heat produced by the percussion of a solid, but the general slowness to see that the compression of air rather than the filling of a vacuum was the fundamental phenomenon which required examination can only have obscured the fact that the heating effects produced in the gas and the solid both

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1. Saussure, Hygrométrie, preface, and Voyages dans les Alpes (Geneva, 1786), iv. 115.

originated in a similar fashion. De Luc and Erasmus Darwin[1] were the only writers to recognize the analogy before 1790 and they, significantly enough, showed less interest than their contemporaries in the work with the evacuated receiver.

The location and scarcity of accounts in the scientific literature are clearly relevant to any examination of the ignorance of adiabatic heating in France. Only two references by French authors before 1798 have been found, both dating from 1790. In that year Cullen's observations were mentioned briefly by J. A. C. Chaptal in his Élémens de Chimie[2] but were misleadingly attributed to evaporation. Although the book was an important one,[3] such a minor remark, the slight importance of which was in any case diminished by Chaptal's interpretation, was all too likely to be overlooked. An equally brief, but even less accessible reference seems to have been made by Monge in the obscure Journal Gratuit[4] in the same year. Monge's article was an extract from one on caloric which he prepared for the Encyclopédie Méthodique but which was never published and most of which was quickly lost. The writer of the article on caloric which eventually did appear in 1816 states that Monge wrote his contribution

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1. De Luc, Météorologie, i. 208 and Darwin, Phil. Trans., lxxxviii (1788), 43.

2. J. A. C. Chaptal, Élémens de Chimie (Montpellier, 1790), i. 70-71.

3. Being reviewed, for example, by C. L. Berthollet in Ann. Chim., vi (1790), 197-203.

4. A copy of the Journal Gratuit has not yet been located, but the article was reproduced in the Enc. Méth. (Physique), ii. 170-174, where the circumstances surrounding its writing and loss are described.

as early as 1782 and that his views on caloric were the subject of much discoussion in Lavoisier's circle, which Monge frequented, about that time.[1] If Monge knew of adiabatic heating by 1782, it seems strange that Lavoisier and Laplace should not have referred to it in their memoir of 1783 and that it should not be mentioned either in Lavoisier's Traité.[2] A possible solution, of course, may be that Monge did not in fact learn of the effect until nearer 1790[3] and that he modified his article for publication in the Journal Gratuit.

The failure of the French to read, or at least to recognize the importance of, the early accounts requires explanation. The authors of these accounts, though few in number, were after all well known figures. Perhaps most important, especially as far as neglect of the German-Swiss school was concerned, was that meteorological enquiry and hygrometry aroused less interest in France than in Switzerland, so that the relevant literature was presumably less widely read by the French. British and, in particular, Scottish science, on the other hand, was well known in Paris at the time when Lavoisier and Laplace were formulating their views on heat, but of the works which would have been discussed Magellan's Essai sur le Feu alone mentioned adiabatic heating,[4] and then only in passing.

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1. See pp.18-19.

2. Especially since Lavoisier had read Cullen's memoir (see Mém. Acad. Sci., (1777), 424n).

3. Even at this date, however, Monge failed to associate the mist in a rapidly evacuated receiver with cooling (see Ann. Chim., v (1790), 11-13).

4. Magellan, Essai, p.185.

Crawford made no published reference to it until 1788, although a comment in the minute-book of the Chapter Coffee House Society of London,[1] dated 21 February 1783, shows that he had performed experiments on the subject by that date and suggests that news of these might already have reached Paris. Speaking of his work with evacuated receivers Crawford reported 'that Mr. Lavoisier had repeated his (Dr. Crawford's) experiments and drawn from them similar conclusions...', but of this contact we know nothing more and the possibility that Lavoisier knew of adiabatic heating by 1783 but that he either considered it unimportant or misunderstood it must remain unconfirmed. By the time Crawford's work became common knowledge five years later, caloric theory was no longer a major subject of debate in France, where most chemists were now preoccupied with the task of establishing the anti-phlogistic chemistry rather than with Crawford's problems which were essentially physical and no longer even novel.

That the effect should have aroused so little interest in France was unfortunate, since most of the treatments given before 1800 lacked the experimental and theoretical rigour which the French caloricists could have brought to bear. The explanations of both Saussure and Pictet, for example, were incomplete in that neither treated both heating and cooling. For both men Lambert was the most important authority, although Saussure, who wrote in 1783,[2] had certainly read Cullen as well and he even quoted from the 1755 paper. Like Arnold, whose work he must have known if only

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1. MS Gunther 4, Museum of the History of Science, Oxford.

2. Saussure, Hygrométrie, pp.129 and 231-233.

through Lambert, Saussure carelessly interpreted Cullen's account as an attempt to attribute the effect to evaporation and so to prove that evaporation occurred more readily and produced greater cooling in the void than in air. In his own experiments Saussure had obtained a temperature change similar to that observed by Cullen and had also shown that the cooling effects obtained with damp and with dried air were identical, so ruling out the possibility that evaporation contributed appreciably to the phenomenon. Vigorously rejecting Cullen's (supposed) explanation he instead followed Lambert in attributing the cooling to the abstraction of fire particles together with the extracted air. Unfortunately Saussure attempted no explanation of the heat evolved when air entered a vacuum, but his chief concern was clearly to refute Cullen rather than to give a full description of adiabatic phenomena.

Saussure's comments provided the starting point for his pupil and close friend Marc Auguste Pictet, who succeeded him in the Chair of Philosophy at Geneva. In 1790 Pictet wrote that he himself had observed a temperature rise of about 2 deg R on allowing air to rush into an evacuated receiver and a similar rise by fitting a thermometer into the end of a condensing syringe and giving a single rapid stroke of the piston.[1] In a manner characteristic of our period Pictet expressed grave doubts concerning the true nature of heat but proceeded to argue in terms of the material theory, which he reluctantly admitted was preferable.[2] Although he vigorously defended the originality of his own theory, maintaining that he had

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1. Pictet, Essay, pp.28-29.

2. Ibid., pp.3-6.

evolved it before Lavoisier's Traité was published,[1] it showed close similarity to current French views. His 'feu' was almost identical with 'calorique' and he even expressed his approval of the French term.[2]

Pictet's work shows a conservatism which strongly emphasizes the difficulty imposed by the way in which adiabatic heating was discovered. Unlike many earlier writers, he was fully aware that the temperature of a gas rose when it was rapidly compressed and that this effect was related to that observed in the air pump receiver; yet he still could not abandon belief in the ability of the void to contain heat as an essential part of his explanation. With the density of fire particles still assumed to determine temperature it was understandably difficult to see how heating resulted from the mere entry of a mass of air into a vacuum, unless additional fire particles were already present in the vacuum ready to be taken up by the air and so to increase its temperature.

Although the confusing attempts to treat a changing mass of gas and a constant volume rather than a constant mass of gas in a changing volume persisted throughout the second period, the realization that the rapid compression of a gas did cause heating was spreading by the 1780s, creating the need for new explanations and diverting attention from the evacuated receiver experiments. How much the French could have contributed at this stage is obvious. They could have argued, as Laplace was later to do, that compression decreased the quantity of latent caloric which a gas could hold and that the excess caloric would thereupon become 'sensible'

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1. Ibid., pp.v-x.
2. Ibid., p.8.

and so raise the temperature. But this type of explanation belonged to the nineteenth century. The much simpler view adopted by Pictet was that heat was expelled from a compressed gas like water from a sponge.

That changes in volume altered the ability of a gas to contain heat was fundamental to all explanations and the one offered by De Luc in 1786[1] was typical in this respect. De Luc's account nevertheless marks an important stage in the history of the effect. Although he was Swiss by birth, his connections with the Swiss school were tenuous, since he had travelled widely and had lived in England since 1783.[2] He still believed that the void did have a definite capacity for heat,[3] but for reasons quite unrelated to adiabatic heating. Seeing the change in volume of a gas as the basic phenomenon, he was able to free his work completely from the influence of the evacuated receiver experiments. It is significant in this respect that it was he who first identified adiabatic heating with the heat evolved in the percussion of a solid.[4] He maintained that a simple change in volume, i.e. in the space between the particles of ponderable matter which could be occupied by 'fire', would affect only what he termed the 'capacité géométrique', while the other contribution to the total capacity, the 'capacité physique', determined solely by the nature of the substance, might or might not vary as well. 'Capacity' for De Luc

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1. De Luc. Météorologie, i. 142-148.
2. D. N. B., art. De Luc.
3. De Luc, Op. cit., 143-144.
4. See p.44.

was synonymous with both specific heat and ability to contain heat so that any decrease in volume, and hence also in the 'capacité géométrique', would be sufficient to cause the liberation of 'fire'. De Luc's explanation may seem that of an Irvinist but in fact he showed no sympathy for Irvine's views and criticized Crawford.[1]

Accounts by Irvinists are disappointingly rare, with the second edition of Crawford's Animal Heat the only major source before 1800. Here Crawford described experiments in which he had observed temperature changes of about 5 deg F on evacuating and filling the receiver of an air pump.[2] The work was carefully performed and throughout he had tried to obviate the effect of moisture. Yet it was original in only one respect, namely in his use of gases other than air. When phlogisticated and dephlogisticated air were used, the temperature changes were, respectively, slightly smaller and slightly greater than those obtained with atmospheric air, but the differences were small. Although Crawford gave no explanation, he appears to have associated the effect with the changes in capacity which he supposed to occur when the volume of a gas varied. Indeed, as we have seen,[3] he almost certainly inferred this dependence of capacity on volume from the adiabatic phenomena. We can assume, moreover, that he saw the heat evolved during the admission of a gas into a vacuum as resulting in some way from compression, since he considered the volume capacity of the

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1. De Luc, Op. cit., 142-148.

2. Crawford, Animal Heat (2nd edn.), pp.250-252.

3. See pp.28-30.

void to be either zero or very small by comparison with that of a gas[1] and so could not have interpreted the effect as a case of a gas of low capacity replacing a vacuum of high capacity, as Dalton, another Irvinist, was later to do.[2]

An interesting anomaly related to Crawford's work occurred in December 1787, not long before the publication of the second edition of the Animal Heat, when Erasmus Darwin independently described his own full experimental investigation of adiabatic phenomena to the Royal Society.[3] Darwin made no reference to earlier sources and so appeared to be claiming an independent discovery. This seems strange when Crawford, in 1788, could refer to the observations made with the air pump as being 'well known',[4] but Crawford of course was speaking as one familiar with the Scottish school of chemists and of this community his comment was no doubt true. The extent to which the effect was known in England, on the other hand, is less easily gauged. The absence of any reference to it in some prominent scientific works published in London before the turn of the century[5] certainly suggests that Darwin's might well have been an

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1. Crawford, Op. cit., pp.266-267.

2. See p.94.

3. E. Darwin, 'Frigorific experiments on the mechanical expansion of air', Phil. Trans., lxxviii (1788), 43-52.

4. Crawford, Op. cit., p.250.

5. e.g. W. Nicholson, The First Principles of Chemistry (1st, 2nd & 3rd edns., 1790, 1792 & 1796) and An Introduction to Natural Philosophy (1st, 2nd, 3rd & 4th edns., 1782, 1787, 1790 & 1796); C. Hutton, A Mathematical and Philosophical Dictionary (1st edn., 1796). In G. Adams, Lectures on Natural...Philosophy (1st edn., 1794), i. 309 and (2nd edn., 1799), i. 383 it is evidently misunderstood.

original contribution. And the fact that his paper was read to the Royal Society and published in their Philosophical Transactions would imply that it was seen as such by members of that body at least.

Yet the situation is an interesting one. In his paper Darwin claimed that he had begun his experiments twelve or fourteen years earlier, i.e. in 1773 or 1775. Then, working with the itinerant teacher John Warltire, he had observed the cooling which accompanied the evacuation of an air pump receiver and with Richard Lovell Edgworth and the great Scottish geologist James Hutton he had investigated the fall in temperature which occurred when the blast of an air gun was directed onto a thermometer bulb. He had also noticed the heat evolved during the compression of air in the receiver of the gun. There is no means of confirming whether these experiments were in fact performed in the period mentioned by Darwin, but Hutton was certainly engaged on a tour of England about this time[1] and in 1774 was introduced in Birmingham to the Lunar Society circle, of which Darwin was a member.[2] It seems reasonable to suppose, then, that Darwin's somewhat unspecific recollection was correct on this point and we may be quite sure from other evidence that he knew of adiabatic heating by about 1776. On page 45 of Darwin's Commonplace Book[3] there appear some notes on winds. Among these is the following passage, which is of parti-

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1. J. Playfair, 'Biographical account of the late Dr. James Hutton', Edin. Trans., v (1805), part 3, 47.

2. R. Schofield, The Lunar Society of Birmingham (Oxford, 1963), p.102.

3. Darwin Papers, Down House, Kent.

cular interest as being the earliest[1] known instance of changes in volume being seen as the sole cause of the thermal effects:

> Now if air be added suddenly rariefied without the addition of heat, as in going into an exhausted receiver, or by being pumped out of it cold is produced...On the contrary when air is condensed heat is produced...

The position of the notes in the book enables us to date this comment fairly precisely. They are followed immediately, on page 47, by a brief reference to a wind gauge which, Darwin states, was described in 'one of the last volumes' of the Philosophical Transactions. The article to which Darwin was presumably referring, by James Lind, was in fact published in 1775.[2] Moreover, the notes are preceded by a section headed 'From Charle's notes at Dr. Black's lectures', 'Charles' being almost certainly Darwin's eldest son by his first wife.[3] Charles studied medicine at Edinburgh, where Black was Professor of Medicine and Chemistry, from 1775 until his death in 1778, so that the notes must have been taken in this period. Since the entries throughout the Commonplace Book follow an approximately chronological order, it seems likely, therefore, that the passage quoted above was written in 1776. Another factor is that the book is inscribed at the front '1776' and, although some subsequent entries date from several years later, it is clear that the early part of it was completed quickly.

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1. Although the idea was very probably expounded in London by Bryan Higgins in 1775 (see his A Syllabus of the Discourses and Experiments..., p.61).

2. J. Lind, Phil. Trans., lxv (1775), 353-365.

3. See Charles Darwin's biographical sketch in E. Krause, Erasmus Darwin (2nd edn., London, 1887), pp.80-83.

Even if we accept this dating, the question of whether Darwin made the discovery independently remains, since there are a number of possible sources in addition to Charles from which he could have learnt of it. The first and strongest possibility is that he had read Cullen's account, which by 1770 had been published in two editions of the Edinburgh Philosophical Society's Essays.[1] The source was by no means obscure and the volume in which Cullen's paper appeared was all the more notable since it included Black's 'Experiments upon Magnesia Alba'. It would be strange indeed if it had escaped Darwin's attention. He would certainly have known of Cullen about the time of the discovery, for it was in the autumn of 1754 that he began his medical studies in Edinburgh.[2] At this time Cullen was still at Glasgow as Professor of Medicine, but the work of such a renowned physician would have been known far beyond his own university. In 1755 Darwin spent some time at Cambridge, but he returned to Edinburgh before setting up as a physician, first in Nottingham in September 1756 and then in Lichfield in November 1756. Cullen had been elected to the Chair of Chemistry at Edinburgh by November 1755 and began lecturing there in the following January, though to a small audience,[3] so that it is even possible that Darwin heard of adiabatic heating from Cullen himself. A letter from Black to Cullen, written in August 1755,[4] indicates that eve-

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1. It was reprinted in Edinburgh Essays (2nd edn., 1770), ii. 159-171.

2. See Krause, Darwin, pp.12-16.

3. J. Thomson, Life...of William Cullen (Edinburgh and London, 1859), i. 90-97.

4. Ibid., 579.

poration under an evacuated receiver was still of current interest and so might well have been mentioned in lectures. In fact, since Cullen's class register[1] makes no mention of Darwin, a personal contact between the two men remains no more than a possibility.

Of the other possible sources available to Darwin perhaps the most likely is his friend James Hutton. Before he was introduced to the Lunar circle by Watt in 1774, Hutton had been closely associated for a number of years with the Scottish chemists, notably Black,[2] among whom the adiabatic effect was probably common knowledge. Even if he did not hear of it in this way, we know that he read and was impressed by Black's paper on magnesia alba [3] and so is unlikely to have ignored the paper by Cullen which immediately preceded it.

Among other possible contacts we should mention James Keir, Darwin's lifelong friend and contemporary in the Edinburgh medical school, who in a letter to Darwin in 1766,[4] referred to Cullen's evaporation experiments. James Watt too could well have told Darwin of the adiabatic effect. After setting up as an instrument maker to the University of Glasgow in 1757 Watt came into close contact with such men as Black and Cullen[5] and it is

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1. Preserved in Edinburgh University Library.

2. Playfair, Edin. Trans., v (1805), part 3, 46.

3. Ibid., 59.

4. A. and J. K. Mcilliet, Sketch of the Life of James Keir (London, n.d.), p.46.

5. S. Smiles, Lives of Boulton and Watt (2nd edn., London, 1866), pp.112-113.

hard to believe that he would not have learned of adiabatic heating in this lively community. In 1767 Watt met Darwin in Birmingham and, although he did not move to Soho until 1774, he immediately joined the Lunar circle, corresponding vigorously with Darwin and the other members.[1]

A further point seems relevant to the problem of the originality of Darwin's work. In the paper of 1787 he described two experiments which he had conducted specifically to prove that the cooling was not the result of either distension of the bulb of the thermometer or of evaporation from its surface.[2] As we have seen, both these rather improbable explanations had been proposed by earlier writers and it seems an extraordinary coincidence that Darwin should quite independently have chosen to refute them in the first announcement of his 'discovery'. Since neither of the experiments in question was conducted before December 1784, this evidence throws little light on the way in which he first learned of adiabatic heating, but it strongly suggests that, contrary to the impression conveyed in his paper, Darwin had read at least some of the literature on the subject by 1787. Indeed, it would be surprising if such members of the Lunar circle as Watt, Josiah Wedgwood or Priestley, among whom the effect was almost certainly well known,[3] had not brought the earlier references to his

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1. Schofield, Op. cit., pp.67-68.

2. Darwin, Phil. Trans., lxxviii (1788), 45-46.

3. See Darwin to Wedgwood, 11 Mar. 1784, in Krause, Darwin, pp.100-101; also Priestley to Benjamin Vaughan, 26 Mar. 1780, in H. C. Bolton, Scientific Correspondence of Joseph Priestley (New York, 1892), pp.19-21. Priestley refers to a demonstration by the itinerant lecturer John Arden, who was also the source of Magellan's knowledge (see Magellan, Essai, p.185). Magellan and Vaughan, as well as Keir, Edward Nairne and Hutton, attended the meeting of the Chapter Coffee House Society on 21 Feb. 1783 at which Crawford's experiments were described (see p.46.).

attention.

With so much of the evidence only circumstantial, we must inevitably leave the problem unresolved. But, whatever our views on the originality of Darwin's account - and this must at least be in serious doubt - there can be no denying its importance. Darwin's was unquestionably the fullest study of adiabatic heating which had yet been undertaken and it was full not simply in respect of the number and variety of his experiments. He was quick to see the possible relevance of his work to two other apparently unrelated phenomena which were badly in need of explanation. The first was the mysterious deposit of snow round the stop-cock where compressed air rushed from a mine pump at Schemnitz in Hungary.[1] The observation had been made as early as 1758, but no satisfactory explanation had yet been offered. By close analogy with an experiment which he and his friend Fox had conducted in December 1784, in which they had examined the cooling which occurred when compressed air was suddenly released from a vessel, Darwin was able to see the snow as resulting from the freezing of water vapour by the rapid expansion of the emerging air. He evidently had a particular interest in the cooling effect, since the notes concerning his experiments with Fox in the Commonplace Book are followed immediately by a diagram[2] which seems to represent a device for attaining low temperatures. Whether it was ever constructed is not clear, but Darwin expressed the hope that it might be possible even to freeze mercury with it. The second phenomenon was the cold

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1. See pp.83-84.

2. Reproduced as plate 9 in Schofield, Op. cit.

experienced in the upper atmosphere. In his notes on winds, which we have dated to 1776, Darwin was already applying his knowledge of the adiabatic effect to meteorological phenomena[1] and in his paper to the Royal Society he ascribed the cold at high altitudes to the expansion of air as it rose and experienced a diminishing pressure. Despite its essential correctness, the explanation attracted little attention, James Hutton and later Cavallo[2] being the only contemporary writers who adopted it.

Although such details of Darwin's work were not generally accepted, the appearance of his paper in the Philosophical Transactions ensured that there could henceforth be no excuse for ignorance of adiabatic phenomena and the paper was understandably an important source for later writers. What in Britain at least had been the concern of fairly restricted groups, such as the Scottish school of chemists, the Lunar Society in Birmingham and the Chapter Coffee House Society in London, now became common knowledge. Interest nevertheless died down after 1788, to be revived only by Dalton in 1800. The account of the second of our three periods therefore ends with Darwin and Crawford in Britain and with Pictet on the Continent. The work of the third period was to be very different, with the true magnitude of the effect, which before 1800 had been seriously obscured by heat losses, being at last appreciated. The most important factor in these advances was to be the entry of the French into the field and it was they who were chiefly responsible for transforming something which was little

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1. See also E. Darwin, The Botanic Garden (London, 1791), 'The Economy of Vegetation', Add. Notes pp.82, 88-89 and 92.

2. Playfair, Op. cit., 66-67n. and T. Cavallo, The Elements of Natural... Philosophy (London, 1803), iii. 94.

more than a curiosity, without apparent relevance to any really major problem, into a phenomenon at the very centre of the study of heat. These eighteenth-century text books which either ignored it or relegated it to a minor position could never have been written after 1800.

Expansion by Heat

Although the first experiments designed specifically to measure the extent to which air was expanded by heat were described by Guillaume Amontons only in 1699,[1] the effect had long been a familiar one. The expansion was known to such ancients as Philo of Byzantium and Hero of Alexandria[2] and had already been applied in the early thermometers of Galileo and Santorio Santorii,[3] but in no case had the need for a closer quantitative study of the behaviour of heated air been felt. For Amontons the immediate incentive was a purely practical one, concerned with the development of his 'moulin à feu', a novel engine which utilized the pressure of hot air to drive a mill-wheel.

In his experiments Amontons in fact measured not the expansion of air but the increase in its pressure when its volume remained constant. The

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1. G. Amontons, 'Moyen de substituer commodement l'action du feu à la force des hommes...', Mém. Acad. Sci., (1699), 112-126.

2. See, for example, the devices in Hero's Pneumatica (Heronis Alexandrini Opera quae supersunt omnia, ed. & tr. W. Schmidt (Leipzig, 1899), i. 176 and 224). For the references in Philo's De Ingeniis Spiritualibus see Ibid., 474-476.

3. F. S. Taylor, 'The origin of the thermometer', Ann. Sci., v (1942), 129-156.

apparatus consisted of a U-tube one limb of which was open to the atmosphere while the other was closed by a bulb, the air under examination being contained in the bulb by a short mercury column in the tube. By observing the change in the levels of mercury Amontons concluded that the pressure of air increased by approximately one third when it was heated from room temperature to the temperature of boiling water. That a similar increase in volume would occur if the pressure and not the volume were maintained constant followed from Boyle's law. Further similar experiments performed in 1702[1] only confirmed Amontons's conclusions, although he now saw clearly how variations in the pressure of air could be used to indicate temperature. In that year he gave the first hint of his understanding of the concept of an absolute zero far below any temperatures previously encountered[2] and in April 1703[3] he formally defined what he termed the 'extreme cold' of his thermometer as that point at which air would exert no pressure. Although Amontons himself did not make the calculation, his data indicate a zero at -239.5°C, if we assume the air pressure to decrease uniformly with temperature. Despite references to it by George Martine,[4] Lambert[5]

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1. G. Amontons, 'Discours sur quelques proprietez de l'air...', Mém. Acad. Sci., (1702), 161-180 and Hist. Acad. Sci., (1702), 1-8.

2. Amontons, Mém. Acad. Sci., (1702), 171.

3. G. Amontons, 'Le thermometre réduit à une mesure fixe & certaine...', Mém. Acad. Sci., (1703), 52.

4. G. Martine, Essays Medical and Philosophical (London, 1740), pp.291-292.

5. Lambert, Pyrometrie, pp.29-30.

(who was very favourable) and Alessandro Volta,[1] Amontons's definition attracted comparatively little attention during the eighteenth century and, when interest in the absolute zero revived with the advent of Irvinist doctrines, it was not even mentioned in the ensuing debate. Even immediate comment, such as that by Lazare Nuguet and Philippe de la Hire,[2] was concerned with the experimental rather than theoretical issues. The effect of heat on the pressure or volume of air would certainly have aroused far greater interest at this time had thermometers of the Amontons type come into general use. Two observers who did adopt this form of thermometry in their meteorological work were Nicolaas Samuel Cruquius[3] in Holland and the Italian mathematician Giovanni Poleni[4] and, as we should expect, both men checked (and substantially confirmed) Amontons's observations. But air thermometry made little headway against the increasingly refined methods involving the use of alcohol and mercury in closed tubes and, although occasional measurements of the expansion of air were made despite the lack of any obvious incentive, it was not until the last quarter of the eighteenth century that the subject became one of major importance. The chief reasons for this development of interest seem to be twofold. First, De Luc's demonstration that air temperature had to be taken into

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1. Le Opere di Alessandro Volta [Edizione Nazionale] (Milan, 1929), vii. 357.

2. L. Nuguet, Mém. de Trévoux (1705), 1790-1807.

3. N. S. Cruquius, Phil. Trans., xxxiii (1724-5), 4.

4. G. Poleni, Phil. Trans., xxxvii (1731-2), 205.

account in measuring altitude with the aid of a barometer created the need for a reliable value for the expansion coefficient of air; and, secondly, the growth of pneumatic chemistry meant that some method was required for correcting the volumes of gases, and not only of air, to a standard temperature. These two new incentives were felt by such clearly distinguishable groups of workers that we shall consider them separately.

De Luc published his account of altitude measurement in 1772.[1] Using a law first derived by Edmund Halley,[2] according to which the difference between the heights of two points was proportional to the difference between the logarithms of the barometric readings taken at the points, he made a large number of determinations of altitude and compared his results with those obtained by trigonometrical methods. By making the comparisons several times at different temperatures he estimated that the discrepancy between the results obtained by the two methods disappeared when the mean temperature of the points at which barometric measurements were made was 16½°R. Further examination showed that the effect of any departure from this mean temperature was, for every deg R, an error of 1/215 of the height calculated by the simple logarithmic law, this figure being also the coefficient of expansion of air in the region of 16½°R.[3]

In view of the growing interest in mountaineering and, from 1763, in

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1. J. A. De Luc, Recherches sur les Modifications de l'Atmosphère (Geneva, 1772), ii. 43-242.

2. E. Halley, Phil. Trans., xvi (1686), 105-106.

3. De Luc, Recherches, ii. 90-92.

ballooning, in both of which pursuits portable barometers were commonly carried,[1] it is not surprising that De Luc's work became well known. Within five years of its appearance it had moved both Sir George Shuckburgh[2] and Colonel William Roy[3] to make direct observations of the expansion of air and consequently to modify some of De Luc's figures, though without rejecting the principles of his treatment. The Swiss physicist Jean Trembley, on the other hand, applied De Luc's indirect method to barometric observations taken by Roy and Shuckburgh, concluding that a modification was required both in the temperature at which the barometric and trigonometrical methods were supposed to be in agreement and in the expansion coefficient.[4] Although it is difficult to cite any other work which was definitely inspired by the problem of altitude measurement, with the possible exception of Saussure's,[5] Laplace's writings alone indicate that both this subject and the closely related one of atmospheric refraction remained important well into the nineteenth century.[6] In turning to consider the effect of the rise of pneumatic chemistry we should therefore not forget that this first demand for the data relating to the expansion of air continued.

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1. See p.72.
2. G. Shuckburgh, Phil. Trans., lxvii (1778), 562-568.
3. W. Roy, Phil. Trans., lxvii (1778), 689-715.
4. Saussure, Voyages, ii. 616-641.
5. Saussure, Hygrométrie, pp.108-111n.
6. See pp.71-72.

If quantitative work in the chemistry of gases was to be meaningful, volumes had to be corrected for variations in both pressure and temperature. For pressure Boyle's law was unquestioningly adopted while for temperature De Luc's figure of 1/215 per deg R appears to have been considered the most reliable, if we judge from Lavoisier and Laplace's application of it in their treatment of combustion and respiration in 1783.[1] But De Luc was not wholly reliable, as subsequent comment had shown, and in any case pneumatic chemistry was not solely concerned with air. As early as 1777 Joseph Priestley had performed some crude experiments on the expansion of all the gases which he knew[2] but when Vandermonde, Berthollet and Monge came to investigate the quantities of hydrogen in various types of iron and steel in 1786, they very properly re-determined the expansion coefficients for air and hydrogen.[3] Although such experiments fulfilled their immediate purpose, they were of limited scope and some four years later Guyton de Morveau and the army engineer and prominent revolutionary Prieur Duvernois (otherwise Prieur de la Côte-d'Or) initiated the thorough investigation of gas expansion which was so obviously needed, still with the problems of pneumatic chemistry in mind.[4] The experiments, conducted

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1. Lavoisier and Laplace, Mém. Acad. Sci., (1783), 396.

2. Priestley, Expts. and Obs...on Air, i. 250; iii. 345-348; and Expts. and Obs. relating to...Nat. Phil., ii. 359.

3. A. T. Vandermonde, C. L. Berthollet and G. Monge, Mém. Acad. Sci., (1786), 164-166.

4. Guyton de Morveau and Duvernois, Ann. Chim., 1 (1789), 256-299 and Enc. Méth. (Chimie) (Dijon, 1789), i. 675-687 (art. Air).

by Duvernois in Guyton's laboratory are significant, since they were concerned not only with a wide range of gases but also with variations in the rate of expansion over different parts of the temperature scale. Previous attempts to compare the expansion of air with that of a thermometric liquid had proved inconclusive. Shuckburgh, for example, saw little reason to doubt that the volume of air increased proportionally to that of mercury,[1] but De Luc[2] and, more especially, Roy[3] were convinced that no such proportionality existed. Unfortunately the quality of Duvernois's experiments was hardly worthy of the importance of the problems and it is clear that the gases which he enclosed in his mercury manometer had not been sufficiently dried. The seven gases under examination expanded to very different extents and their volumes all increased far more rapidly at higher temperatures, a sure indication of the presence of water vapour.

Despite their shortcomings, Duvernois's results had the air of authority. For Riche de Prony they provided the data for an elaborate attempt to derive an expression relating the volume of a gas to its temperature,[4] and they were quoted as standard in less original work also.[5]

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1. Shuckburgh, Op. cit., 565-566.

2. De Luc, Recherches, i. 282. See also Ibid., ii. 161-169.

3. Roy, Op. cit., 695.

4. R. de Prony, Nouvelle Architecture Hydraulique (Paris, 1796), ii. 163-175 and J. Éc. polytech., i (an IV), 36-49.

5. See, for example, Nicholson, Chemistry (1st edn.), p.522; (2nd edn.), p.536; (3rd edn.), 554; Thomson, Chemistry (1st edn.), i. 269 and Enc. Brit. (3rd edn.), supplement, i. 259.

Indeed, they were so authoritative as to go unchallenged even by such an eminent physicist as J.A.C. Charles who, with the Robert brothers, his companions in his early work on balloons, had already shown that all insoluble gases at least were equally expanded by heat.[1] Such open criticism as there was, by Volta, came from neither Britain nor France and was consequently only too easily overlooked.

Volta's chief concern in his work[2] was probably thermometry, although in examining his motives it is worth observing that he was a noted mountaineer.[3] He was familiar with far more earlier work on the subject of gas expansion than any other writer and he appears to have been particularly influenced by Lambert and Johann Friedrich Luz,[4] both authorities who were never cited by the British or French. While he would not commit himself on Lambert's assertion that the expansion of air was proportional to the quantities of heat added, his experiments, conducted between 1791 and 1793 with a Drebbelian thermometer incorporating oil instead of water, showed that from the freezing point to the boiling point of water dry air expanded

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1. J. L. Gay-Lussac, Ann. Chim., xliii (1802), 156-158. The participation of the Robert brothers is mentioned only in the MS notes for lesson 25 of a physics course given by Charles about 1806 (Library of the Institut de France, Paris). The experiments appear to have been conducted in 1786 or 1787, with an apparatus now in the Conservatoire National des Arts et Métiers, Paris (exhibit 1584).

2. A. Volta, 'Della uniforme dilatazione dell'aria', in Volta, Opere, vii. 347-375. See also the letters on pp.323-344.

3. M. Cermenati, Alessandro Volta, Alpinista (Turin, 1899).

4. The reference to Luz given by Volta (Opere, vii. 354n) is J. F. Luz, Vollständige und auf Erfahrung gegründete Beschreibung... (1774), p.414, a copy of which has not yet been located.

by almost exactly 1/216 of its volume at 0°R for every deg R rise in temperature as measured on the mercury thermometer. Volta thus anticipated a result obtained independently by Gay-Lussac some ten years later.[1]

So the eighteenth century came to a close with the data relating to the expansive properties of gases in quite as unsatisfactory a state as those concerning their specific heats. Moreover, the inadequacy of the situation, aggravated as it was by the fact that adiabatic phenomena were virtually unknown to those who could have applied them most effectively, was all too little recognized. By most eighteenth-century writers the existing results were readily accepted, if only as fair approximations, and at least the general principles of such problems as the nature of heat and the structure of gases appeared to be settled. The need for the far higher standard of experimentation which was to give new stimulus to the study of gases so soon after the turn of the century had not yet been felt.

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1. See p.70.

CHAPTER 2

The Special Status of Gases

The work on the thermal properties of gases before 1600 had done little to suggest that matter in the gaseous state deserved special attention. The expansion coefficients of gases had been found to be as varied and unpredictable as those of liquids and solids, and their specific heats similarly had shown no sign of regularity. Only adiabatic heating seemed in any way an unusual phenomenon and even this had hardly attracted the attention which it deserved. In France it was almost unknown, even by 1800, while elsewhere, even if it was no longer exclusively associated with the entry of a gas into a vacuum, it was all too easily dismissed as an instance of heating by compression analogous to the more familiar effect which accompanied the percussion of a solid. Gases, it seemed, were no more than modified forms of liquids and solids, with their properties altered but not in any fundamental sense different.

Two events early in the new century served to change this opinion radically and to give gases a unique status. The first was the discovery, made independently by John Dalton and Joseph Louis Gay-Lussac, that, for any given increment in temperature, all gases expanded to the same extent. Taken in conjunction with the equally simple Boyle's law, this constituted strong evidence that a certain fundamentality was to be associated with the gaseous state and that laws, particularly those relating to caloric, might be deduced in their simplest form from observations on gases. The second event was the sudden and rapid spread of knowledge of the adiabatic

effect, especially in France. Dalton again was largely responsible, but Laplace's removal of the notorious discrepancy between the experimental and theoretical values for the speed of sound, which had existed since Newton, not only ensured lasting prominence for the effect but also gave the first reliable, and somewhat surprising, indication of its true magnitude. The intense interest in the thermal properties of gases in the first three decades of the century, with which this work is chiefly concerned, owed much to these two events and we shall therefore need to examine them in some detail.

Expansion by Heat

In October 1801 John Dalton read four papers on various subjects relating to gases and vapours to the Liberary and Philosophical Society of Manchester. It was in the last of these[1] that he announced his conclusion that 'all elastic fluids under the same pressure expand equally by heat'.[2] He claimed to have conducted 'a great many experiments', in which he had observed the expansion of air, hydrogen, oxygen, nitric oxide and carbon dioxide in a manometer tube. Although he fully recognized the importance of drying the gases, he admitted that he had succeeded in this only for air and so readily ascribed minor deviations from his 'law' to the presence of water vapour. The observations on air were therefore the definitive

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1. J. Dalton, 'On the expansion of elastic fluids by heat', Manchester Memoirs, v (pt.2) (1802), 595-602.

2. Ibid., 602.

ones and these showed an increase in volume of 325 parts in 1000 between 55°F and 212°F.

Gay-Lussac announced a similar conclusion to the First Class of the Institute (the revolutionary successor of the Académie des Sciences) on 31 January 1802,[1] when he was still only twenty-three. Although Dalton's paper had already been read, and possibly even published,[2] there is no evidence that Gay-Lussac knew of it. Of undoubted importance, however, was his familiarity with Charles's experiments conducted some fifteen years earlier and to these he paid due acknowledgement. Gay-Lussac seems to have been more successful than Dalton in drying the nine gases which he used and he concluded confidently that between 0°C and 100°C all the permanent gases expanded by 1/266.66 of their volume at 0°C for every deg C rise in temperature. Even the insoluble gases were found to expand in exactly the same way as air, in contradiction to Charles's conclusion on this point. As we should expect from the remarkable consistency of his results, Gay-Lussac's experimental procedure was more sophisticated than Dalton's. The gas under examination was enclosed in a flask which was heated in a water bath and, as heating proceeded, gas was allowed to escape through an exit tube fitted with a tap. When the flask had stood for about twenty minutes in boiling water, the tap was closed and the whole apparatus cooled. The volume of gas expelled could now be determined by opening the

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1. J. L. Gay-Lussac, 'Recherches sur la dilatation des gaz et des vapeurs', Ann. Chim., xliii (1802), 137-175.

2. Thomson, Chemistry (4th edn., Edinburgh, 1810), i. 488.

flask over water and measuring the volume of water which entered. The same principle was also used in a simpler alternative method in which the tap was dispensed with. For the soluble gases no direct measurements were made and their expansion in a tube inverted over a mercury bath was merely compared with that of air similarly heated in an identical tube.

That two essentially correct measurements of gas expansion should have been made almost simultaneously and yet independently clearly requires comment. Was this the result of pure coincidence? If not, what were the contemporary problems which required the information? Unfortunately only Gay-Lussac gave any indication of the motives for the work, but his comments suffice to show that the results would have been seen as a very welcome addition to physical knowledge. He wrote:

> ...on a besoin tous les jours, en physique et en chimie, de ramener un volume donne d'un gaz d'une temperature à une autre, de mesurer la chaleur dégagée, ou absorbée, dans le changement de constitution des corps, celle dégagée, ou absorbée par le même corps en passant d'une température a une autre; dans les arts, de calculer les effets d'une machine mue par le feu, de bien apprecier les dilatations de plusieurs corps; en météorologie, de determiner la quantité d'eau tenue en dissolution par l'air, quantité qui se varie avec sa température at sa density, et suivant une loi qu'on ne connait pas encore. Enfin, dans la construction des tables de réfraction astronomique, et dans l'application du baromètre à la mesure des hauteurs, il est indispensable de connaitre exactement et la température de l'air et la loi de ses dilatations.[1]

Most of this passage speaks for itself, but the last sentence is particularly interesting for its allusion to two topics with which Laplace was concerned about this time. Indeed, the expansion coefficient of air

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1. Gay-Lussac, Op. cit., 139-140.

figured so prominently in Laplace's recently published accounts of atmospheric refraction and of the use of the barometer to measure altitude[1] that we can be almost certain that it was he who requested Gay-Lussac to conduct the experiments.[2] Both problems, moreover, were of more than academic interest. With regard to the former, it was obviously a constant concern of astronomers that it should be possible to correct for refraction in the atmosphere and so determine the true position of stars. Laplace's treatment, which was repeated in the Mécanique Céleste,[3] was the best known, but J. T. Mayer (the younger) gave another detailed account in 1810, using his own figure for the coefficient.[4] The second of Laplace's problems had been a familiar one for some thirty years, but contemporary interest in mountaineering and ballooning ensured its continued importance and Gay-Lussac himself was actually to use the barometric method of altitude measurement, incorporating his own revised expansion coefficient, in two balloon flights which he made in 1804.[5]

In the 1802 paper[6] Gay-Lussac warmly expressed his gratitude to Laplace

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1. P. S. Laplace, Exposition du Système du Monde (2nd edn., Paris, an VII), pp.81, 82 and 86.

2. P. S. Laplace, Traité de Mécanique Céleste (Paris, 1805), iv. 270.

3. Ibid., 269-276.

4. J. T. Mayer, 'Commentatio de apparentiis obiectorum terrestrium...', Commentationes Soc. Reg. Scientarum Gottingensis Recentiores, i [Commentationes mathematicae] (1811).

5. J. L. Gay-Lussac, 'Relation d'un voyage aérostatique', Ann. Chim., lii (1804), 75-94. For Laplace's amendment to his earlier treatment of altitude measurement see Laplace, Op. cit., 289-293.

6. Gay-Lussac, Ann. Chim., xliii (1802), 140.

and to Claude Louis Berthollet for their encouragement and material assistance in the experiments. His acquaintanceship with these two great French scientists had begun only recently when, in 1800 on his return from Egypt, Berthollet had asked for a pupil from the École Polytechnique to act as his assistant in the laboratory which he had established in his country house at Arcueil just outside Paris.[1] Gay-Lussac, newly graduated, was chosen and so entered into close contact not only with Berthollet but also with Laplace, Berthollet's neighbour at Arcueil. The collaboration was not always to prove a salutary one, as we shall see for example in Gay-Lussac's reluctance to accept the atomic theory and in his firm belief in the physical reality of caloric,[2] but during the early years of the century, when Laplacian science was pre-eminent in France, an entrée to Arcueil was a most valuable asset for any aspiring scientist.

Another problem in which Laplace took a particular interest was the search for a rational scale of temperature. The chief difficulty was that there was no guarantee that the mercury in a conventional thermometer expanded uniformly or, as Gay-Lussac put it in terms of current caloric theory, 'que des divisions égales de son échelle représentent des tensions égales de calorique'.[3] The work of the eighteenth century had of course given no reason to suppose that gases were any more suitable in this

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1. D. F. J. Arago, 'Gay-Lussac', in Oeuvres Complètes de François Arago (2nd edn., Paris, n.d.), iii. 7.

2. See pp.145-146 and 281.

3. Gay-Lussac, Op. cit., 139.

respect. Moreover, gas thermometers were unwieldy in practice and the mercury-in-glass instrument had quite recently received influential support from both De Luc and Crawford.[1] But the discoveries of Dalton and Gay-Lussac quickly revived interest in gas thermometry. Gay-Lussac's first experiments could not help, since they did not involve the gradual variation of temperature in the water bath, but a new procedure, which he must have adopted before 1805,[2] allowed the expansion of gases to be compared with the readings on a mercury thermometer over a range of temperatures up to the boiling point of water. No account was given at the time, but the method was presumably that later described by Biot, who recorded that the expansion coefficient determined with Gay-Lussac's new apparatus was precisely that obtained in the original experiments and was the same for all gases.[3] Gay-Lussac had apparently shown also that the expansion of the gas was proportional to the readings on the mercury thermometer between 0°C and 100°C and Laplace would seem to have known something of his results when, in 1805,[4] he recommended the air thermometer as the ultimate standard and the mercury thermometer as a reliable everyday instrument. Laplace was of course far-sighted in this, but it was only after Dulong and Petit's vigorous advocacy of gas thermometry in 1818[5] that the method

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1. De Luc, Recherches, i. 285-330 and Crawford, Animal Heat (2nd edn.), p.53.

2. See note 4 below for reference.

3. J. B. Biot, Traité de Physique (Paris, 1816), i. 182-190.

4. Laplace, Op. cit., 270 and p.xxii.

5. See p.272.

became widely accepted as a standard of comparison. The delay is hardly surprising when we compare the first class experimental work which Dulong and Petit conducted in support of their claim with this unconvincing argument, which was the best that Laplace could offer:

> ...si l'on concoit que le volume d'air restant toujours le même, sa température augmente; il est très-naturel de penser que sa force élastique dont la chaleur est la cause, augmentera dans le même rapport. En le soumettant dans ce nouvel etat, à la pression qu'il éprouvait dans le premier; son volume croîtra comme sa temperature. Le thermomètre à air me paraît donc indiquer exactement les variations de la chaleur...[1]

Dalton had no mentor of the stature of Laplace and his work gives little indication of the problems which he considered might benefit from the new data. It is possible that mere dissatisfaction with the existing results provided sufficient incentive, and this at least was the impression conveyed by Dalton.[2] However, the paper which resulted was more than an account of experimental procedure and observations, for Dalton immediately applied his results in a highly original derivation of a theoretical expression relating the volume of a gas and its absolute temperature.[3] In examining Dalton's argument two points must be born in mind. First, and most important, he was a convinced Irvinist, rejecting any idea that some caloric in bodies existed in a latent state.[4] His commitment is nowhere more apparent than in the first part of volume 1 of his New System of Chemical

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1. Laplace, Op. cit., p.xxii.
2. Dalton, Manchester Memoirs, v (pt.2) (1802), 595.
3. Ibid., 601.
4. Dalton, Nicholson's Journal, /2/ v (1803), 36.

Philosophy,[1] which he devoted largely to an account of caloric theory based on Irvinist principles and in which, significantly, one of the few illustrations (see Plate 1) shows the cylinders of uniform cross section which Crawford[2] had already used to explain his views on the quantities of heat in bodies. The second point is that Dalton accepted as a physical truth Newton's purely mathematical demonstration[3] that Boyle's law could be accounted for if it was supposed that the adjacent particles of a gas expanding isothermally repelled one another with a force inversely proportional to the distance between them. Caloric theory, of course, had given new authority to the static gas hypothesis by providing a ready explanation of the repulsive forces, but in 1801 the implications of the theory had not yet been examined in detail. Unfortunately the cryptic nature of Dalton's account prevents us from knowing exactly how he tackled the problem of relating volume and temperature theoretically, but the following is a possible reconstruction of his argument.

Dalton naturally chose to consider the expansion of air at constant pressure between 55°F and 212°F, the range of his own experiments, and he would presumably have had to treat the process in two stages. In the first, the heating of the air at constant volume from 55°F to 212°F the total heat content would have increased from, say, Q_{55} to Q_{212}, while the inter-

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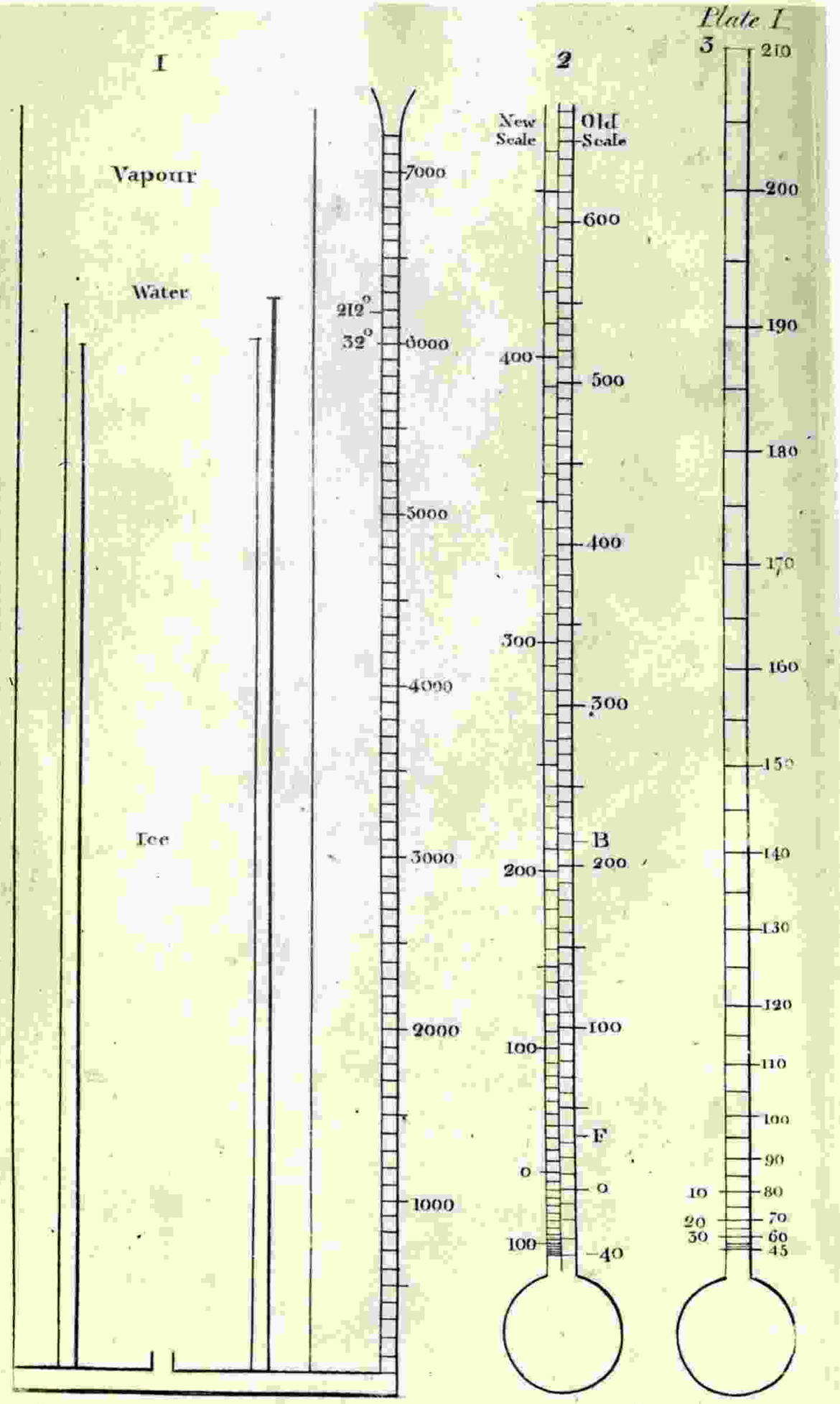
1. J. Dalton, A New System of Chemical Philosophy (Manchester, 1808), i (pt.1).

2. Crawford, Animal Heat (2nd edn.), p.379. See also J. Leslie, An Experimental Enquiry into the Nature and Propagation of Heat (London, 1804), p.529.

3. Newton, Principia, ed. F. Cajori (Cambridge, 1934), i. 300-302.



EXPLANATION OF THE PLATES.

PLATE I. Fig. 1. is intended to illustrate the author's ideas on the subject of the capacities of bodies for heat. See page 3. There are three cylindrical vessels placed one within another, having no communication but over their margins; the innermost is connected with a lateral and parallel tube graduated, and supposed to represent the degrees of a thermometer, the scale of which commences at absolute cold; if a liquid (supposed to represent heat) be poured into the tube, it will flow into the inner vessel, through an aperture at the bottom, and rise to the same level in the vessel and the tube. Equal increments of heat in this case are supposed to produce equal increments of temperature. When the temperature has arrived at a certain point (suppose 6000°) the body may be supposed to change its solid form to the liquid, as from ice to water, in which case its capacity for heat is increased, and is to be represented by the second vessel. A considerable portion of liquid must then be poured into the tube before any rise will be perceived, because it flows over the margin of the innermost vessel into the lateral cavity of the second; at length it reaches the level, and then a proportional rise will ensue, till the body becomes converted into an elastic fluid, when the thermometer again becomes stationary—whilst a great portion of heat is entering into the body; now assuming a new capacity.

Fig. 2. is a comparative view of the old and new divisions of the scale of the mercurial thermometer. See Table, page 14. The interval from freezing to boiling water is 180° on both scales, and the extremes are numbered 32° and 212° respectively. There are no other points of temperature in which the two scales can agree.

Fig. 3. is a view of the divisions of a water thermometer, conformably to the new scale of the mercurial; the lowest point is at 45°; the intervals from 45° upwards, to 55°, 65°, 75°, &c. are as the numbers 1, 4, 9, &c. Also, 30° and 60° coincide, as do 20° and 70°, &c.

PLATE II. Fig. 1. represents an air thermometer, or the expansion of air by heat; the numbers are Fahrenheit's, and the intervals are such as represented in the 7th column of the table, at page 14.

Fig. 2. is the logarithmic curve, the ordinates of which are erected at equal intervals, and diminish progressively by the ratio $\frac{1}{2}$. The intervals of the abscis or base of the

particle force, originally F_{55}, would have become F_{212}. Since Dalton assumed, explicitly though without justification, that this force was proportional to Q, it followed that $\frac{F_{212}}{F_{55}} = \frac{Q_{212}}{Q_{55}}$. His Irvinist views would now have allowed him to go one stage further, for he could argue that $\frac{Q_{212}}{Q_{55}}$ was in turn equal to $\frac{T_{212}}{T_{55}}$, the ratio of the absolute temperatures before and after the heating. In order to relate this ratio to the increase in volume which would have occurred if the air had been allowed to expand at constant pressure, it was necessary to consider a second process, the isothermal expansion of the air to the point where the pressure, and hence also P, fell to the values which they had before the heating. Dalton must have supposed, and here he was using Newton's result, that the force between the gas particles varied in inverse proportion to the distance d between them, so that $\frac{F_{212}}{F_{55}} = \frac{d_{212}}{d_{55}}$, where d^3_{55} and d^3_{212} were of course proportional to the volumes which the air would have occupied at 55°F and 212°F respectively had it been heated at constant pressure in a single process. It followed simply that $\frac{T_{212}}{T_{55}} = \frac{d_{212}}{d_{55}}$ and hence, on the assumption that the particles were spherical and of volume proportional to d^3, the insertion of Dalton's own experimental values for the expansion yielded an absolute zero at -1540°F. Dalton in fact made only an approximate calculation, obtaining a figure of -1515°F, which he declared was 'in more than fortuitous' agreement with Crawford's (app. -1500°F).[1] It should be noticed that even here he had not abandoned his belief in the correctness of the more traditional Irvinist

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1. Crawford, Op. cit., p.265.

method of determining the zero. Indeed by 1808, when he placed it at about -6000°F,[1] he relied solely on the latter method.

Although Dalton's argument provoked some discussion,[2] there is no evidence that it was anywhere accepted as correct. Even such an admirer of Dalton as Thomas Thomson, who discussed it fully, expressed serious reservations.[3] But, if its influence on the subsequent development of caloric theory was slight, the new relationship was of no small significance to Dalton himself. Above all, in predicting that gases expanded more rapidly at higher temperatures, it strengthened his conviction that the traditional mercury thermometer was inadequate, since his own experiments had shown an expansion of 167 parts in 1000 between 55°F and 133½°F but of only another 158 parts between the latter temperature and 212°F. His suspicions with regard to the mercury thermometer had apparently[4] been first aroused during his experiments on vapour pressure, the subject of the second of his four papers of October 1801.[5] He had noticed that for equal increments in temperature the pressures of all the vapours examined increased in an approximately geometrical progression, the same in all cases

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1. Dalton, Op. cit., 82-99.

2. 'Π', Nicholson's Journal, 27 iv (1803), 220-224; Dalton, Ibid., v (1803), 34-36; L. W. Gilbert, Gilb. Ann., xii (1803), 316-317 and Ibid., xiv (1803), 287-292.

3. See p.108.

4. According to Dalton, New System, i (pt.1), 10-11.

5. J. Dalton, 'On the force of steam...', Manchester Memoirs, v (pt.2) (1802), 550-574.

but with a ratio which, instead of being constant, diminished slightly with rising temperature as measured on the mercury thermometer. In 1808[1] Dalton recalled his immediate surprise at this approach to regularity and his concern to discover why the regularity was not perfect. His first thought had been to reject the traditional thermometer as inaccurate, but 'overawed by the authority of Crawford' he had hesitated. However, his subsequent work on gas expansion only confirmed his suspicions, for he now saw that if mercury could be shown to expand not uniformly, but more rapidly at higher temperatures, then either the deviation from a perfect geometrical progression might be removed or his cube root law of expansion might be vindicated. All this was only hinted at in 1801[2] and by 1808,[3] when he eventually tackled the problem, the situation had been changed and his rejection of the theoretical treatment of gas expansion. This step had almost certainly been taken not as a consequence of any doubts concerning the Irvinist or Newtonian principles on which he had based the treatment but because he had now perceived a possible analogy between the behaviour of heated gases and the variations in the pressure of a saturated vapour with temperature. To establish the analogy it was necessary to define a new temperature scale in which the expansion of mercury and water, and probably of all pure liquids, was taken as proportional to the square of the 'true' temperature measured from their respective freezing points. On this scale, Dalton maintained, both the

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1. Dalton, New System, i (pt.1), 10-11.

2. Dalton, Manchester Memoirs, v (pt.2) (1802), 601-602.

3. Dalton, New System, i (pt.1), 9-12. His new views appear to have been formulated by 1807 (see A. W. Thackray, Manchester Memoirs, cviii (1965-6), 39).

pressure of vapours and the volume of gases would increase in a geometrical progression (i.e. exponentially) with temperature, and this was evidently sufficient justification for the adoption of the new scale. In fact it probably remained so until after 1818, when Dulong and Petit's experiments on expansion[1] made his position untenable. Not until 1827 do we learn that Dalton had abandoned the campaign for the scale.[2]

Although Gay-Lussac differed essentially from Dalton in that he found volume to increase in an arithmetical progression with increasing temperature, there were certain consequences of their work on which both men were agreed. The new law of expansion, whether Dalton's or Gay-Lussac's, gave a unique status to gaseous matter and this comment made by Dalton in 1801 is typical of what was very quickly to become a commonplace[3] in treatments of caloric:

> This remarkable fact that all elastic fluids expand the same quantity in the same circumstances, plainly shews that the expansion depends solely upon heat: whereas the expansion in solid and liquid bodies seems to depend upon an adjustment of the two opposite forces of heat and chemical affinity, the one a constant force in the same temperature, the other a variable one, according to the nature of the body; hence the unequal expansion of such bodies.[4]

Here, as Dalton immediately saw, was the first evidence since Boyle's

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1. See pp.272-273.

2. Dalton, New System (Manchester, 1827), ii. 288-289.

3. See, for example, C. L. Berthollet, Essai de Statique Chimique (Paris, 1803), i. 161; R. J. Haüy, Traité...de Physique (2nd edn., Paris, 1806), i. 144; J. Playfair, Outlines of Natural Philosophy (Edinburgh, 1812), i. 233. For an even clearer, but later, exposition see P. S. Laplace, Connaissance des Tems...pour l'an 1825 (Paris, 1822), 386-387.

4. Dalton, Manchester Memoirs, v (pt.2) (1802), 600.

law of the essential simplicity of gases and the belief which he held about this time that the particles of all gases under the same conditions of temperature and pressure were equally spaced[1] was almost certainly a result of his discovery. In 1801, however, it was in the further investigation of caloric theory that the most exciting possibilities lay, although Dalton's comment was cautious:

> It seems.../he declared/ that general laws respecting the absolute quantity and the nature of heat, are more likely to be derived from elastic fluids than from other substances.[2]

The French were still more impressed by the fundamentality of behaviour which it appeared was to be associated with the gaseous state. Laplace, as we have seen, was quick to advocate the use of the air thermometer as a standard and when in 1806 Biot and Arago undertook a study of refraction it was on gases that they chose to work, citing as a principal reason for their choice the absence of inter-molecular forces in this state.[3] Nearly three years later the special status of gases was put beyond all doubt by Gay-Lussac's discovery that, when gases combine chemically, they do so by volumes which bear a simple numerical relationship to that of the product.[4] This simple behaviour Gay-Lussac too associated with the absence of inter-molecular forces of attraction. He wrote:

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1. Dalton, New System, i (pt.1), 168.

2. Dalton, Manchester Memoirs, v (pt.2) (1802), 600.

3. J. B. Biot and D. F. J. Arago, Mém. Inst. Fr., vii (1806), 301-302.

4. J. L. Gay-Lussac, 'Mémoire sur la combinaison des substances gazeuses', Mém. Soc. Arcueil, ii (1809), 207-234.

> L'attraction des molécules dans les solides et les liquides est donc la cause qui modifie leurs propriétés particulières, et il paroît que ce n'est que lorsque elle est entièrement détruite, comme dans les gaz, que les corps se trouvant placés dans des circonstances semblables, présentent des lois simples et régulières.[1]

The work of Dalton and Gay-Lussac on gas expansion must therefore be seen as more than the timely discovery of a new familiar law. For a calorist it had a far greater significance and one which we can hardly appreciate today. Yet it was only partially responsible for the period of intense activity in the study of the thermal properties of gases which followed and we turn now to the second of the two crucial events which served to direct attention to the special relevance of gases for the theory of heat.

Adiabatic Heating

If we except the brief references by Chaptal and Monge in 1790, the first mention of the adiabatic effect in the French literature dates from 1798, when J. C. Delamétherie, editor of the Journal de Physique, described a report communicated to him by Pictet of the cold observed on releasing air from a compression pump.[2] Delamétherie seems to have misinterpreted Pictet's suggestion that the effect could be made even more striking by placing a little water in the receiver and observing the formation of ice round the exit valve, for the explanation he offered was that

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1. Ibid., 208.

2. J. C. Delamétherie, 'Note sur un froid considérable...', J. Phys., xlvii (1798), 186.

the water was carried off by the escaping air in the form of a vapour and so required latent heat which it took from the rest of the water and in particular from the drops round the valve. We may be sure that the analogy with cooling by the evaporation of ether, mentioned by Delamétherie, was not suggested by Pictet. It may possibly have its origin in Chaptal's earlier mistaken interpretation.

Delamétherie's somewhat confused account could all too easily have been overlooked but Arsène Nicolas Baillet, an inspector of mines who also taught at the École des Mines, was quick to appreciate the true significance of Pictet's communication. In a paper to the Société Philomathique[1] and a letter to Delamétherie[2] he reported an analogous effect first observed in the mines of Schemnitz in Hungary[3] by Gabriel Jars of Lyons in 1758. Jars had noted that, when air compressed by a water column over forty metres high in Hoell's column-of-water engine was suddenly allowed to escape, compact ice was deposited on any object placed in the way of the issuing air. The phenomenon had already attracted considerable attention. It had been described, though not explained, in the Philosophical Transactions in 1762,[4] apparently quite independently of Jars, and, as we have seen,[5] Darwin had used it in 1787 as evidence that the rapid expan-

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1. A. F. Silvestre, Rapport Général des Travaux de la Société Philomathique ...depuis le 23 frimaire an VI jusqu'au 30 nivôse an VII (Paris, 1799), pp. 21-22.

2. A. N. Baillet, J. Phys., xlviii (1799), 166-167.

3. G. Jars, 'Description d'une nouvelle machine...', Mémoires...présentés à l'Académie Royale des Sciences par divers Savans, v (1768), 67-71.

4. N. M. Wolfe, 'Descriptio fontis Hieronis...', Phil. Trans., lii (1762), 547-554.

5. See p.57.

sion of air gave rise to cooling. Baillet, without reference to Darwin, similarly attributed the formation of ice to the cooling of the air, which through its contact with the water column was of course saturated with vapour. He maintained that the fall in temperature of the expanded air accorded well with the recent work of Crawford and Lavoisier but, since Lavoisier appears to have had no views on the matter,[1] he was presumably referring specifically to Crawford's conjecture that the capacity of a gas increased with rarefaction.

Even Baillet's comments did little to arouse interest and nearly three years passed before the subject was again referred to in the French journals, this time by J. M. Coupé[2] who, in 1801, attempted to account for some recent instances of several days of unusual cold or heat immediately preceding periods of, respectively, mild and cool weather, by reference to large-scale adiabatic effects. He suggested that when a cold, northerly air stream moved southwards it compressed and so expelled heat from the air in its path and that the mild weather caused by this heat gave way to cold when the northerly stream eventually forced its way past the impeding air. Coupé's was not in fact the first attempt to apply the adiabatic effect in meteorology,[3] but it nevertheless passed virtually unnoticed.[4]

Of course strange effects observed on mine pumps and large-scale

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1. Although see p.46.

2. J. M. Coupé, 'De la chaleur qui précède l'arrivée d'un vent froid...' J. Phys., liii (1801), 262-264.

3. See p.58.

4. Although he did not mention Coupé, Joseph Mollet was almost certainly referring to his work in the Mémoire sur deux faits nouveaux..., pp.23-24. (For full reference see p.97, n.2).

meteorological phenomena had little obvious connection with traditional physical problems. The numerous existing accounts in the British, Swiss and German literature, including now an important review article by the young German poet and novelist, Ludwig Achim von Arnim,[1] continued to be ignored by the French and it was only after Laplace's success in applying adiabatic phenomena to a really major problem that they accepted the heating produced by the compression of a gas as a fact to be reckoned with in the theory of heat. The material theory, as we shall see, responded impressively to the new challenge and what might have proved a serious threat only served to strengthen the position of caloric.

Laplace's success was to account for the error in Newton's expression for the velocity of sound. In the first edition of the Principia[2] Newton had demonstrated that the velocity in air was given by

$$v = \sqrt{\frac{P}{\rho}} \qquad \ldots\ldots(1)$$

where P represented the 'vis elastica' or pressure of the air and ρ its density. Calculation from this expression yielded 968 ft per sec for v, a figure lying well within the wide range of existing experimental values, which varied from roughly 600 ft per sec, as measured in a very crude fashion by Roberval,[3] to 1474 ft per sec, Mersenne's figure.[4] Moreover

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1. L. A. von Arnim, Gilb. Ann., ii (1799), 238-245.
2. Newton, Principia (London, 1687), pp.369-372.
3. M. Mersenne, Hallistica et Acontismologia (Paris, 1636), pp.83 and 140.
4. M. Mersenne, De l'Utilité de l'Harmonie (Paris, 1636), pp.44-46. (This work is part of the Harmonie Universelle).

it agreed with Newton's own simple observations made in the court of Trinity College, Cambridge, the results of which varied from 920 to 1085 ft per sec. In the second edition in 1713[1] Newton obtained 979 ft per sec from his original formula, the modification in the figure resulting from his use of a different value for the ratio between the densities of water and air. But new and more reliable experimental determinations of the velocity of sound had now been made and Newton was convinced that even his revised figure was too low. Corrections for the bulk of the air particles, which he had previously not taken into account, and for water vapour in the atmosphere led to a final value of 1142 ft per sec, in exact, and no doubt intentional, agreement with the figure reported by William Derham in 1708.[2] However, Newton's attempts to account for the discrepancy were far from satisfactory and the problem continued to attract leading mathematical physicists throughout the eighteenth century. Euler in 1727[3] calculated that the true figure lay between 1101 and 1259 ft per sec, depending on the temperature, but by 1759 he too recognized that the experimental value considerably exceeded the theoretical figure which he adopted at this time.[4] The discrepancy, he added, was unexplained. Lambert similarly rejected existing explanations and looked for the answer in the presence of heavy

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1. Newton, Principia (2nd edn., Cambridge, 1713), pp.342-344.

2. W. Derham, Phil. Trans., xxvi (1708), 2-35.

3. L. Euler, Dissertatio physica de sono (Basle, 1727), consulted in L. Euleri Opera Omnia (Leipzig & Berlin, 1926), series 3, vol. i. 182-196.

4. Ibid., 442-443 (in 'De la propagation du son', originally published in Hist. Acad. Sci. Berlin, xv (1759), 185-209).

foreign particles in the air which raised its density without contributing to its elasticity.[1] Lagrange, who obtained a theoretical figure of 975 ft per sec, would seem to have shared Lambert's view.[2] Despite the attentions of such men as these, as well as of the Bernoullis and d'Alembert,[3] the explanations offered carried little conviction and the problem was still wide open when Laplace turned to it, probably in 1802.

The first intimation of Laplace's solution was given in that year by Jean Baptiste Biot,[4] then a young professor of physics at the Collège de France. Laplace, it seems, had asked Biot to examine how the velocity was affected by the heat and cold which he supposed to occur in the successive regions of compression and rarefaction constituting the sound wave. The effect of the temperature variations was essentially to invalidate the assumption, which had hitherto been fundamental to all calculations, that during the passage of the sound the pressure of the air was everywhere proportional to its density. Biot made constant reference to Lagrange's earlier treatment, but we may summarize the argument as follows, eliminating the mathematical complexities.

Air pressure at any point was given by

$$P = gHn\rho$$

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1. J. H. Lambert, Hist. Acad. Sci. Berlin, xxiv (1768), 70-79.

2. J. L. Lagrange, Mécanique Analytique (Paris, 1788), 510-511.

3. For a summary of other work see C. A. Truesdell's introduction to Euler, Opera Omnia (Zurich, 1956), series 2, vol. xiii. pp.xix-lxxii.

4. J. B. Biot, 'Sur la théorie du son', J. Phys., lv (1802), 173-182.

where H was the reading on a mercury barometer, g the acceleration due to gravity, n the ratio of the density of mercury to that of air and the density of the air. The variations in density in the sound wave, if isothermal conditions were assumed to hold, could be expressed by

$$\rho' = \rho(1 + s)$$

where s was the (small) fractional change in density, taken as positive for compression, and ρ was the density of the undisturbed air. Biot supposed that the effect of the fractional compression s was to heat the air and so to increase the pressure by an additional factor (1 + ks), where k was a constant of proportionality. In fact a solution of this sort was not entirely novel, for Lagrange had already examined the implications of putting the pressure of air in a sound wave proportional to some power m of the density, i.e. $P \propto \rho^m$,[1] a correct expression, of course, for adiabatic volume changes. Lagrange even calculated that m should be 1½, if the experimental and theoretical velocities were to agree and his value for m (γ in modern notation) was thus very close to the present accepted value. How such an appreciable deviation from Boyle's law could have escaped detection was a difficulty which Lagrange, ignorant of adiabatic phenomena, naturally could not answer. Unfortunately Biot did not adopt Lagrange's expression, but his own expression for the pressure of a gas undergoing adiabatic volume changes, $P' = g\delta n \rho (1 + s)(1 + ks)$, was a good approximation provided s was small. From it, neglecting terms in s^2, Biot obtained

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1. J. L. Lagrange, Mélanges de Philosophie et de Mathématique de la Société Royale de Turin, ii (1760-1), 152-154.

$$v = \sqrt{g\Pi n\ (1 + k)},$$

which reduces to the more familiar $v = \sqrt{\gamma \frac{P}{\rho}}$ if we substitute our term γ for Biot's constant (1 + k). The effect of Newton's error in assuming the compressions and rarefactions to take place isothermally had thus been to put k = 0. Under these conditions the velocity became $\sqrt{g\Pi n}$, the quantity which Lagrange had calculated as 975 ft per sec. An independent determination of k, which confirmation of his treatment required, was unavailable and Biot tried instead to use the data relating to the expansion of gases by heat, in a strikingly naive fashion. First, he assumed, quite erroneously, that the heat evolved in the adiabatic compression of a gas was equal to that which was released by the gas in a similar contraction while cooling at constant pressure. Thus, to use modern notation, he supposed that a unit mass of gas, on being compressed by, say, 1/266 of its initial volume, would give out c_p units of heat. Now Gay-Lussac's experiments had shown that an increase in temperature of 80 deg R would cause a gas to expand by 0.35 of its volume at 0°R, so that Biot, disregarding any distinction between c_p and c_v, could argue that a compression of $\frac{0.35}{80}$ would raise the temperature of the gas by 1 deg R. Showing a misplaced confidence in the results of Amontons, Biot now declared that such a temperature change would effect a fractional increase of 1/240 in the pressure of the gas and he equated this increase to $k.\frac{0.35}{80}$, i.e. to ks, to obtain 0.95 for k and a value for v considerably greater than the currently accepted experimental value. That the inequality of the coefficients of Gay-Lussac and Amontons implied the rejection of Boyle's law seems, surprisingly, to have escaped him. A far more accurate result was obtained by equating

$\sqrt{gHn(1 + k)}$ to 1107 ft per sec, the velocity determined experimentally for the Académie des Sciences in 1738 by a group of workers under Cassini de Thury.[1] The appropriate value for k was 0.2869. If the velocity of 1151 ft per sec determined by Cassini, Picard and Roëmer in 1677[2] was used, k became 0.3922, still closer, albeit fortuitously, to the correct value of 0.4031. It is interesting to note that, since Lagrange was using a figure for the ratio of the density of mercury to that of air which was too big, the use of the correct velocity would have yielded an even worse value for k. The discrepancy between the values deduced from the laws of gas expansion and by comparison with the experimentally determined velocities aroused no specific doubts concerning the assumptions made in the former method, and Biot, while admitting that there might be errors in the basic hypotheses, suggested that some of the heat evolved in the regions of compression was emitted as radiation without raising the temperature of the air and so did not affect the velocity.

Despite these difficulties, there could now be few who doubted that small temperature changes did occur in sound waves. And five years later Biot provided further striking evidence by his demonstration that sound was transmitted through various saturated vapours.[3] The experiment was a decisive one since, unless heat were liberated in the regions of compression,

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1. Cassini de Thury, Mém. Acad. Sci., (1738), 135.

2. J. B. du Hamel, Regiae Scientarum Academiae Historia (Paris, 1698), p.158.

3. J. B. Biot, Mém. Soc. Arcueil, 11 (1809), 94-103.

liquefaction would take place and hence the passage of sound would be prevented.

Biot's paper of 1802 was more than a spectacular beginning to the study of adiabatic phenomena in France. It provided also a convincing intimation that earlier authorities had seriously underestimated the magnitude of the effect, for, on the false but plausible assumption that the rise in temperature was proportional to the degree of compression, Biot concluded that reduction in volume by half would raise the temperature of the air by either 86 deg C (for k = 0.2869) or 118 deg C (for k = 0.3922). For many years Biot's remained the most acceptable method of determining the true temperature changes, although it was Siméon Denis Poisson's figure, given in 1807,[1] which became standard in the literature, being used by Sadi Carnot,[2] for example, and by both pairs of competitors in the Institute's prize competition of 1812.[3] Poisson's treatment was essentially that of Biot, though with the refinement that account was taken of the effect of air temperature on velocity. Poisson also differed in using a lower value for the ratio between the densities of mercury and air and he concluded that, if the theoretical and experimental velocities were to agree, k must be 0.4254. By assuming, like Biot, that the temperature change was proportional to the degree of compression, though limiting his assumption to cases where the compression was small, Poisson

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1. S. D. Poisson, J. Éc. polytech., vii (1808), 319-392.

2. S. Carnot, Réflexions sur la Puissance Motrice du Feu (Paris, 1824; Blanchard reprint, 1953), pp.43-54 and 79-81.

3. See pp.153 and 158.

deduced that a sudden decrease or increase in volume of 1/116 would raise or lower the temperature by 1 deg C.

When Biot wrote he would have been unaware that an attempt to obtain the direct experimental evidence for the magnitude of adiabatic heating which he sought had already been made by John Dalton. Although Dalton's paper was read to the Manchester Literary and Philosophical Society in June 1800,[1] it was not published in England until 1802 and notice of it appeared in France only in January 1803.[2] Dalton correctly interpreted the rapidity with which the temperature variations occurred on evacuating and filling an air pump receiver as indicating that the true temperature variations were far greater than those observed on a thermometer but were simply obscured by heat losses to the surroundings and to the thermometer itself. Perhaps the most conclusive evidence he obtained to demonstrate this was that a thermometer with a large heat capacity indicated considerably less variation than a smaller instrument in the same circumstances. To measure the true temperature changes he used two quite separate methods. In the first he noted that the maximum rate at which a small thermometer suspended in an evacuated receiver rose when air was suddenly admitted was 1 deg F in 3½ sec. He then showed that a similar rate of fall of temperature was obtained when the temperature of the thermometer was 50 deg F above that of the surrounding air and hence con-

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1. J. Dalton, 'Experiments and observations on the heat and cold produced by the mechanical condensation and rarefaction of air', Manchester Memoirs, v (pt.2) (1802), 515-526.

2. Ann. Chim., (1803), 103-107 and J. Mines, xiii (1803), 257-267.

cluded, presumably on the basis of Newton's law of cooling, that the temperature of the air surrounding it in the first case was 50 deg F above that of the thermometer when the mercury was rising most rapidly. His second method was far more satisfactory and is of particular interest as a possible precursor of the familiar method of Clément and Desormes for determining γ. The respect which Clément and Desormes were to accord Dalton's work[1] supports this view of their debt to him, although Dalton was using an observation which, if we are to believe Baillet and Hauy,[2] was already a familiar one in laboratories but which had not been satisfactorily explained. A capillary tube sealed at one end and containing a short mercury thread, was placed in a receiver. The air in the receiver was compressed to a pressure of two atmospheres, so that the length of the short air column trapped by the thread was halved. The air was then allowed to escape rapidly from the receiver until the thread regained its original position, whereupon the tap was quickly closed. It was observed that, on standing, the length of the enclosed column of air decreased by one tenth, although it was restored to its original length when the tap was re-opened. An analogous effect occurred when air was admitted to a receiver evacuated to one quarter of atmospheric pressure, although in this case the length of the air column increased by slightly more than 1/10 after the tap was first closed. Dalton's explanation of this was a

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1. Clément and Desormes, J. Phys., lxxxix (1819), 323 and 324.

2. A. N. Baillet, J. Mines, xiii (1803), 267; Hauy, Traité (2nd edn.), i. 139-140.

somewhat confused version of the truth, which was that the tap had been closed while the pressure of the air had been temporarily increased by heat. Thus, although the pressure fell below atmospheric once temperature equilibrium had been restored, it had been sufficient to restore the mercury thread to its original position when the air was heated. Since his own experiments on gas expansion indicated that a temperature increment of about 50 deg F was necessary to raise the pressure by one tenth, Dalton naturally saw the estimate of the temperature changes obtained by his first method as being confirmed.

Dalton's experimental examination of the subject, although thorough so far as it went, was restricted to work on an evacuated receiver and the explanation which he adopted was coloured accordingly. It was an interesting union of Crawford's views on capacity with Lambert's concept of a vacuum able to contain heat. Dalton, who accepted Crawford's explanations of heat of reaction and latent heat, was in little doubt that changes in the volume specific heat of air with compression and rarefaction accounted for the thermal effects. The heat produced by the rapid entry of air into a vacuum, he could argue, arose merely from the replacement of the void, which had the greatest[1] volume capacity of all, by air, with a lesser capacity. Although Dalton's conviction that his work might lead to a method of determining the capacities both of the void and of various

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1. On p.526 of the version of his paper which appeared in the Manchester Memoirs the capacity of the vacuum is erroneously stated to be less than that of an equal volume of air.

gases was to provide the starting point for Clément and Desormes, he unfortunately never pursued the matter himself.

Dalton's explanation was soon effectively attacked,[1] but the competence of his experimental investigation was generally recognized and, if only because it was so widely reprinted and translated,[2] the paper did much to stimulate interest at about the same time that Biot's announcement was made. Moreover, in experiments designed for the purpose Dalton dispelled the persistent myths that distortion of the thermometer bulb or evaporation might account for the observed effects. That such confirmation of the true nature of the phenomena was still required is evident from Baillet's comments on the summary of Dalton's paper which appeared in the Journal des Mines,[3] for, while Baillet himself accepted an explanation in terms of the increasing capacity of air with rarefaction, he felt obliged explicitly to reject the view of 'some teachers' that the distension and contraction of the receiver was the cause. Also, somewhat earlier, Alexander Tilloch had referred to an opinion that the heat observed on compressing air in a cylinder arose from the friction of the piston against the cylinder wall.[4]

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1. See pp.139 and 163.

2. To the references given in the Royal Society's Catalogue of Scientific Papers, 1800-1863 the following should be added: Nicholson's Journal, iii (1802), 160-166; Bull. Soc. Phil., (1803), 163-164; Repertory of Arts and Manufactures, [2] ii (1803), 118-125.

3. Baillet, J. Mines, xiii (1803), 268.

4. A. Tilloch, Phil. Mag., viii (1800), 213.

If further evidence was needed both for the genuineness and the true magnitude of the effect, it was soon provided in a series of striking discoveries. On 29 December 1802 the French Institute heard a letter from Joseph Mollet, professor of physics at the École Centrale in Lyons, describing a light which accompanied the discharge of an air gun in the dark and the ignition by the rapid compression of air of a small piece of linen fixed in the exit tube of a condensing pump.[1] Both observations had been first made by chance by a workman at the armoury in Saint-Étienne earlier in that year. Pictet's brief report in Tilloch's Philosophical Magazine[2] quickly caught the attention of William Nicholson, who in April 1803 inserted a note in his own journal claiming that the effect with the air gun had already been observed, about eighteen months previously, by a Mr. Fletcher, at a weekly meeting 'for philosophical experiments and conversations' held at Nicholson's house.[3] In Paris Mollet's communication seems to have been more sceptically received and the referees[4] appointed by the Institute were unable to reproduce his observations. Undeterred, Mollet continued his experiments in collaboration with Ennemond Eynard, a doctor and member of the science section of the Lyons Academy, and with two other

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1. For accounts of the events described here see J. B. Dumas, Histoire de l'Académie Royale des Sciences, Belles-Lettres et Arts de Lyon (Lyons, 1839), 232-242 and J. Mollet, Mémoire sur deux faits nouveaux... (Lyons, 1811), pp.3-8.

2. M. A. Pictet, Phil. Mag., xiv (1803), 363-364.

3. W. Nicholson, Nicholson's Journal, [2] iv (1803), 280.

4. Presumably J. A. C. Charles and L. Lefèvre-Gineau. See Proc. Verb., ii. 606 (8 nivôse an XI).

friends, Haex and Gensoul. In fact it was these three colleagues of Mollet who first heard of the workman's observations at Saint-Étienne. Although he never managed to produce the flash associated with the discharge of the air gun satisfactorily, Mollet now discovered that a similar flash occurred when air was compressed in a cylinder by means of a closely fitting piston. This new observation and the now well established ignition of an inflammable material such as tinder by the same method he described first to the Institute in November 1803[1] and then to the Lyons Academy in January and March 1804.[2] This time the Institute's referees, Charles and Fourcroy, reported favourably and in May 1804 they even performed Mollet's experiments before their colleagues.[3] In Lyons there was still some scepticism, but Mollet appears to have successfully answered suggestions that the cause of the ignition was not the rise in temperature of the air and to have systematically refuted the alternative explanations which were proposed. Having established, to his own satisfaction at least, that air was in fact heated by compression, Mollet gave his explanation on the basis of caloric theory, to which he was unreservedly committed, even though he avoided the actual word 'calorique'. He distinguished clearly between latent and free heat, both of which he supposed to exist in gases, but he attributed the rise in temperature on compression not to the change

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1. Proc. Verb., iii. 28 (6 frimaire an XII).

2. J. Mollet, Mémoire sur deux faits nouveaux, l'inflammation des matières combustibles, et l'apparition d'une vive lumière, obtenues par la seule compression de l'air (Lyons, 1811). Read on 27 Mar. 1804.

3. Proc. Verb., iii. 95-96 (17 floréal an XII).

of some heat from the latent to the free state, as several later caloriste were to do, but to the expulsion of a certain amount of free heat.

One historian of the Lyons Academy, J. B. Dumas, was to hail Mollet's discoveries as some of the greatest contributions ever made to science by the Academy[1] and, while we should not be deceived by Dumas's excessive enthusiasm and by his resentment against those Parisian scientists who, he thought, had tried to steal credit for the work, there can be no doubt that the academicians of Lyons were by far the most important figures in the early experimental study of adiabatic phenomena in France. One further debt which the nineteenth-century world owed to Lyons was for the domestic fire-making device known as the fire-piston, or 'briquet pneumatique', in which the ignition of tinder in a closed cylinder was put to practical use. Henry Balfour, in his account of the origins of the fire-piston,[2] inclined to the view that the widespread use of the instrument by natives in certain parts of South-East Asia during the nineteenth century might indicate a completely independent discovery in that region. But since there is no conclusive evidence to rule out the possibility of its having been introduced from the West, Mollet and his colleagues must retain priority for the discovery. Mollet had first suggested that the piston and cylinder might possibly be used for fire making in March 1804[3] but it is not until February

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1. Dumas, Op.cit.

2. H. Balfour, 'The fire-piston', in Anthropological Essays presented to Edward Burnett Tylor (Oxford, 1907).

3. Mollet, Op. cit., p.13.

Fire-pistons

1. Brass model of fire-piston (length 5¾ inches) made c.1834 in France. This instrument is unusual in that the compressed air escapes through a number of small holes before encountering the tinder. On this type see the Lenny Museum, III (1834), 264-5.

2. Fire-piston with piston of steel (brass head) and cylinder of brass (length 4¼ inches); bought in Scotland.

3. Fire-piston with piston of steel (brass head) and cylinder of brass; English. Length 3 inches.

4. Brass fire-piston, possibly English. Length 2¾ inches.

5. French fire-piston (length 3 inches) of a type re-introduced c.1830.

(The lengths given are those of the cylinders only)

The instruments numbered 1, 2 and 3 are items 1,20, 1,31 and 1,30 in the Bryant and May collection of fire-making appliances in the Science Museum, London. Instruments 4 and 5 are in the Pitt Rivers Museum, Oxford. The illustrations appear by courtesy of the curators of the museums concerned.





PLATE 2

1806 that we find any evidence of the commercial manufacture of the instrument. The Journal de Physique for that month[1] contained a brief announcement that the instrument maker Dumotiez of Paris was producing the fire-piston in various sizes and designs. That Dumotiez was the manufacturer is hardly surprising when we note that it was in his workshop exactly two years earlier that tinder was first successfully ignited in Paris by the compression of air.[2] Another early manufacturer was Dubois, a Lyons founder, who patented a design based on a prototype which Lynard constructed and demonstrated publicly in August 1806.[3] According to Mollet, writing in 1811,[4] Dubois's instruments had the advantage over Dumotiez's that the tinder was contained in a small cavity at the end of the piston. After a single sharp stroke the piston was quickly withdrawn and the tinder, now glowing, could be easily applied. In Dumotiez's instruments, as in Mollet's early designs,[5] the tinder was contained in the end of the cylinder which therefore had to be rapidly unscrewed before a light was obtained. This type of fire-piston must have been similar to one patented in London by Richard Lorentz in February 1807,[6] and the 'foreigners residing abroad' who communicated the invention to him may well have been connected

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1. 'Briquet pneumatique par Dumotiez', J. Phys., lxii (1806), 189.
2. Mollet, Op. cit., p.3.
3. Dumas, Op. cit., p.236.
4. Mollet, Op. cit., pp.30-31.
5. Dumas, Op. cit., p.233.
6. Patent specification no. 3007 (1807) at the Patent Office, London.

with Dunotiez. In Lorentz's version the only difference was that the compressed air passed through a narrow aperture before meeting the tinder. Only one surviving example of a fire-piston constructed on this principle is known (see Plate 2, item 1) and all the others which still exist have the tinder cavity at the end of the piston. The fact that Dunotiez's instruments became especially well known, even by 1811,[1] suggests, despite Mollet's account, that Dunotiez had already adopted Dubois's superior design by that date. The fire-piston was mentioned frequently in the first thirty years of the century and Davy, Sadi Carnot and Berzelius[2] are just three of the many writers who referred to it in terms which imply considerable familiarity. Yet, despite a brief resumption of manufacture in France about 1900,[3] the fire-piston seems to have been too inconvenient and unreliable ever to have seriously threatened the conventional tinder-box and it was rapidly replaced by the friction match after 1830.

The knowledge that tinder could be ignited by compression alone no doubt provided the stimulus for a perilous, though successful, attempt to form water from a suitable mixture of oxygen and hydrogen by this method. Who actually performed this experiment is in some doubt. The anonymous author of the article 'Compression' which appeared in 1814 in the Encyclopédie

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1. J. F. Dessaignes, J. Phys., lxxiii (1811), 50.

2. H. Davy, Elements of Chemical Philosophy (London, 1812), p.90; Carnot, Réflexions, p.50n; J. J. Berzelius, Traité de Chimie, tr. ... J. L. Jourdan (Paris, 1829), i. 91.

3. See Plate 2, item 5.

Méthodique (Physique)[1] states that it was done in the École Polytechnique by J. H. Hassenfratz at the instigation of Laplace, but that Biot, who had been present, described it to the Institute as if it were his own work. The existing accounts[2] certainly convey the impression that Biot did in fact perform the experiment and that Hassenfratz was little more than an assistant, so that, if the author of the article in the Encyclopédie Méthodique is to be believed, Hassenfratz was the victim of a successful piece of deception.[3] According to Biot, the gases were contained in the chamber of an air gun and a single stroke of the piston sufficed to effect a combination accompanied by a violent explosion. A further explosion, which shattered the chamber, provided sufficient warning of the danger for the experiments to be abandoned. The results of further experiments by Hassenfratz, which were not mentioned by Biot, and in which Hassenfratz believed he had formed nitrogen dioxide and ammonia gas, were apparently too unreliable to be published, but in a letter to Nicholson's Journal dated 17 December 1805[4] Thomas Northmore of London described how he had produced a number of different compound gases by merely compressing their constituent elements. The experiments had been conducted with the aid of the 'late chemical operator' of the Royal Institution, but nothing more

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1. Enc. Méth. (Physique), ii. 507. The author may well have been Hassenfratz himself.

2. The fullest is J. B. Biot, Ann. Chim., liii (1805), 321-327.

3. For a similar incident involving Biot and Arago see Arago, Oeuvres Complètes (1st edn., Paris, 1859), xi. 702-703.

4. T. Northmore, Nicholson's Journal, [2] xii (1805), 368-374.

is known of them.

We have so far said little about Mollet's other observation, that light was emitted in the compression of air. The effect was to attract considerable attention before Thenard finally showed it to be spurious in 1830.[1] Biot was one writer who was quick to see the production of light as important. In 1803 Berthollet suggested that the function of the electric spark in effecting the combination of gases in a eudiometer was essentially to compress, and consequently to heat, the gas in the vicinity of the spark to the point where a reaction occurred.[2] Writing late in 1804, when he knew of Mollet's observations, Biot went so far as to suggest that the light of the spark arose from the rapid compression of the adjacent gas.[3] Since Biot's own experiments had failed to show that light was evolved by compression, his extreme reserve in making the suggestion was more than justified.

Mollet's observation soon became involved in another, even more fundamental problem, namely the possible identity of caloric and light. The most influential exponent of the view that the two fluids were essentially identical appears to have been Monge, who presumably expressed his opinions on the matter in the unpublished article on caloric which he wrote in 1782 for the Encyclopédie Méthodique.[4] Although most of the

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1. L. J. Thenard, Ann. Chim. Phys., xliv (1830), 181-188.

2. Berthollet, Statique Chimique, i. 307.

3. Biot, Op. cit. On the dating of Biot's work see the brief account in Bull. Soc. Phil., (1804), 259.

4. See pp.44-45.

article was soon lost, its contents were familiar to many of Monge's contemporaries. Fourcroy, Berthollet and Biot,[1] for example, were among those who took his view seriously. The discovery that light as well as caloric was emitted in the compression of gases might have been expected to strengthen Monge's case, as Mollet pointed out,[2] but owing largely to Jean Antoine Saissy, a doctor from Lyons, it was the contrary opinion which gained ground. In 1811 J. P. Dessaignes of Vendôme announced that he had produced light by compressing oxygen, nitrogen and hydrogen in the course of his work on phosphorescence,[3] the subject for which, two years earlier, he had won the Institute's prize for physics.[4] He was satisfied that the effect was not one of phosphorescence and that it arose from the expulsion of caloric by the compression of gas molecules. By 1813,[5] moreover, he was convinced that light was produced when air entered a vacuum. In a paper presented to the Lyons Academy[6] Saissy disputed Dessaignes's evidence, claiming that light was only observed in gases which contained oxygen. Thus it occurred most readily in pure oxygen, rather less so in air and hydrogen chloride (which, like all acids on Lavoisier's theory of

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1. A. P. Fourcroy, Système de Connaissances Chimiques (Paris, 1802), i. 131-134; Berthollet, Op. cit., i. 191-205; Biot, Traité, iv. 600-617.

2. Mollet, Mémoire sur deux faits nouveaux..., pp.27-28.

3. Dessaignes, J. Phys., lxxiii (1811), 50-51.

4. Dessaignes, J. Phys., lxviii (1809), 444-467 and lxix (1809), 5-35.

5. Proc. Verb., v. 250 (4 Oct. 1813).

6. Dumas, Hist. Acad. Lyon, pp.237-239 and J. L. N. F. Cuvier, 'Histoire de la Classe...Partie physique', p.lxxxviii in Mém. Inst. Fr., xiii (1812).

of acidity, was thought to be a compound of oxygen), and not at all in nitrogen or hydrogen for example. Saissy's results were confirmed by experiments conducted in Berthollet's laboratory[1] and by Mollet, Aynard and two other referees appointed by the Lyons Academy. Although, in reporting, Mollet was clearly reluctant to abandon the view that the emission of caloric was the cause,[2] he accepted as highly likely Saissy's suggestion that the 'base' of oxygen was a combination of light with some unknown ponderable substance but that light was a constituent of no other gas. Since there was no doubt that caloric, on the other hand, existed in all gases, this was strong evidence for the dissimilarity of the two imponderables, as Georges Cuvier pointed out.[3] It is worth noting that Saissy's view was not unlike an early opinion of Humphry Davy, who had supposed oxygen gas to be the base oxygen combined with light,[4] but it seems unlikely that Saissy would have read the obscure journal in which Davy wrote.

A striking characteristic of these early discussions of adiabatic phenomena is the absence of any attempt to interpret them in terms of a vibrational theory. In fact, far from supporting the evidence which Count Rumford had so recently obtained with solids,[5] the new discoveries, by virtue of the ease with which they could be accommodated on the assumption

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1. Thenard, Op. cit., 182.
2. J. Mollet, J. Phys., xc (1820), 114-115.
3. Cuvier, Op. cit.
4. Collected works of Davy (London, 1839), ii. 36-49. See also p.121, n.1.
5. Rumford, Phil. Trans., (1798), 80-102.

of the materiality of heat, merely strengthened caloric theory. The production of heat by the percussion of solids had generally been explained by supposing that a slight decrease in volume reduced the solid's capacity (taken in its loosest sense of ability to hold caloric), so that heat was expelled. That compression must diminish capacity in this sense seemed all too obvious to calorists, although the actual experimental evidence was slender, amounting to no more than Thomas Wedgwood's observation that the specific heat of the clay used in his father's celebrated pyrometer fell by one third when its volume was halved by strong heating.[1] And this, in any case, would have been significant only to an Irvinist. Even so, the explanation resisted Rumford's attacks, despite the latter's experimental demonstration, made with Irvinists obviously in mind, that the specific heat of the shavings from his bored canon was not smaller than that of the unbored metal. The growing familiarity of adiabatic phenomena, which intimately related decrease in volume with the production of heat, can only have made his task more difficult. In 1792 Wedgwood[2] had followed De Luc and Darwin in comparing the heating effects obtained on striking solids and on compressing gases and soon after 1800 the analogy had become a commonplace.[3] How compression accounted for the heat evolved in friction,

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1. T. Wedgwood, Phil. Trans., (1792), 280.

2. Ibid.

3. See, for example, Cavallo, Natural Philosophy, iii. 97; Leslie, Heat, pp.167-168; Dalton, New System, i (pt.1), 97; Berthollet, Statique Chimique, i. 165; Mollet, Mémoire sur deux faits nouveaux..., p.15; Bailly, Traité (2nd edn.), i. 141-142; Thenard, Traité (1st edn.), i. 81-82.

which was accompanied by no obvious decrease in volume, was a problem which concerned some caloricts,[1] but most avoided it either by obscuring the distinction between percussion and friction or, like Dalton,[2] by explicitly denying it.

Caloric theory thus withstood a shock which, as it might seem to observers familiar with the inter-convertibility of heat and work, could perhaps have proved fatal. The theory was in fact never in danger from the wealth of new evidence. In the very early years of the century it was still in the process of development, still growing, and hence flexible enough to allow an easy process of assimilation. But the situation in which the heats of percussion or compression could be satisfactorily explained by some vague analogy with the expulsion of water from a sponge did not last long. The two advances in the study of gases and heat which we have examined in this chapter soon stimulated new experimental and theoretical work and it was this new work, far more careful and rigorous than anything that had gone before, which allowed caloric theory to develop still further and eventually to reach its most sophisticated form during the mid-1820s in Laplace's caloric theory of gases.

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1. e.g. Thomson in Enc. Brit. (3rd edn.), supplement, i. 277-279 and Chemistry (1st edn.), i. 361-368; J. Murray, Elements of Chemistry (Edinburgh, 1801), i. 164-165 and A System of Chemistry (1st edn., Edinburgh, 1806), i. 434-439 & (2nd edn., Edinburgh, 1809), i. 423-428.

2. Dalton, Op. cit., 97.

CHAPTER 3

The Rival Caloric Theories

Theories of Heat in Britain

Irvine's views on heat continued to exert a powerful influence in Britain after 1800. As we might expect, they were generally interpreted in terms of caloric theory, since, for most chemists at least, the existence of caloric was still axiomatic and only the details of its behaviour remained to be worked out. Among chemists, it seems, the work of Rumford, Davy and Thomas Young, all of whom seriously questioned the materiality of heat about the turn of the century, had remarkably little effect. But even among caloristes Irvine's views had their opponents, most of them men who claimed that they were following Joseph Black. The miscellaneous writer Robert Heron, writing in 1800, was one who did not actually mention Black, but he argued vigorously for the existence of caloric in two states, the 'free' and the 'combined'.[1] A still more notable critic of Irvine was Thomas Thomson, a convinced calorist in the early years of the century.[2] Thomson strongly supported Black's claim that Irvine had not adequately explained changes of state, maintaining that it was the quasi-chemical combination of caloric with a solid or liquid which brought about fluidity

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1. Heron, Chemistry, pp.71-78.

2. Thomson, Chemistry (1st edn., 1802), i. 259. Cf. his less confident statement in Enc. Brit. (3rd edn., 1801), supplement, i. 250.

or vaporization accompanied by a consequent change in specific heat.[1] Moreover, the fact that some caloric thus existed in a latent state in bodies naturally invalidated Irvine's method for determining the absolute zero of temperature.

> Dr. Irvine's theorem, /Thomson declared in 1801/ therefore, is insufficient for ascertaining the real zero; and hitherto no method has been discovered which can solve this problem. We are therefore entirely ignorant of the quantity of caloric which exists in bodies.[2]

This was not to say, of course, that he had no interest in the problem and in 1804 he commented that the most promising attempt so far had been Dalton's deduction from his law of gas expansion, although he added that such a method yielded a measure only of that caloric which contributed to the inter-particle repulsion in the gas state and so threw no light on the caloric which remained even if the gas were liquefied.[3]

Like Thomson, William Henry of Manchester had attended Black's lectures on chemistry at Edinburgh in the 1790s.[4] He was a good friend of Dalton but, although they had at least one common interest, in the solubility of gases,[5] they were opposed on the subject of heat. The most

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1. Enc. Brit. (3rd edn.), supplement, i. 269 and Thomson, Chemistry (1st edn.), i. 326-328.

2. Enc. Brit. (3rd edn.), supplement, i. 271 and Thomson, Chemistry, i. 337.

3. Thomson, Chemistry (2nd edn.), i. 400-404.

4. D. N. B., art. Henry.

5. See W. Henry, Phil. Trans., xciii (1803), 33 and Nicholson's Journal, /27 viii (1804), 297-301.

detailed account of Henry's views appeared in a paper which he read to the Manchester Literary and Philosophical Society in June 1801.[1] The real motive for the paper was to answer the criticisms recently made by Rumford and Davy, but Henry made it quite clear that it was not caloric theory in general but Black's version only that he was defending.[2] In fact Henry went still further than Black since he supposed that the caloric which existed in a latent form in bodies and brought about changes of state was in a truly chemical combination and had a characteristic affinity, exactly like ordinary ponderable matter. Irvine, he maintained, had merely indicated the point of total privation of uncombined caloric.[3]

John Murray and John Leslie, both of whom taught for considerable periods at Edinburgh, were more conventional Irvinists. In 1804 Leslie was particularly vigorous in rejecting the view that some latent caloric existed in a state of combination in bodies[4] and both men expressed approval for at least the principles of Irvine's method for the determination of the absolute zero,[5] Leslie placing it at -1320°F, Murray at about -1500°F

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1. W. Henry, 'A review of some experiments which have been supposed to disprove the materiality of heat', Manchester Memoirs, v (pt.2) (1802), 603-621.

2. See also Henry's An Epitome of Chemistry (London, 1801), pp.7-13.

3. Henry, Manchester Memoirs, v (pt.2) (1802), 612-613.

4. Leslie, Heat, p.532. See also his Preliminary Dissertation in Enc. Brit. (7th edn., Edinburgh, 1842), i. 644-646. On Murray see Murray, Elements (1801), i. 143-152; System (1st edn., 1806), i. 406-412 and 'Notes' pp.66-72 and (2nd edn., 1809), i. 396-402 and 658-663.

5. Leslie, Heat, pp.170 and 532-533. In the 1842 Encyclopaedia Britannica article he had modified the figure to -1500°F. Murray, Elements, i. 155-156; System (1st edn.), i. 386-423 and 'Notes' pp.66-106, and (2nd edn.), i. 377-413 and 658-694.

or rather higher. They were quite satisfied that a sudden change in capacity adequately explained the absorption of heat on melting and vaporization and they argued against Black's opinion on this point with a thoroughness which emphasizes the importance of the dispute over the state of caloric in bodies during the first decade of the nineteenth century.

The easy assimilation of the adiabatic phenomena by the caloric theory continued after 1800, thanks not only to the great calorists such as Dalton and Laplace but also to lesser authorities whose influence was chiefly felt through their text-books. Murray's treatment[1] was typically Irvinist, with changes in capacity proposed as the cause of the effects. Indeed, he even adopted Dalton's explanation of the evacuated receiver experiment, although wrongly attributing it to Crawford. Thomson, as we should expect, rejected such explanations, although he accepted that variations in capacity did accompany volume changes.[2] Instead he presented this simple mechanical picture, which could also be applied to account for the heat produced in the percussion of a solid:

> When the particles of a body are forced nearer each other, the repulsive power of the caloric combined with them is increased, and consequently a part of it will be apt to fly off.[3]

Leslie's explanation was similar to Murray's, for, although he criticized the term 'capacity' as misleading,[4] it is difficult to see how his 'specific

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1. Murray, System (1st edn.), i. 366-369.

2. Enc. Brit. (3rd edn.), supplement, i. 277-278 and Thomson, Chemistry (1st edn.), i. 361-362.

3. Enc. Brit. (3rd edn.), supplement, i. 278 and Thomson, Chemistry (1st edn), i. 362.

4. Leslie, Heat, pp.529-530.

attraction', which was the property that determined the quantity of heat in a body, differed essentially from the more familiar expression. Since it was a change in this attraction which occasioned the emission and absorption of heat in both adiabatic phenomena and changes of state, Leslie's treatment showed little originality. In his interpretation of the evacuated receiver experiments,[1] however, Leslie put forward an unusual view, although even here the extent of his originality is open to doubt, since in attributing the heating solely to the compression by the incoming gas of the small quantity of gas which remained in even the best obtainable vacuum he was merely repeating an explanation proposed by Cleghorn in 1779.[2] Whether or not he had read Cleghorn is unclear, but the possibility that he had done so must remain, especially in view of a marked reluctance on his part to acknowledge other authorities.[3] His attempt to apply the explanation to the determination of specific heats, on the other hand, certainly was original.[4] He argued that, if various gases at the same pressure were admitted to a receiver in which the air pressure had been reduced to, say, one tenth or one hundredth of atmospheric, the extent to which the remaining air was compressed, and hence the quantity of heat evolved, would be identical, whatever gas was admitted. The temperature changes occurring with different gases would thus be determined

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1. Ibid., pp.533-534.

2. See pp.40-41.

3. This is apparent throughout Leslie's Heat.

4. Dalton's earlier suggestion that the evacuated receiver experiments might be used for this purpose had been based on a quite different analysis (see Dalton, Manchester Memoirs, v (pt.2) (1802), 526).

solely by their volume specific heats, once correction for the very considerable heat losses through the walls of the receiver had been made. Unfortunately Leslie put his method to the test for hydrogen and air only, observing an identical temperature change in each case. The conclusion that the volume specific heats of the two gases were equal in fact accorded well with Crawford's results.

Probably the most extravagant of all the calorists of the period about 1800 was Alexander Tilloch, a Scot living in London, who in December 1799 delivered a far from convincing attack on the view that caloric could exist in two states to the Askesian Society of London, 'a select number of gentlemen' who since March 1796 had 'associated for their mutual improvement in the different branches of natural philosophy'.[1] A paper read before a small private society such as this would normally have been lost but Tilloch, as editor of the Philosophical Magazine, had a ready vehicle for his opinions and of this fact he took full advantage.[2] In November 1800 he enlarged on an earlier suggestion of his that the volume of the 'matter of heat' expelled in a compression or, indeed, in a chemical reaction might be equal to the change which occurred in the volume of the ponderable matter. He argued, furthermore, that heat not only possessed volume but was also subject to gravitational attraction and so could be

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1. Phil. Mag., vii (1800), 355n.

2. A. Tilloch, 'A brief examination of the received doctrines respecting heat or caloric', Phil. Mag., viii (1800), 70-78, 119-126 and 211-221.

weighed.[1] In this, of course, he was reviving a persistent eighteenth-century idea and neglecting Rumford's recent experimental refutation.[2] Tilloch's arguments generally betray an inadequate understanding of the issues involved and, despite their novelty, they are therefore of small importance in the history of caloric theory, a theory which had exponents of far greater weight than anyone whose work we have examined so far in this chapter.

On the Irvinist side the greatest name was undoubtedly that of Dalton. We have already seen how his commitment to Irvine's views influenced his work on adiabatic phenomena and also on the absolute zero of temperature, which to him, as to any Irvinist, was 'an object of primary importance in the doctrine of heat'.[3] In all this work there was much that was original, but Dalton's originality is probably nowhere more apparent than in his views on the size of gas particles. His novel attempt of 1801 to relate particle diameter and the absolute temperature of a gas expanding at constant pressure was only one aspect of this interest. By the time he abandoned the attempt, between early 1805 and March 1807,[4] the subject of particle size and in particular its dependence on the nature

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1. A. Tilloch, 'An attempt to prove that the matter of heat...possesses not only volume but gravity', Phil. Mag., ix (1801), 150-167.

2. Rumford, 'An inquiry concerning the weight ascribed to heat', Phil. Trans., (1799), 179-194.

3. Dalton, New System, i (pt.1), 83.

4. See the syllabuses for lectures delivered by Dalton in Thackray, Manchester Memoirs, cviii (1965-6), 36 and 39. The V^3 law was rejected explicitly in Dalton, New System, i (pt.1), 12.

rather than the temperature of a gas had gained a new and far greater significance with the emergence of his atomic theory. From the start size was as much a characteristic of the Daltonian atom as weight. By the time the first table of particle weights first appeared in his note-book, on 6 September 1803 or very shortly afterwards,[1] Dalton had already rejected his earlier idea that under similar conditions of temperature and pressure the particles of all gases were equally spaced[2] and by 19 September the first list of fourteen gas-particle diameters had been drawn up.[3] In view of his later descriptions of gas particles composed of huge but weightless atmospheres of caloric surrounding a small, heavy central atom,[4] it may seem surprising that it was apparently not until the early months of 1806 that he began to examine the implications of his new concept in the light of his Irvinist theory of heat. Was it not immediately obvious that the diameters were somehow related to the quantities of heat in different gases and hence also to their specific heats? The problem of deriving the relationship was, of course, a difficult one, but an additional reason

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1. H. E. Roscoe and A. Harden, A New View of the Origin of Dalton's Atomic Theory (London, 1896), p.28.

2. Ibid., p.27, where the rejection is clearly implied in the passage from p.246 of volume 1 of Dalton's note-book.

3. Ibid., p.41. For the method of calculation see Ibid., pp.24-25.

4. See Ibid., pp.71 and 73-74 for comments dated 23 May and 17 June 1806. Also Dalton, New System, i (pt.1), 143-144 and i (pt.2), (Manchester, 1810), 548 and plates 7 and 8. For similar, earlier views, probably unknown to Dalton, see B. Higgins, Experiments and Observations relating to acetous acid... (London, 1786), p.306 and W. Higgins, A Comparative View of the Phlogistic and Antiphlogistic Theories (2nd edn., London, 1791), pp.14-15, 81 and 174-175.

for the delay may lie in Dalton's 'first theory of mixed gases'[1] which he held at this time and which even led him to doubt for a while whether the repulsive forces between particles should be attributed to caloric at all.[2] It was only towards the end of 1805, when he finally abandoned this theory,[3] that he unequivocally restored to caloric its customary rôle and, even more important, gave variations in particle size between different gases a special importance as the basis of his amended or 'second' theory of mixed gases.[4]

With this new and eminently satisfactory application of particle size fresh in his mind and with the difficulties which his first theory raised for caloric now removed, Dalton returned to the subject of heat between March and June 1806. According to Roscoe and Harden[5] some fifty pages of notes attest to his interest in this period and it is significant that he paid considerable attention to the relationship between the sizes of the particles of various gases and the quantities of caloric which they contained. The earliest comment appeared in a short manuscript article 'On heat' dated 23 May 1806.[6] Here Dalton made his first attempt to relate

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1. The term used by L. K. Nash in Isis, xlvii (1956), 101-116 to denote Dalton's first attempt to explain the uniform diffusion of gases through one another.

2. Dalton, Manchester Memoirs, 2nd i (1805), 436 and New System, i (pt.1), 189. See also the notes for his 1810 Royal Institution lectures in Roscoe and Harden, Op. cit., p.16.

3. For this dating see A. W. Thackray, Isis, lvii (1966), 44-45.

4. First described in Dalton, New System, i (pt.1), 187-192.

5. Roscoe and Harden, Op. cit., p.71.

6. Ibid., pp.71-72.

particle size to the characteristic attraction for heat, an attraction which he was careful to distinguish from chemical affinity. He summarized his views as follows:

> The virtual diameters of atoms of matter will therefore vary in like circumstances according to their attraction for heat; those with a strong attraction will collect a large and denser atmosphere around them, whilst those possessing a weaker attraction will have a less dense atmosphere, and consequently the virtual diameter, or that of the atom and its atmosphere together, will be less, though the atmospheres of both have precisely the same disposition to receive or to part with heat upon any change of temperature.[1]

Such an assertion that the density of caloric was greatest in those atoms with the largest diameters[2] clearly required further examination and another comment, quite separate from the above article but evidently written about the same time, shows Dalton in search of a more specific relationship. It reads:

> Query, does not the quantity of heat in a given volume of gas vary as the diameter of the atoms under like pressure? No.[3]

Unfortunately Dalton offered no explanation for this rejection, so that we can only guess at the considerations which, by 1 June and on the very next page after this last note, had led him to try a quite different approach. He now wrote:

> I. It seems clear that the attraction of any atoms for heat must be as their diameters in an elastic state, whatever be the law of attraction.
> II. It seems also true that the law of attraction, whatever it may be, will not affect the relative quantities of heat around

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1. Ibid., p.72.
2. For a similar view see B. Higgins, Op. cit., p.315.
3. Roscoe and Harden, Op. cit.

> different kinds, in like circumstances.
> III. Further, the absolute quantities of heat around different atoms must be as the cubes of the diameters of these atoms. Consequently all elastic fluids of given pressure and temperature contain the same heat in the same bulk.[1]

His revised opinion, given in paragraph III, that under similar conditions the density of caloric was the same in all gases, irrespective of the size of their particles, seems to have been preferable to that which he had held a few days earlier in just one respect, namely in that it predicted specific heats in rather better, if not good, agreement with Crawford's experimental values. It seems, therefore, that it is in a concern to reconcile the consequences of his caloric theory of gases with the results of Crawford's experiments, or at least with his explanation of heats of reaction, that we must look for an understanding of the motives for Dalton's work. It is impossible, of course, to be certain on this point, but his views on the state of caloric in gases appear to have led to no other consequences which were capable of independent verification. Admittedly the volume specific heats obtained by Crawford[2] were by no means equal, as would have been expected if Dalton were correct, but still less did they increase with increasing particle size,[3] the corollary of Dalton's earlier opinion.

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1. Ibid., p.73.

2. Conveniently listed in Dalton, New System, i (pt.1), 66.

3. The particle diameters which Dalton adopted at this time were probably very similar to those listed in his note-book on 14 Sep. 1805 (Roscoe and Harden, Op. cit., p.65; see Thackray, Op. cit., on the dating). Slight modifications in the particle weights between Nov. 1805 and Aug. 1806 (Ibid., 55) would have had little effect on the calculated diameters.

Since Dalton was still working on the problem during the printing of the New System,[1] it is not surprising that the definitive version of his views which appeared in the first part of the book showed yet another fundamental change. He now proposed three main possibilities:

> 1. Equal weights of elastic fluids may have the same quantity of heat under like circumstances of temperature and pressure...
> 2. Equal bulks of elastic fluids may have the same quantity of heat with the same pressure and temperature...
> 3. The quantity of heat belonging to the ultimate particles of all elastic fluids, must be the same under the same pressure and temperature.[2]

In his conviction that a relationship of this type existed at all he was evidently guided by his belief in the essential simplicity of gases,[3] but the justification for the particular choice which he made was slight. The first possibility was convincingly dismissed, however, by reference to any exothermic reaction between gases, for, with the conservation of caloric accepted as axiomatic by all caloricts, it was obvious that the total quantity of heat in the compound resulting from such a reaction must be less than that present initially in the reactants, even though there had been no overall change in weight. The second possibility was less easily disposed of, but Dalton, arguing of course as an Irvinist, showed that it predicted a specific heat for carbon which was quite incompatible with experiment. It is interesting to note that as recently as June 1806 this evidence, although available, had apparently not constituted an objection.

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1. Dalton, Op. cit., 66.
2. Ibid., 68-70.
3. See pp.80-81.

The third possibility was the acceptable one. In justification Dalton began by dismissing any idea that the numbers of particles in either equal weights or equal volumes of different gases were equal. To readers unfamiliar with the polyatomic elementary molecule Dalton's argument on this point was unanswerable, for how could it be supposed that the size of a (compound) atom of nitric oxide was the same as those of its constituent gases when it was known that virtually no decrease in volume occurred in the reaction between equal volumes of nitrogen and oxygen? Was the total number of 'atoms' not halved in the process? The argument thereafter was less convincing. Dalton's arbitrary claim that the effect of a sudden increase in the affinity of an atom for heat would be to reduce the size of its existing atmosphere, and hence also the volume of the gas, rather than to attract more caloric was quite unfounded and in clear disagreement, as we see, with the views which he had held in 1806. Nevertheless Dalton proceeded to the obvious conclusion, namely that equal quantities of caloric were contained not in equal volumes or equal weights of different gases but in equal numbers of particles and that therefore the specific heat of any gas must be inversely proportional to its atomic weight. A comparison between experiment and the specific heats predicted on this basis was possible for six gases, but only in the case of air did Dalton find real support for his speculations. Not surprisingly, he now took good care to exclude air from the general criticism of the accuracy of Crawford's results which had appeared in a chapter of the New System printed off earlier.[1] His confident, if negative, claim that there was no

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1. Compare Dalton, Op. cit., 63 with Ibid., 67.

'established fact' which could disprove his treatment was only too true in 1808 but it reflected the standard of earlier experiments on the specific heats of gases rather than any intrinsic merit in his own work. Within a few years this unsatisfactory state of affairs had changed. In particular, the French Institute's prize competition for 1812 established as correct results which could not conceivably be reconciled with Dalton's and which, moreover, refuted the basic principles of his theory of heat. Irvinist doctrines and Crawford's explanations of animal heat and heats of reaction thereafter became untenable, at least for those less committed and more open-minded than Dalton. The possibility that anyone might take his theoretical treatment of specific heats seriously thus became even more remote after 1812 than it had been before.

The considerable attention which we have devoted to the material theories of heat in this period fairly reflects their dominance over the rival vibrational theories, but in England especially there was dissent. Rumford's views, for all their vagueness, were widely known and were at least mentioned by most text-book writers, some of whom admitted the difficulty of explaining the heat produced by friction on the caloric theory.[1] Davy's experiment of melting ice by rubbing together two pieces of ice in a vacuum were also familiar,[2] despite the obscurity of Thomas Beddoes's

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1. See p.106.

2. For evidence that Davy's work was known see Henry, Manchester Memoirs, v (pt.2) (1802), 603 and T. Young, A Course of Lectures on Natural Philosophy (London, 1807), i. 653. The latter is cited hereafter as Young, Natural Philosophy.

journal in which the description was published.[1] In 1801 Davy acquired a more prominent forum for the exposition of his vibrational theory, for it was in that year that he began lecturing at the Royal Institution in London, and he appears to have taken full advantage of his position.[2] Thomas Young was another supporter of the vibrational theory who lectured at the Royal Institution about this time, in his capacity as professor of natural philosophy between 1801 and 1803. In the syllabus for his course in 1802[3] and again in the revised version of the lectures, which he published five years later,[4] Young emphasized that, although the material theory was especially successful in accounting for heats of reaction, yet all the principal thermal phenomena could be explained equally well on the vibrational theory and, in the important case of friction, very considerably better. Young's views on the undulatory nature of light lent additional support, since they suggested a ready explanation of radiant heat in terms of vibrations in the all-pervading subtle elastic medium which were similar to, but 'larger and stronger than those of light'.[5] Perhaps the most sur-

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1. H. Davy, 'Essay on heat, light, and the combinations of light' in Works, ii. 5-86. The ice-rubbing experiment is described on pp.11-12. The paper appeared originally, early in 1799, in Contributions to Physical and Medical Knowledge, principally from the West of England, collected by Thomas Beddoes, M.D.

2. H. Davy, A Syllabus of a Course of Lectures on Chemistry (London, 1802), pp.53-54.

3. T. Young, A Syllabus of a Course of Lectures on Natural and Experimental Philosophy (London, 1802), pp.146-149. Cited hereafter as Young, Syllabus.

4. Young, Natural Philosophy, i. 653-657.

5. Young, Syllabus, p.149 and Natural Philosophy, i. 654.

prising feature of Young's theory of heat is the lingering influence of Irvine and Crawford. Young described their work in some detail in his lectures[1] and gave a particularly sympathetic account of their method for de termining the absolute zero. The disagreement between the various results obtained by this method inevitably gave rise to serious reservations and, while Young felt that there could be no objection to accounting for the heat absorbed or emitted in a change of state or of volume by reference to changes in capacity, he maintained that the heats evolved in friction and combustion defied explanation in this way. Nevertheless he accepted a value of about -1400°F for the absolute zero as 'a tolerable approximation'[2] and proceeded to apply it in a novel but uncritical treatment of the adiabatic effect.[3] In this he adopted the explanation of the heat produced by air entering a (partial) vacuum which Cleghorn and Leslie had already given.[4] He supposed that, if the density of the small amount of air remaining in the receiver before the tap was opened was 1/x of that of atmospheric air, then its capacity would be diminished x^{n} times when it was re-compressed to its original density and a quantity of heat proportional to $1450\left(1 - \frac{1}{x^{n}}\right)$ would be expelled, where 50°F (i.e. 1450 deg F above the absolute zero) was taken as the initial temperature. If now

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1. Young, Natural Philosophy, i. 650-652.
2. Ibid., 652.
3. Ibid., 632 and ii. 408-409.
4. See pp.40-41 and 111-112.

all this heat were absorbed by the compressed gas alone, its temperature would increase by 1450 $\left(1 - \frac{1}{x^n}\right).x^n$ deg F, but, since in fact the heat would be shared by x times as much air, the rise in temperature would be only 1450 $\left(x^{n-1} - x^{-1}\right)$ deg F. We shall term this expression (1). He went on to show that, if n were assumed to be small, this expression was a maximum when x = 2.7, so that the greatest heat would be obtained by opening a receiver evacuated to about two fifths of atmospheric pressure. Young recognised the unreliability of Dalton's data on the subject and showed that they yielded a value of $\left(\frac{1}{11.2}\right)$ for the constant n, compared with 1/8, which was the figure required to reconcile the experimental and theoretical velocities of sound. With n = 1/8, expression (1) gave 131.2 deg F for the temperature change produced in doubling or halving the density of air, without heat loss, and 1 deg F for a compression of 1/180. The general agreement between this and the similar figures derived by Biot and Poisson is noteworthy but, as we have already mentioned, it was Poisson's figure which became standard and Young's treatment passed unnoticed.

Davy's objections to fluid theories were to be far more comprehensive than those of Young, who adopted them in his accounts of both electricity and magnetism.[1] Yet Davy's first attack, dating from 1799, was directed specifically at caloric.[2] He claimed that to attribute the mutual repulsion between particles of ponderable matter to caloric was merely to post-

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1. Young, Natural Philosophy, i. 658-695.

2. Davy, Works, ii. 20-23.

pone the difficulty and to leave the repulsion between the particles of caloric themselves unexplained. Some years later his attitude had hardened still further and in some notes for a lecture which he delivered in 1809 we find the following stricture on all fluid theories:

> Vulgar idea -- like that of the peasant, every thing done by a spring; so every thing must be done by a fluid. The ether was the ancient fluid; then there was a phlogistic fluid: we have had the magnetic fluid, the vitreous fluid, the resinous fluid; and within the last few years there has been a fluid of sounds; and, in a book which I lately received from France, published by M. Azais,[1] all the phenomena of nature are explained by a gravic fluid.[2]

Davy's confidence in his attitude to fluids would already have been strengthened by his realization that chemical heat might be electrical in origin[3] and in a lecture in 1812 he again referred specifically to caloric:

> I do not think we have at present any means of deciding upon this question of the nature of heat; and its effects may be studied, - and it may be employed as an instrument of experiment, without the necessity of adopting any hypothetical views respecting its cause. It is my intention merely to give a caution with respect to the adoption of the chemical solution, - which is by far the most generally received. Indeed the matter of heat or caloric is sometimes talked of with the same confidence as water, or any common ponderable bodies...The truly philosophical inquirer into nature will not consider it as a disgrace, that he is unable to explain every thing; he will wait, and labour with hope, tempered by humility, for the progress of discovery; - and he will feel that truth is more promoted by the minute and accurate examination of a few objects, than by any premature attempts at grand and universal theories.[4]

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1. The French philosopher Pierre Hyacinthe Azaïs.
2. Davy, Works (London, 1840), viii. 348.
3. See pp.277-278.
4. Davy, Op. cit., 350.

In fact, by this time Davy was not so uncommitted on the nature of heat as he appears here. In his Elements of Chemical Philosophy, which also appeared in 1812, he cited the phenomena of friction and percussion, as well as certain unspecified exothermic reactions in which no decrease in capacity occurred, as evidence against the caloric theory, concluding:

> The immediate cause of the phenomena of heat then is motion, and the laws of its communication are precisely the same as the laws of the communication of motion.[1]

Davy provided revealing evidence for the rôle of adiabatic heating in the dispute over the nature of heat in his reference to the effect as one which was particularly well explained on the material theory.[2] Nevertheless he could offer a physical picture for this and, indeed, for all other thermal phenomena by supposing, quite gratuitously, that the particles of gases and liquids possessed, in addition to the familiar vibrational motion supposed to occur in solids, a rotational motion about their own axes, this motion being more rapid in gases.[3]

> Temperature [he explained] may be conceived to depend upon the velocities of the vibrations; increase of capacity on the motion being performed in greater space; and the diminution of temperature during the conversion of solids into fluids or gases, may be explained on the idea of the loss of vibratory motion, in consequence of the revolution of particles around their axes, at the moment when the body becomes fluid or aeriform, or from the loss of rapidity of vibration, in consequence of the motion of the particles through greater space.[4]

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1. Davy, Chemical Philosophy, pp.94-95.
2. Ibid., p.93.
3. Ibid., pp.95-96.
4. Ibid., p.96.

Such unfounded speculation was clearly vulnerable, but caloric theory was still so secure that contemporary comments, whether favourable or unfavourable, are hard to find. The most distinguished critic was Berzelius, himself no calorist, but his claim that Davy had not explained how the motion of compression was converted to rotational motion in the gas particles[1] seems to miss the point, since it was an increase in the rapidity of vibrational, and not of rotational, motion which was manifested as a heating effect, even in gases. Davy's views nevertheless had little to recommend them to chemists of the time and it was only when they were revived by James Joule over thirty years later[2] that they exerted any appreciable influence.

Davy, like Young, was not entirely free from the influence of Irvine and Crawford and even he accepted that the specific heat of a gas decreased with compression,[3] a view with which his theory of heat was in good agreement. The influence was still more marked on another non-calorist, the Westphalian chemist Friedrich Christian Accum, who had lived in London since 1793[4] and who, in 1803, had lectured at the Surrey Institution. Writing in 1805 Accum showed no preference for either the material or vib-

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1. Berzelius to Davy, n.d., in Jac. Berzelius Bref, ed. H. G. Söderbaum (Uppsala, 1912), ii. 41. The hypothesis of rotational motion also raised difficulties for J. B. Emmett in Ann. Phil., ix (1817), 423.

2. J. P. Joule, Phil. Mag., [3] xxvi (1845), 301-382.

3. Davy, Op. cit., p.90.

4. D. N. B., art. Accum.

rational theory[1] but he was none the less satisfied that the phenomena of latent heat, chemical and animal heats, friction and percussion were adequately explained by changes in capacity.[2]

So, throughout the first decade of the nineteenth century, the attitudes of British scientists to the theory of heat continued to be dominated by the legacy of Black, Irvine and Crawford. Neither caloricts nor vibrationalists strayed far from the basic principles laid down by these men and this at least gives a certain unity to the work of the period in Britain.

Theories of Heat in France

In France theories of heat lacked the unifying influence which they had in Britain and the systems adopted there tended to be more varied and also more complex. With caloric being called upon to explain such a wide diversity of phenomena as radiation, temperature, specific heat, expansion, change of state and the repulsive forces between gas particles, some degree of complexity was to be expected, but the multiplicity of forms which it was thought caloric could adopt was truly formidable about 1800. The easiest of solutions was, after all, simply to postulate as many sorts of caloric, each of them with its own characteristic properties, as there were phenomena to explain, and, although no one went quite so far as this, the current

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1. W. Nicholson, Natural Philosophy (5th edn., London, 1805), ii. 114 (in the section on chemistry, which Accum re-wrote).

2. Ibid., 122.

terminology reflects how attractive this type of solution was. Thus we find such terms as combined, latent, radiant, sensible and free heat (or caloric) all in common use, to say nothing of the quantities absolute and specific heat. However, it is important to note that in all versions of caloric theory only one fluid was concerned and its properties were merely modified by its state of combination with ordinary matter. The situation was in this respect quite different from that prevailing in the two-fluid theories of electricity and magnetism.

The arbitrary way in which characteristic properties had to be attributed to each of the forms of caloric was an obvious weakness and it was very properly the concern of early nineteenth-century writers to try to justify this procedure. One approach is seen in the attempts which were made to draw a close analogy between the behaviour of caloric and that of ponderable matter and it was in this way that the chemist and doctor Joseph Marie Socquet[1] tackled the problem. Although French by birth, Socquet never made much impact on Parisian science and, after serving as a doctor in the Sardinian and French armies, he eventually returned to Turin, where he had been educated at the university. His lengthy Essai sur le Calorique,[2] published in 1801, does not therefore belong to a really major tradition in French science and it is significant that he acknowledged as his mentor on the subject, not a leading Parician scientist, but Montgolfier.[3] However,

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1. For biographical details see Michaud, Biographie Universelle (Paris & Leipzig, n.d.), art. Socquet.

2. J. M. Socquet, Essai sur le Calorique (Paris, 1801).

3. Ibid., p.viii n.

the principles which he adopted in treating calorio were not untypical.

He wrote:

> L'action du calorique sur les corps y produit différens phénomènes, qu'il est important de bien distinguer et dont nous allons tâcher de nous rendre raison, à l'aide des seuls principes évidens que nous fourniront la chimie et la physique, en considérant le calorique comme un corps réel et non une simple modification de la matière, et lui appliquant, ainsi qu'aux autres substances, les lois d'affinité, de pression, &c.[1]

In accordance with the resolve expressed in this passage, Socquet distinguished four states in which caloric could exist, as caloric of composition, of capacity, of temperature, or as radiant caloric. Caloric of composition[2] was chemically combined with the ultimate particles of matter, forming one essential constituent of them. A molecule of water, for example, would contain a certain quantity of caloric of composition which would remain unchanged so long as the molecule continued to exist. Caloric of capacity,[3] on the other hand, was retained in a body by a purely physical force, 'affinity of adhesion', the mechanism being exactly that which bound dissolved gases to their solvent. Particles of caloric, like those of a dissolved gas in water, were supposed to penetrate any substance and to adhere to the surface of the molecules composing it with a force inversely[4] proportional to the square of the distance from the surface, so that capa-

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1. Ibid., p.6.

2. Ibid., pp.9-10.

3. Ibid., pp.10-13.

4. Socquet appears to have made a slip throughout the seal, for he refers everywhere to this force as being directly proportional to the square of the distance.

city was determined not simply by the innate affinity of the molecules for caloric but also by the extent of the surface area of the molecules to which caloric could adhere.[1] Since he adopted an inverse square law, we must assume that Socquet considered the force of adhesion to be gravitational and he certainly believed that caloric had weight.[2] Finally, the pores which necessarily existed between the molecules were filled by caloric of temperature.[3] Although this was not subject to the force of adhesion, it was still not in a state of perfect freedom, being retained in a body by external pressure, which counteracted the tendency of all caloric to expand under the influence of its natural elasticity and hence to escape as radiant caloric. Caloric of temperature, unlike all other types of caloric, could be detected by a thermometer and in this important respect it differed from radiant caloric, which was supposed to move so rapidly that it was detectable only if it were slowed down by the material of the thermometer and so essentially ceased to be radiant caloric.[4]

Socquet clearly fulfilled his aim to the extent that the attributes he bestowed on caloric were ones which he supposed to be established in physics and chemistry, but the weakness of his system is only too apparent. The properties which he supposed the different types of caloric to possess

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1. Socquet, Op. cit., pp.29 and 43-44. Cf. a similar view in Bergman, Opuscula, iii. 423.

2. Socquet, Op. cit., p.108.

3. Ibid., pp.13-16.

4. Ibid., p.99.

were assigned in a patently arbitrary fashion and, furthermore, some of the principles which he classed as 'evident', notably the mechanism by which gases were retained in a liquid, were by no means beyond dispute.

Yet it was some time before the analogy between caloric and ponderable matter was seen to be a fruitless one, and the most successful attempt to establish it was still to be made, by C. L. Berthollet in his Essai de Statique Chimique of 1803. Although the underlying principle was similar to Socquet's, his treatment was far more convincing. Indeed, the success which he considered he had had in justifying the analogy might even be seen as additional evidence for the materiality of heat, as he claimed in this passage:

> Si l'on ne veut pas regarder cette conformité entre les propriétés du calorique et celles d'une substance qui subit une combinaison, comme une preuve rigoureuse de son existence substantielle, on ne pourra se refuser à convenir que l'hypothèse de son existence n'a aucun invonvénient, avec l'avantage de n'introduire dans les explications des phénomènes que des principes généraux et uniformes.[1]

The strength of Berthollet's approach was that the phenomena with which he compared the behaviour of caloric formed part of the single coherent system of chemical affinities which he had so recently devised and which he was now convincingly expounding. Of course the truth of the system itself was by no means proved, but its obvious thoroughness, to say nothing of Berthollet's authority, ensured that it could not be lightly dismissed. The behaviour of acids provided the model for caloric, so that the combination of caloric with ponderable matter became no more (and no less) mysterious

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1. Berthollet, Statique Chimique, i. 180.

than any familiar chemical reaction. Just as the quantities of a given acid which were required to produce neutralization varied according to the base with which the acid combined, so different quantities of caloric were required to produce the same effect, for example a certain rise in temperature, in different bodies, the quantities in the two cases being proportional to the mass of the body (or base) and to its innate affinity for caloric (or for the acid).[1] This approach imposed one salutary restriction, since Berthollet could now abandon any attempt to explain the precise mechanism which held caloric in a body and so was able to reduce the range of his problems. In this he was breaking with a minor research tradition which went back well into the eighteenth century and of which Bocquet's unfruitful physical picture of the various ways in which caloric was held in bodies was only one highly developed example. It was a tradition in which Bergman, De Luc and even Lavoisier[2] had participated by their attempts to devise physical explanations for the difference between the specific heats of various substances in terms of the structure and properties of their ultimate particles. Berthollet's analogy allowed other simplifications to be made also. It was no longer necessary to ascribe special properties to each of the forms of caloric, and a single affinity now sufficed, as it did for acids. Rather less plausible, however, was his explanation of temperature changes, which he considered to be the result of opposition to the naturally expansive

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1. Ibid., 176-177.

2. Bergman, Opuscula, iii. 423; De Luc, Météorologie, i. 141; Lavoisier, Traité, i. 18-21. For a later instance of this same approach see Joseph Mollet's attempt of 1817 to account for the varying specific heats of gases and the different temperature changes occurring in the evacuated receiver experiments in terms of the sizes of gas particles (J. Phys., xc (1820),

force of caloric.[1] In the case of solids and liquids it was the forces of cohesion between the molecules which resisted this expansive force and so caused heating when caloric was added. In the case of gases, in which the inter-molecular forces of attraction had been overcome, the resistance was provided by external pressure. It followed that, as soon as the resistance was removed, caloric would combine with a solid or liquid without affecting its temperature and this, Berthollet supposed, was what occurred during a change of state. When the resistance was increased, on the other hand, as in the compression of a gas or in the percussion of a solid, a rise in temperature resulted, even without the addition of more caloric.

It would be interesting to know to what extent Laplace was associated with the development of Berthollet's views on caloric, for he and Berthollet were already good friends. At all events, Laplace contributed two important notes on caloric to the Mémoi. In these he showed a particular interest in adiabatic heating, as we should expect so soon after his success with the velocity of sound problem, but the carelessness of his argument in the first, hastily written note[2] suggests that he had not yet given serious thought to caloric theory. He argued that, if gas in a vessel fitted with a manometer were compressed isothermally to half its initial volume, then the number of gas molecules pressing on the surface of the mercury in the manometer would be doubled. Now the pressure and hence also the force on the mercury surface were known to be doubled in the process, so that the

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1. Berthollet, Op. cit., i. 155-156.

2. Ibid., 245-247.

repulsive force exerted by each molecule must remain the same. Such a conclusion, implying as it did that the force between two gas particles was independent of the distance between them, was of course quite irreconcilable with Newton's opinion on the matter. Disagreement of this sort, which was based purely on a careless slip, is surprising in such a good Newtonian as Laplace and can only suggest that he had not read the Principia on this point. The consequences for caloric theory were important. Laplace assumed, apparently quite arbitrarily, that the magnitude of the inter-particle force depended solely on the quantity of what he termed 'free heat' (chaleur libre) in a given volume of gas, so that in any isothermal compression the quantity of free heat expelled would be proportional to the change in volume. It followed from Laplace's theory that, since temperature was the only factor which could vary the inter-particle force, it too was determined by the density of free heat.

Laplace recognized the fundamental error of his argument so quickly that there was still time to insert a revised note[1] before the printing of volume one of the Essai had been completed. He now maintained that to compress a gas to, for example, one eighth of its original volume would increase the number of molecules pressing on a given surface by a factor not of eight but of two. The proof was essentially Newton's and it led to the familiar law of inverse proportionality relating the force and the distance between gas molecules. Laplace's law of force was thus in

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1. Ibid., 522-523.

no way original but, as Dalton also had realized, it now had to be integrated with caloric theory. The intimate relationship between temperature, the repulsive force between molecules and the density of free heat, which Laplace had established in his earlier note, could no longer be fully maintained. There was no mention of free heat and he supposed now that the force was determined simply by the density of 'heat'. If the Newtonian law of force were to be accounted for on this basis, it followed that the density of heat must increase in any isothermal compression. Thus, when a gas was compressed to half its original volume, less than half of its 'heat' must be expelled. Although Laplace did not mention it, his argument had shown incidentally that the temperature of a body was not determined by the density of heat in it.

Laplace was apparently content with this rather vague conclusion and it was left, unexpectedly perhaps, for Joseph Mollet of Lyons to take the argument a stage further.[1] To do this he had to make one additional supposition, namely that the repulsive force between two particles not only depended on, but was also proportional to, the density of heat in the gas. He could then argue that, if this force were doubled when a gas was compressed to one eighth of its original volume, then the density of heat must likewise be doubled. Three quarters of the free heat present in the gas originally

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1. Mollet, Mémoire sur deux faits nouveaux... (1811), pp.20-21. Although this paper is stated to have been read in Mar. 1804, the possibility that Mollet modified it subsequently, perhaps after reading Hally, cannot be ruled out.

must therefore have been expelled.

The Abbé René Just Haüy, then professor of mineralogy at the Muséum d'Histoire Naturelle in Paris, reproduced Mollet's argument, though without acknowledgement and with some reservations, in 1806.[1] In his views on caloric theory expounded in successive editions of his Traité élémentaire de Physique there is nevertheless evidence of originality. Berthollet's chemical analogies and the search for mechanisms had no place in his system and throughout he maintained a strict agnosticism in his attitude to the nature of heat,[2] as also to the fluids of electricity and magnetism, emphasizing that he was using the language of materiality merely for its convenience. He tried to preserve a similar impartiality in his treatment of the rival versions of caloric theory which, for a Frenchman, were seen as those of Irvine and of Lavoisier and Laplace. In the first edition, in 1803, he succeeded in presenting the views of both sides on such topics as change of state[3] and adiabatic heating[4] without committing himself, but three years later, when the second edition appeared, there had been a slight, but significant, change. He now went so far as to admit that the version adopted by Lavoisier and Laplace in 1783 presented a clearer picture of liquefaction and vaporisation.[5] Moreover, he showed

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1. Haüy, Traité (2nd edn.), i. 138.

2. Haüy, Traité (1st edn., Paris, 1803), i. 90; (2nd edn.), i. 80; (3rd edn., Paris, 1821), i. 80.

3. Haüy, Traité (1st edn.), i. 109-110.

4. Ibid., 116-118.

5. Haüy, Traité (2nd edn.), i. 128.

in detail how their clear distinction between the heat which brought about expansion and that which caused temperature changes could be used to account for adiabatic phenomena.[1] It seems clear that the latter application was not entirely original. In 1802 Biot had mentioned how in the compression of air 'une partie de sa chaleur latente...passe à l'état de chaleur sensible',[2] and in the first edition of the Traité Haüy had referred in passing to certain physicists who maintained that some heat entered into combination with any gas undergoing expansion.[3] Nevertheless his account of 1806 must stand as the first clear exposition of a principle which was to become quite crucial in Laplace's subsequent development of the analytical caloric theory. It also led him to the soundest understanding which had yet been obtained of the distinction between c_p and c_v.[4]

In their conviction that the density of caloric was greatest in a gas at high pressure Laplace, Pollet and Haüy were contradicting a fundamental point in Dalton's Irvinist theory,[5] but it was left for Gay-Lussac to deliver the first explicit criticism in a paper on the adiabatic effect

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1. Ibid., 135-141.
2. Biot, J. Phys., lv (1802), 176.
3. Haüy, Traité (1st edn.), i. 116-117.
4. See pp.178-179.
5. See p.94.

which he read to the Institute in September 1806.[1] The motive for Gay-Lussac's interest was the vexing problem of specific heats. About two years earlier, in the course of their work on the proportions in which hydrogen and oxygen combined to form water,[2] Gay-Lussac and his friend Alexander von Humboldt had observed that a complete union of the two gases did not occur if a large excess of oxygen was present. When the oxygen in excess of that which actually entered into combination was replaced by nitrogen, the reaction ceased at very nearly the same point. Assuming that the rapid absorption of the heat of reaction by the excess gas had brought the temperature below that required for ignition, they concluded that oxygen and nitrogen, since they were equally effective in this, had identical volume specific heats. It was a natural extension, although one hardly confirmed by further experiments with excess hydrogen and carbon dioxide, to suppose that all gases might be similar in this respect and, after returning from a year's tour of Italy, Switzerland and Germany with Humboldt,[3] Gay-Lussac set about examining the possibility at Arcueil, with the approval of Berthollet and Laplace, who appear to have shown considerable interest.[4]

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1. J. L. Gay-Lussac, 'Premier essai pour déterminer les variations de température qu'éprouvent les gaz en changeant de densité et considérations sur leur capacité pour le calorique', Mém. Soc. Arcueil, i (1807), 180-203.

2. See A. Humboldt and J. L. Gay-Lussac, J. Phys., lx (1805), 129-168.

3. See D. F. J. Arago, 'Gay-Lussac' in Arago, Oeuvres Complètes (2nd edn.), iii. 20-29.

4. Gay-Lussac, Mém. Soc. Arcueil, i (1807), 182.

While paying due acknowledgement to Dalton's experimental work,[1] Gay-Lussac proceeded to demolish the English chemist's theoretical analysis of the adiabatic effect. He did not deny that the cooling which accompanied the escape of compressed air from a vessel indicated that heat would have to be absorbed in order to restore the remaining air to its original temperature. But the conclusion that there must have been an overall increase in the density of caloric in the vessel once the initial temperature had been regained was quite unfounded, unless it could be shown that the amount of caloric absorbed exceeded that carried off by the escaping air. Although this question could not be finally resolved, Gay-Lussac convincingly demonstrated that a vacuum, far from containing more caloric than an equal volume of gas, in fact contained none at all. He did this[2] by enclosing one bulb of a sensitive air thermometer in the Torricellian vacuum above the column of a mercury barometer and then showing that no temperature changes occurred when the volume of the vacuum was changed by tipping the tube. Leslie's analysis of the evacuated receiver experiments was likewise dismissed, for Gay-Lussac observed that the temperature changes which followed the opening of the tap increased, rather than decreased, as the density of the small amount of air remaining in the receiver diminished.

Because of the significance which it holds for a reader familiar with the principle of energy conservation, one of the experiments described in Gay-Lussac's paper has attracted particular attention. In the experiment

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1. Ibid., 182-183.

2. Ibid., 191.

dry air at atmospheric pressure was contained in one of two twelve-litre spherical vessels which were connected by a narrow tube fitted with a tap. The air was then suddenly allowed to escape into the other vessel, which was evacuated, and any temperature changes were observed on alcohol thermometers in each of the vessels. This and other experiments conducted with air at initial pressures of one half and one quarter of an atmosphere and with different gases left Gay-Lussac in no doubt that the rise in temperature in the vessel which was initially evacuated was exactly equal to the fall observed in the other and that the temperature changes occurring with any particular gas were proportional to its initial pressure. But it was from his observation that the changes in temperature were greatest for gases of low density that Gay-Lussac drew his most important and ill-founded conclusions. His reasoning was as follows:

> ...si nous remarquons que tous les gaz se dilatent également par la chaleur, et que, dans nos expériences, en occupant des volumes plus grands, mais égaux, ils ont absorbé des quantités de calorique d'autant plus grandes qu'ils ont moins de pesanteur spécifique, nous tirerons cette conséquence importante, savoir que les capacités des gaz pour le calorique, sous des volumes égaux, suivent un rapport croissant quand leurs pesanteurs spécifiques diminuent.[1]

The assumption made here that the large temperature variations observed with gases of low density indicated that they required the greatest quantities of caloric in order to expand was, of course, quite unjustified since their specific heats were unknown. However, once the assumption was made, the rest followed easily. Gay-Lussac's reference to the equality of

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1. Ibid., 200-201.

the expansion coefficients suggests that he was assuming, with Haüy and probably Laplace,[1] that the amount of heat necessary simply to cause expansion was proportional to that required to effect the same degree of expansion accompanied by heating at constant pressure. It followed that the quantities of heat absorbed for equal increases in volume were proportional to the heat capacity of the gas in question, and Gay-Lussac duly concluded that the volume specific heats were greatest for gases of low density. One other consequence, derived by the same reasoning, was that the volume specific heat of any gas decreased as it was rarefied. In fact, if we are correct in our reconstruction of Gay-Lussac's argument, we must assume that he supposed the volume specific heat of the gas to be proportional to its density. This, however, was not the case for variations between different gases. Consider Gay-Lussac's conclusion on this point:

> Les capacités des gaz pour le calorique sous des volumes égaux, sont d'autant plus grandes, que leurs pesanteurs spécifiques sont plus petites.[2]

One writer[3] has recently followed Delaroche and Bérard,[4] the winners of the Institute's prize competition of 1812, in supposing that Gay-Lussac thought the volume specific heats of all gases under similar conditions of temperature and pressure to be inversely proportional to their densities.

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1. See p.179.
2. Gay-Lussac, Op. cit., 202.
3. M. P. Crosland, Ann. Sci., xvii (1961), 12.
4. Delaroche and Bérard, Ann. Chim., lxxxv (1813), 79.

but this is surely to read too much into the passage. Gay-Lussac's results would not support such a conclusion and both here[1] and in 1812[2] he explicitly stated that the exact form of the relationship between specific heat and density was unknown to him.

Even Gay-Lussac must have seen his investigation as no more than a modest contribution to a familiar problem. It was work which was hardly worthy of such a great scientist and the modern reader is struck not only by the unconvincing nature of the argument but also by Gay-Lussac's failure to notice the fact, which now seems so significant, that no overall absorption of heat took place when a gas expanded into a vacuum. It was five years before he returned to the subject but, when he described his recent experiments on specific heats of gases to the Institute on 20 January 1812,[3] he showed as much interest as ever. The simple method of mixtures which he used was one of striking crudity, for all the confidence which he placed in it. Equal volumes of two gases, one at a high and the other at a low temperature, were allowed to mingle and their final temperature was taken. No serious attempt appears to have been made to eliminate heat losses and it is not surprising that the results were inaccurate. Detecting no difference between the capacities, Gay-Lussac concluded that the volume specific heats not only of the gases examined but possibly of all gases were iden-

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1. Gay-Lussac, <u>Op. cit.</u>, 201.

2. Gay-Lussac, <u>Ann. Chim.</u>, lxxxi (1812), 103.

3. J. L. Gay-Lussac, 'Extrait d'un mémoire sur la capacité des gaz pour le calorique', <u>Ann. Chim.</u>, lxxxi (1812), 98-108.

tical. The result flatly contradicted his earlier conclusion, yet such was his confidence in its correctness that he now (wisely) chose to reject his theoretical interpretation of the 1806 experiments.

However, it was not long before his opinion changed yet again. In July 1812 he inserted a short article in the Annales de Chimie[1] in which, as a result of further experiments with a larger version of his method of mixtures, he accepted that the volume specific heats of gases were far from equal. But the subject now held less interest for him since he had learned that two of his 'friends' were tackling it by what he acknowledged to be a far superior method. There can be little doubt that the 'friends' referred to were Delaroche and Bérard rather than their rivals in the Institute's 1812 competition, Clément and Desormes, although the latter pair did claim friendship with Gay-Lussac.[2] The reason for this conclusion lies above all in the fact that Delaroche and Bérard conducted their experiments at Arcueil,[3] where Gay-Lussac was a prominent member of Berthollet's circle, although we might also note that they had submitted a preliminary report on their work to the Institute on 5 February 1812,[4] of which Gay-Lussac, as one of the judges for the competiton, would presumably have known.

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1. J. L. Gay-Lussac, 'Note sur la capacité des fluides élastiques pour le calorique', Ann. Chim., lxxxii (1812), 106-108.

2. Clément and Desormes, J. Phys., lxxxix (1819), 428, 436 and 443.

3. Delaroche and Bérard, Op. cit., 110n.

4. Ibid., 81.

Although the competition thus put an end to Gay-Lussac's immediate interest in the problem, as well as to his intention of presenting a much fuller treatment,[1] his article does throw light on the sort of questions which it was thought necessary to answer in 1812. Prominent among these was the dependence of specific heat on temperature and Gay-Lussac duly showed that the capacities of equal weights of air at -20°C and 52°C were in the ratio 1 to 1.206. Further experiments, in which air was mixed with hydrogen and carbon dioxide at various temperatures not only showed that the volume specific heats of these gases were far from equal but also confirmed that the variations with temperature were considerable. It is worth pointing out here that his view of the dependence of the volume specific heats of the various gases on their densities had been quite reversed since 1806, for he now found that they were greatest for those gases with the largest density.

Gay-Lussac's results were soon to be superseded, as he himself realised. It is conceivable that they were seen by the contestants in the Institute's competition as in some sence 'official' but, despite his eminence, it seems more likely that Gay-Lussac was himself influenced by Delaroche and Bérard in the way we have mentioned. However, there can be no denying that his theoretical views on caloric, which owed much to his early experiments, were to exert a crucial influence on the course of the competition.

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1. Gay-Lussac, Mém. Soc. Arcueil, i (1807), 201 and Ann. Chim., lxxxi (1812), 106.

he 1812 Competition

On 7 January 1811 the First Class of the Institute announced the following subject for its next prize competition in physics:

> Déterminer la chaleur spécifique des gaz, et particulièrement celle de l'oxigène, de l'hydrogène, de l'azote et de quelques gaz composés, en la comparant à la chaleur spécifique de l'eau; déterminer, au moins par approximation, la différence de chaleur spécifique qui est produite par la dilatation de ces gaz. Les concurrens sont invités à indiquer les principales conséquences de ces nouvelles déterminations dans les théories physiques.[1]

Entries were to be submitted by 1 October 1812 and the name of the winner of the 3,000 franc prize would be declared in January 1813.

The announcement left the motives for setting this subject in little doubt. After pointing out the great discrepancies between existing values for the specific heats of gases, it continued:

> La Classe des Sciences physiques et mathématiques de l'Institut rappelle l'attention des physiciens sur cet objet dont il est facile de faire sentir l'importance. En effet, tant que la chaleur spécifique des gaz sera indéterminée, on ne pourra faire aucune recherche exacte sur la chaleur dégagée dans diverses combinaisons, ni sur celle que produisent les animaux. On peut espérer que la détermination de la chaleur spécifique des gaz conduira à la solution de la question indécise, s'il existe dans les corps du calorique à l'état de combinaison, ou si toute la chaleur dégagée dans les combinaisons est due au changement de la chaleur spécifique des corps qui se combinent.

Gay-Lussac was predictably enough a member of the Class's committee which had been elected in December 1810 to choose the subject.[2] His interest in

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1. 'Prix pour...1813', Mém. Inst. Fr., xi (1811), p.xcv.

2. Proc. Verb., iv. 399 (3 Dec. 1810). The other members were Desfontaines, Cuvier, Berthollet and Bosc.

specific heat was already well known and his recent work on combining volumes had given him a special familiarity with the heat evolved in reactions between gases, as well as convincing him that the laws of nature were to be observed in their simplest form in gaseous matter.[1] The changes in capacity which were supposed to accompany reactions were thus an obvious subject for investigation and one which was of interest not simply to Irvinists. Even Gay-Lussac himself had used the principle that the capacity of an oxide was less than the mean of the capacities of its constituent elements to determine a rough value for the specific heat of oxygen in January 1812.[2] Nevertheless, in any such examination it was Irvine's theory and Crawford's explanations of animal heat and heats of reaction which were vulnerable and the competition must therefore be seen as an attempt to provoke a confrontation between the two main versions of caloric theory. The debate during the first decade of the century, intensified by the publication in 1805 of important papers by Irvine and by Lavoisier and Laplace,[3] had already clarified the issues and in most cases sides had been taken. In France, as we have seen, the climate of opinion was such that the Irvinists could have little prospect of success.

The experimental determination of the specific heats of gases presented notoriously difficult problems, but others besides Gay-Lussac were showing

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1. See pp.61-62.

2. Gay-Lussac, Ann. Chim., lxxxi (1812), 104-106.

3. See pp.11 and 25-26.

an interest. In August 1812, for example, Joseph Mollet communicated a letter to the Institute[1] in which he appears to have concluded that the volume specific heats of all gases were equal.[2] And in a description of a new calorimeter which he read in February of that year Count Rumford had emphasized how the apparatus might be used for measuring the specific heats of gases.[3] Yet, despite this interest, the competition attracted only two entries.

Following a custom which appears to have grown in popularity since the successful collaboration of Lavoisier and Laplace, the contestants worked in pairs. All four would have been well known to the committee of judges, which consisted of Berthollet, Mally, Charles, Thenard and Gay-Lussac,[4] and three of them, François Delaroche,[5] Nicolas Clément[6] and Charles Bernard Desormes,[7] had already been unsuccessful candidates for admission to the Institute. The fourth, Jacques Étienne Bérard, a chemist from Montpellier, was working at Arcueil by 1808[8] and was a member of the circle

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1. Proc. Verb., v. 85 (10 Aug. 1812).

2. Mollet, J. Phys., xc (1820), 115-117.

3. Rumford, Nicholson's Journal, xxxii (1812), 113.

4. Proc. Verb., v. 105 (12 Oct. 1812).

5. Ibid., iv. 131 (24 Oct. 1808). Delaroche was a candidate for a place in the botany section.

6. Ibid., iv. 143 (5 Dec. 1808). Clément was a candidate for a place as corresponding member in the chemistry section.

7. Ibid., iv. 315 (22 Jan. 1810). Desormes was a candidate for a place in the chemistry section.

8. Gay-Lussac, Mém. Soc. Arcueil, ii (1809), 216.

there by 1816,[1] being held in particular affection by Berthollet, who wanted him to be his heir.[2] Bérard in fact declined and eventually returned to Montpellier as professor in the Faculty of Medicine. Little is known of his partner Delaroche except that he was a doctor, came from Geneva[3] and died in 1813 soon after the competition. He had published a number of papers on physiology and on animal and radiant heat since 1806, one of which was reported on very favourably by Gay-Lussac, Berthollet and Biot in 1810.[4] Equally glowing judgement had been passed on a paper by Bérard[5] and on two written jointly by Clément and Desormes.[6] In all three cases Gay-Lussac was one of the two referees, with Chaptal, Berthollet and Thenard respectively. Clément's[7] interest was industrial chemistry and, with Desormes, whose daughter he later married, he ran a factory for the manufacture of alum at Verberie (Oise). In November 1819

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1. Mém. Soc. Arcueil, iii (1817), p.vii.

2. See Bérard's obituary in the Montpellier newspaper Union Nationale for 13 June 1869, p.4.

3. See Alexandre Marcet to Berzelius, Jul 1814, in Berzelius, Bref (Uppsala, 1913), iii. 106.

4. Proc. Verb., iv. 299-301 (15 June 1810). See also Ibid., 274.

5. Ibid., iv. 321-323 (26 Feb. 1810).

6. Ibid., iv. 481-482 (27 May 1811) and 508-509 (29 July 1811).

7. For biographical details see Dictionnaire de Biographie Française (Paris, 1959), art. Clément-Desormes. The N. B. G. follows C. Louandre and F. Bourquelot, La Littérature Française contemporaine, 1827-1844 (Paris, 1848), ii. 16-17, in erroneously treating Clement and Desormes as one man. The error arises from Clément's adoption of the surname Clément-Desormes after his marriage.

he became professor of applied chemistry at the Conservatoire National des Arts et Métiers in Paris and it was while teaching there that he became a good and significant friend of Sadi Carnot.[1] Desormes[2] was an early product of the École Polytechnique but, despite the numerous papers which he wrote jointly with Clément, he is perhaps equally well known for his political activities as a liberal in the Department of the Oise.

The memoirs of both pairs of contestants[3] were of a remarkably high standard, but the outcome could hardly have been in doubt. Clément and Desormes used so many concepts which were quite alien to the caloric theory as it was taught in France at this time,[4] that they must have been fortunate to receive even 'une mention très particulière'[5] when the result was announced in December 1812. There was surely no question of unfairness, although a recent article maintains that Clément and Desormes did make this complaint.[6]

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1. See pp.204-206.

2. For biographical details see Dictionnaire de Biographie Française, art. Desormes.

3. F. Delaroche and J. É. Bérard, 'Mémoire sur la détermination de la chaleur spécifique des différens gaz', Ann. Chim., lxxxv (1813), 72-110 and 113-182. N. Clément and C. B. Desormes, 'Détermination expérimentale du zéro absolu de la chaleur et du calorique spécifique des gaz', J. Phys., lxxxix (1819), 321-346. The original of the latter paper, entitled simply 'Détermination expérimentale du zéro absolu de la chaleur', is in the Académie des Sciences, Paris. It differs only very slightly from the published version.

4. The views expressed in Hachette's Programmes d'un Cours de Physique (1809) probably reflect contemporary orthodox opinion. On these see p.264.

5. Proc. Verb., v. 130 (21 Dec. 1812).

6. B. S. Finn, 'Laplace and the speed of sound', Isis, lv (1964), 12.

It was simply unwise to contradict principles which Gay-Lussac, by his work in the preceding years, could only consider as established, and this Clément and Desormes did repeatedly in their memoir, with inevitable consequences.

Although Delaroche and Bérard's theoretical conclusions were the more acceptable, there was little to choose between the contestants as far as their values for the specific heats of different gases were concerned. Moreover, their results agreed remarkably well with those accepted today, especially in the case of Delaroche and Bérard, and both papers were agreed on one point, namely that the volume specific heats of all gases were not in fact equal.

Yet these were not the real issues. Far more significant both in ensuring their victory and for the future development of caloric theory was that Delaroche and Bérard appeared to have put the opinions of Lavoisier and Laplace on the state of heat in bodies beyond all reasonable doubt. The doctrines of Irvine and Crawford, some of which were retained in a restricted form by Clément and Desormes, were never again a serious rival. The victory for the French orthodoxy was crushing and decisive.

The constant-flow method which Delaroche and Bérard used was based on unexceptionable principles. They were inevitably critical of all existing data, but their reason for rejecting Crawford's work is particularly interesting, since it was undoubtedly an important factor in the design of their apparatus. The objection went beyond the mere lack of sensitivity of Crawford's method, as we see in this passage:

> Ce procédé, outre son peu de précision, avait l'inconvénient de ne point donner la chaleur spécifique, dans l'acception que nous venons de donner à ce mot, puisque les gaz, ainsi renfermés, ne pouvaient ni se dilater ni se condenser.[1]

their opinion that the specific heats of gases should normally be measured at constant pressure rather than at constant volume was probably widely accepted, except by Irvinists, by 1812,[2] but this was the first occasion on which it had been explicitly taken into account in the design of an experiment. A constant-flow method was the obvious answer and Delaroche and Bérard devised two experiments of this type. In the first the gases were allowed to flow through a spiral tube inside a cylindrical copper calorimeter filled with water. When equilibrium conditions were established, the gases, which had been heated before entry and which cooled during their passage through the spiral tube, left the apparatus at the same temperature as the water in the calorimeter. It could then be assumed that the heat lost by the gases in cooling equalled the heat given up by the calorimeter to its surroundings and a simple calculation yielded their specific heats. For the second experiment Delaroche and Bérard acknowledged their debt to the suggestion which Rumford had made in his paper of February 1812.[3] In t is they did not wait for the establishment of equilibrium conditions, but simply compared the temperature rises caused by the flow of different hot gases when the water in the

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1. Delaroche and Bérard, Op. cit., 84n.
2. See p.179.
3. See p.147.

calorimeter was initially cold. The striking agreement between the results obtained by the two methods inevitably provided strong evidence for their accuracy.

More than a straightforward determination of specific heats was required, however. Of the supplementary problems probably the most important was the dependence of the specific heat of a gas on its density. A modification of their first experiment allowed Delaroche and Bérard to pass air through the apparatus at a pressure of 100.58 cm of mercury, as well as at atmospheric pressure. The result, that the volume specific heat at this higher pressure was to that at the ordinary pressure of 74.05 cm as 1.2396 to 1, was decisively, though not seriously, in error. Since the ratio of the pressures was 1:1.3583, it followed that the specific heat by weight had decreased in the ratio 1: 0.9126 as a result of the pressure increase. We now know that it should not have varied at all, but in 1812 it was the expected result and the confidence which Delaroche and Bérard placed in it almost certainly owed a good deal to this fact. They based it on only two experiments conducted on air at the single higher pressure of 100.58 cm, the steady variation of pressure being impossible with their apparatus. The discrepancy between the specific heats deduced from the two experiments, 1.2127 and 1.2665, of which 1.2396 was the mean, should in itself have made them suspicious, but without further examination they proceeded to extrapolate the results to other pressures and confidently assumed that they applied equally well to all gases. Their error, although of less than 10%, was to prove one of the most influential in

the whole history of the study of heat. Backed by the prestige associated with victory in the Institute's competition, the result quickly became standard and was to mislead many later calorists.

Delaroche and Bérard never lost sight of the central issue in the competition, which was to determine the form which caloric theory was to adopt. (The materiality of heat, we should note, was never in question). The way in which specific heat had been found to vary with pressure was perfectly consistent with Irvine's principles, but one deduction from the results did seem to tell against Irvine. Calculating the effect of compressing air adiabatically on the basis of Poisson's conclusion that a decrease in volume by 1/116 would raise its temperature by 1 deg C, Delaroche and Bérard used Irvine's theory to relate the heating to the change in specific heat which they had supposed to occur. The calculation placed the absolute zero of temperature at -306.4°C, appreciably higher than any figure previously suggested. But the authors set little store by such an argument. The whole basis was far too insubstantial and in any case they had stronger evidence for their attack on Irvine.

The need for a comparison between the specific heats of the same substance in the liquid and vapour states had long been recognized, but the high temperatures which it was necessary to maintain in work on vapours had proved a serious obstacle. Crawford's crude calculation[1] had shown naturally enough that the specific heat of steam was greater than that of

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1. See p.77.

water, but from a comparison of the heating effects of damp and dry air Delaroche and Bérard concluded, though with justified reserve, that the specific heats in the two states were as 0.8470 : 1.00, a result which, once established as accurate, would itself overthrow Irvine's theory of heat.

Still more convincing was their examination of the effect of chemical reaction on specific heat. According to Irvine's argument it followed that, in any reaction in which no temperature change occurred, the specific heat of the resulting compound would be [ac + (1 - a)d], where the masses of the reactants were a and (1 - a) and their specific heats by weight c and d. In any exothermic reaction, however, the predicted specific heat would be below this value and Delaroche and Bérard's results concerning the influence of changes of density on specific heat suggested that any decrease in volume would have a similar effect. In no case where heat was emitted or where contraction occurred could a specific heat greater than that determined by the above method be accounted for. The experimental values for certain compounds formed in exothermic reactions were in fact less than the calculated figures, but for red lead oxide and, even more strikingly, for water, in the formation of which much heat was liberated and a large decrease in volume occurred, the specific heat <u>exceeded</u> the calculated figure. The evidence was 'insurmountable', for no conceivable error in the specific heats of oxygen and hydrogen could account for the discrepancy. While Delaroche and Bérard did not exclude completely the possibility that the specific heat of a com-

pound might be related to those of its constituents,[1] there could be only one conclusion:

> ...il faut donc, si nous ne nous faisons pas illusion à cet égard, abandonner absolument l'hypothèse d'après laquelle le dégagement de chaleur, qui a lieu dans les combinaisons, serait attribué uniquement au changement de capacité des corps pour le calorique, et admettre en conséquence ainsi que l'ont fait Blake [sic], MM.Lavoisier et De Laplace, et un grand nombre de physiciens, l'existence du calorique à l'état de combinaison dans les corps. La connaissance de la chaleur spécifique de l'oxigène suffirait seule pour faire adopter cette opinion; car elle est si peu considérable, qu'il est presque impossible d'expliquer la grande quantité de chaleur qui se dégage dans la combustion de la plupart des corps, si l'on ne suppose pas que cette chaleur y existait à l'état de combinaison; aussi, dans l'hypothèse contraire a-t-on été obligé de supposer que la chaleur spécifique de ce gaz était au moins quinze fois aussi grande qu'elle ne l'est réellement.[2]

The contrast with the approach of Clément and Desormes was a marked one. Whereas Delaroche and Bérard conducted a simple, straightforward determination of specific heats, based on principles and coming to conclusions which could have aroused no objection among the judges, Clément and Desormes used an indirect method, the theory of which could only have met with disapproval, especially from Gay-Lussac. Moreover, the two perfectly fair attempts at direct determinations which they did make they reduced to the status of digressions, for in their view of the problem such results could not be regarded as in any sense final. The most important determination and the one to which they gave the greatest attention was of the heat capacity of the vacuum. That the void did in fact possess a definite

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1. See p.230.

2. Delaroche and Bérard, Op. cit., 174-175.

capacity for heat was, as usual, based chiefly on the ease with which it accounted for the phenomena accompanying the entry of gas into an evacuated container. In particular, as Clément and Desormes later pointed out,[1] it answered one problem which may well have caused more concern to caloricts than the literature suggests, namely the puzzling fact that cooling did not first occur when a gas expanded into a vacuum. Not until 1822 do we find another reference to the problem, this time by Gay-Lussac and J. J. Welter,[2] who based their solution on their observation that air rushing from a vessel where it had been kept under pressure experienced no fall in temperature. They interpreted this as indicating that the passage of air through a narrow aperture caused heating which counteracted the normal cooling effect and they argued that this was precisely what happened when a vacuum was suddenly opened. Almost inevitably, a year later,[3] came the best of all solutions, an experimental demonstration that the initial cooling did in fact occur!

The principle of Clément and Desormes's method for the measurement of the heat capacity of the void was to determine experimentally the amounts of caloric present in a vacuum of fixed volume at two different temperatures and hence to find the amount required to effect the rise from one temperature to the other. Since they supposed that air entering an evacuated chamber was heated because it absorbed all the caloric previously held by

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1. Clément and Desormes, J. Phys., lxxxix (1819), 436-438.
2. J. L. Gay-Lussac and J. J. Welter, Ann. Chim. Phys., xix (1822), 437.
3. A. de la Rive and J. Marcet, Bib. Univ., xxii (1823), 273-279.

the void, this could be achieved in an ideal experiment simply by measuring the heating effects obtained at each of the two chosen temperatures. But such factors as the imperfection of the vacuum and heat loss made any experiment far from ideal and it was to removing, or at least to allowing for, such imperfections that Clément and Desormes devoted a large part of their memoir. They sought to lessen heat loss by using a large spherical glass vessel of 28.4 litres capacity which they only partially evacuated. This arrangement above all reduced the time for which air was actually entering and ensured that the rise in temperature and hence also the rate of loss of heat were small. For their analysis of the effect of using a partial and not a perfect vacuum, Clément and Desormes looked to Gay-Lussac's work of 1806 on adiabatic expansion. They argued that, since the temperature changes in Gay-Lussac's two vessels had been equal and opposite, the total quantity of caloric present was unchanged by the expansion. Thus any volume of air at half atmospheric pressure, for example, was exactly equivalent to half that volume of air at one atmosphere together with an equal volume of evacuated space. A similar argument could be applied to air at any other pressure below atmospheric. Since Clément and Desormes found it most satisfactory to reduce the pressure in their vessel by only about 14 mm of mercury, the heat produced on admitting air was to be attributed to the destruction of only approximately half a litre of vacuum. Temperature measurement was effected by the ingenious method which is now generally associated with their name even though the principle had already been used for the same purpose by Dalton.[1] Clément and

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1. See [illegible]93-94.

Desormes used a rather more sensitive, conventional type of manometer fitted externally to the vessel instead of the capillary tube which Dalton suspended inside. After repeating the experiments with carbon dioxide instead of air in an attempt to correct for the remaining heat losses by using a gas of higher capacity, they concluded that at 12.5°C the total quantity of caloric in a vacuum would raise the temperature of an equal volume of air measured at atmospheric pressure by 114 deg C. They were not slow to point out the agreement between this figure and the heating predicted by Poisson in 1807.[1] From their opinion that the heat evolved in the mechanical compression of a gas resulted from the destruction of a certain volume of void it followed that the effect of compressing a gas by 1/114 of its original volume was essentially to destroy this same volume of evacuated space, producing a temperature rise in the remaining gas of 1 deg C. Thus Clément and Desormes were simply substituting 114 for Poisson's 116.

It now remained only to discover the quantity of caloric present in the same volume of evacuated space at a higher temperature, but in this they encountered the problem which led them to their only direct determinations of specific heats. It was clearly essential to know the specific heat of air, which was the thermometric fluid in their experiments, and in particular to ascertain how it was affected by temperature changes. Of the two types of experiment which they devised the first was a constant-flow

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1. See p.91-92.

method[1] in which the heat given up by the gas in cooling was measured by the melting of ice, but unsuitable winters prevented any extensive use of the apparatus, or of Lavoisier and Laplace's ice-calorimeter with which they began their work. Their second method was the more successful. In this, air at various pressures and a number of other gases were heated in a closed spherical vessel surrounded by a water bath and fitted with an external manometer which was used to measure the pressure and hence also the temperature of the enclosed gas. A comparison of the rates of heating (as also, in a supplementary experiment, of cooling) yielded a simple means of calculating the volume specific heats. That they were here measuring specific heat at an approximately constant volume, whereas in their flow method they would have found a constant pressure figure, does not appear to have concerned them, but their comment that the expansion occurring in their second method was so small as to necessitate no 'correction'[2] suggests that it was the constant-volume value which they saw as the 'true' specific heat.

Using a slightly modified apparatus, Clément and Desormes repeated their experiments on air entering a partial vacuum at 13°C and 98°C. After corrections for the effect of temperature on the capacity of the air, made by applying their experimental results on the assumption that isothermal

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1. The description of this method was omitted from the printed version of the paper.

2. Clément and Desormes, J. Phys., lxxxix (1819), 337.

expansion and expansion accompanied by heating influenced the capacity in exactly the same manner, they concluded that the quantities of caloric contained in equal volumes of vacuum at 15°C and at 96°C would raise the temperature of an equal volume of air at atmospheric pressure by 102 and 132.24 deg C respectively. Thus it followed that the caloric which raised the temperature of the void by 80 deg C would heat the air by only 30.24 deg C, so that the relative volume capacities of air and vacuum were as 80 : 30.24 or 1000: 377.

Two completely fortuitous agreements confirmed Clément and Desormes's confidence in their analysis of adiabatic heating. First, their conception of a partial vacuum as a mixture of a perfect vacuum and of air at normal pressure led directly to a simple relationship giving the volume specific heat of air at any pressure:

$$C' = \frac{NC + nc}{N + n} \qquad \ldots(1)$$

where C', C and c were the volume specific heats of air at low pressure, air at atmospheric pressure and the void respectively. N and n were the volumes of air at normal pressure and of vacuum which were supposed to be equivalent to volume (N + n) of low-pressure air. On inserting the specific heats which they had determined experimentally at three pressures below atmospheric, they obtained three remarkably similar values for c/C and a mean of 410/1000. Even in this calculation the consistency was obtained purely by chance and could not have occurred if their experimental data had been accurate. But to Clément and Desormes it was convincing and the point

could not now be missed that the values of c/C, calculated by two quite different methods showed extraordinary similarity. The capacity of the void was duly set at 400 where that of an equal volume of air at atmospheric pressure was 1000.

The other fortuitous agreement was between two values for the absolute zero of temperature deduced from two quite unrelated principles. The first method of calculation depended on their observation that the quantity of caloric in a vacuum at 16°C was to that at 98°C as 102 : 132.24. Arguing on Irvinist lines and assuming the capacity to be independent of temperature, Clément and Desormes concluded that, where x was the absolute temperature at 16°C,

$$x : 80 :: 102 : 30.24$$

and hence that the absolute zero was at -251.8°C. A modified procedure, also involving the capacity of the void, gave -267.5°C. Their second method of calculation was essentially the one originally suggested by Amontons,[1] although they based it on the expansion rather than the pressure coefficient of gases. Naturally they used Gay-Lussac's results, but only after checking them themselves, and so placed the zero at -266.66°C. The calculation is notable for its correctness, since of earlier nineteenth-century writers only Dalton and J. T. Mayer[2] had adopted anything resembling

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1. See p.60.

2. J. T. Mayer, 'Commentatio de lege vis elasticae vaporum', Commentationes Soc. Reg. Scientarum Gottingensis Recentiores, 1 (1811), commentationes mathematicae, 28-29. On Dalton see pp.76-78.

Amontons's definition of the zero, and Dalton, as we have seen, had applied it in a most unconvincing fashion. This neglect seems particularly surprising when we recall that the common eighteenth-century belief that gases expanded to widely differing extents when heated, which presumably diverted attention from Amontons's definition, had been rejected as early as 1802.

For Clément and Desormes, however, the important point was the agreement between the results of two completely different methods of procedure. Once again, it seemed, their basic principles had been more than adequately confirmed.

To what extent their preconceived theoretical ideas influenced the selection of what they considered to be the true readings we cannot know. As it stands, their memoir is a plausible document in which experimental results strongly vindicate their theoretical analysis of adiabatic heating. Such was their confidence that the specific heats listed in the final table were given not merely for equal volumes, as we should expect, but relative to that of an equal volume of vacuum. Moreover, the variations in specific heat with density were determined not experimentally but by calculation with equation (1). Only in fixing the specific heats of different gases relative to air were experimental results used directly.

On 21 December 1812 Delaroche and Bérard's victory was announced to the Institute.[1] The report of the committee was unfortunately never published, despite a request that it should be, and it has not survived. Yet

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1. Proc. Verb., v. 130.

the reasons for the decision are clear enough. Although it would be wrong to see the two memoirs as simply representing the rival versions of caloric theory and the result as a straightforward victory for Lavoisier and Laplace over Irvine and Crawford, there is something of this in the situation. Clément and Desormes had never denied the possibility that some caloric might exist in a combined state in bodies[1] but, on the other hand, they had never given any support to this view. Instead they sought to avoid the issue by working in terms of the caloric of the void, in which there could be no question of latent caloric. Irvine's principles might reasonably be expected to hold here and, as we have seen, they were applied, if only in a restricted form. Their idea that a vacuum could have a definite capacity for heat also had Irvinist overtones, not least in the mind of Gay-Lussac who, in discrediting the concept in 1806, directed his attack particularly at Dalton.[2] Clément and Desormes apparently saw their own analysis of the evacuated receiver experiment as being identical to Dalton's, but one essential difference was that the French writers found the capacity of the void to be less than that of an equal volume of air and their explanation was therefore in fact rather different. Of course, the results of both pairs of contestants supported Dalton's position to the extent that, when extrapolated to pressures greater than atmospheric,

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1. Clément and Desormes, Op. cit., 326-327. However, in later years they apparently thought the existence of latent caloric 'une hypothèse inutile' (see Thenard, Traité (4th edn., Paris, 1824), i. 84).

2. See p.139.

they predicted a decrease in specific heat by weight with increasing pressure. In fact the agreement between the two memoirs on this point was extremely close, for while Delaroche and Bérard observed an increase in volume capacity of 22.3% when the pressure increased from 75.30 to 100.50 cm of mercury, Clément and Desormes predicted 21.5% for the same increment.[1]

It certainly appeared that the theory of heat had received important clarification as a result of the competition, but problems remained. In particular the effect of temperature and pressure on specific heat had not been adequately investigated and there was a growing realization that the choice between constant-pressure and constant-volume measurements might be an important one. On 21 December 1812 Gay-Lussac, speaking on behalf of a committee consisting of Berthollet, Haüy, Cuvier, J. N. Hallé and himself,[2] announced the subject for the next competition, the result of which was to be declared in January 1815.[3] It was as follows:

> Déterminer la chaleur spécifique des fluides élastiques de 20 en 20 degrés centigrades, entre la température de la glace fondante et celle de l'eau bouillante, et sous deux pressions différentes, mais dans le rapport de un à deux, soit en ne faisant point varier leur volume, soit en le laissant se dilater librement par l'action de la chaleur.[4]

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1. Clément and Desormes, J. Phys., lxxxix (1819), 429. On the scale where the volume specific heat of air at 75.30 cm of mercury is 1000, the specific heat at 1000.50 cm, as given by Delaroche and Bérard's results, should not be 1.2396, as Clément and Desormes wrote in 1819, but 1.223. This brings the figures of the contestants into even better agreement.

2. Proc. Verb., v. 130.

3. But see p.165, n.3.

4. From p.1 of a pamphlet announcing the subjects for prizes to be awarded in 1815 and 1817 by the Classe des Sciences Mathématiques et Physiques of the Institute. The pamphlet was printed for the public meeting held on 9 Jan. 1815.

he setting of this subject was in no sense a criticism of Delaroche and Bérard's highly esteemed results, but merely an extension based on problems arising out of the previous competition. The competition was not a success and little record of it has survived.[1] On 5 December 1814 Berthollet announced that no paper of sufficient merit had been received and recommended that the subject be withdrawn.[2] If we are to judge by the one entry which has come to light, the decision was fully justified. The memoir[3] came from one Vincent Frédéric Olmi, a teacher of natural science at the Lycée in Moreze (Tarn), who tried to extend the well known dependence of the expansion coefficient of a gas on humidity to specific heat, claiming that variations in specific heat were caused simply by the quantities of water vapour present in the various gases. In fact he did not tackle the problem seriously and gave none of the results which he presumably obtained with his 'Hygro-Calorimètre-Pneumatique', an instrument designed to determine simultaneously the expansibility, specific heat and humidity of a gas.

As we shall see in Chapter 6, it was not long before serious doubt was cast on the accuracy of Delaroche and Bérard's results. For the moment,

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1. It is not mentioned, for example, in E. Maindron, Les Fondations des Prix à l'Académie des Sciences (Paris, 1881).

2. Proc. Verb., v. 455. See also Ibid., 407 (17 Oct. 1814).

3. V. F. de Olmi, 'Mémoire sur la détermination de la chaleur spécifique des fluides élastiques', in the Académie des Sciences, Paris. The paper, profusely dedicated to Laplace, is dated 5 Oct. 1813 and refers on the title page to the fact that the prize was to be awarded in January 1814. It is possible, therefore, that the competition on which Berthollet reported in December 1814 had been originally set for January 1814 and deferred.

owever, they won general acceptance and they continued to exert a powerful influence on caloriets until the 1850s. But of far more immediate and decisive importance for the future of caloric theory was the convincing way in which Delaroche and Bérard had refuted the Irvinist doctrines and, by their victory, given official sanction to the rival version associated with the names of Lavoisier and Laplace.

After 1812

For the caloricists something of a mopping-up operation followed the 1812 competition. The basic principles of caloric theory were now established beyond reasonable doubt and the problems which remained, such as those set in the competition of 1815, although important, were not of a fundamental nature. Thus, despite the disappointing outcome of the latter competition, Gay-Lussac could declare with every confidence in 1816:

> ...on peut affirmer aujourd'hui que la capacité d'un composé ne dépend pas de la quantité absolue de chaleur qu'il renferme.[1]

The impression that the pattern for the future development of caloric theory had been settled was further strengthened by the failure of Clément and Desormes to publish their paper until 1819, by which time they could have had even less hope of success than in 1812. By 1819 the intensity of the debate over the state of caloric in bodies had died down. New and even more fundamental issues, touching on the very existence of the fluids of heat and light, had now arisen, while for those who remained caloricists

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1. Gay-Lussac, Ann. Chim. Phys., i (1816), 216.

Welsrocks and Bérard's results and opinions were proving so successful as to require no modification. Yet, despite this quietening of the debate, it was a paper interpreted by Clément and Desormes as a major attack on their theory of heat[1] which seems to have encouraged them to publish their work. The paper, by Gay-Lussac,[2] appeared in 1813. It advocated the application of the cooling associated with the rapid expansion of a gas to the attainment of low temperatures, a proposal which was, of course, to be taken up in later years. The ignition of tinder by the compression of air to one fifth of its original volume in a fire-piston, which Gay-Lussac saw as indicating that a temperature of at least 300°C had been attained, showed that the heating effect might even exceed that predicted by Poisson. So there was surely no reason to doubt that much higher temperature changes would occur if the air were compressed still more strongly and rapidly and, conversely, that equivalent degrees of cold might be attained if air at very high pressure was suddenly allowed to expand. There might be no limit to this cold, Gay-Lussac argued, and, if this were so,

> ...la détermination du zéro absolu de chaleur doit paraître une question tout-à-fait chimérique.[3]

Such a conclusion could hardly fail to arouse Clément and Desormes, even though they were not mentioned by Gay-Lussac. In successive issues

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1. Clément and Desormes, J. Phys., lxxxix (1819), 428 and 444. Gay-Lussac was nowhere mentioned by name.

2. J. L. Gay-Lussac, 'Sur le froid produit par la dilatation des gaz', Ann. Chim. Phys., ix (1818), 305-310.

3. Ibid., 310.

of the Journal de Physique in November and December 1819 they published first the paper which they had entered for the competition and then a detailed reply to the supposed attack.[1] Their observation, made at the beginning of this reply, that the nature of heat was still unknown[2] suggests that they had made some concession to the changing climate of opinion. But their argument remained essentially unaltered and they made no attempt to reconcile it with any but the material theory. Indeed, much of the reply was taken up with a vigorous re-affirmation of their belief in the capacity of the void. Gay-Lussac, they maintained, had drawn the wrong conclusion from his demonstration that changes in the volume of a vacuum did not cause heating. The difference when a gas was present was simply that the gas presented an obstacle to the escape of heat through the walls of the container. In a vacuum, where there was no such obstacle, the heat escaped without being detected by the thermometer. Moreover, how else was the heating which accompanied the entry of air into a vacuum to be explained? Rejecting all the other possibilities, they retained their own explanation, which had now received further support from the recent application of Bréguet's metallic thermometer to the problem. Experiments with this highly sensitive instrument had shown that when air entered a vacuum its temperature rose by 70 deg C.[3] the highest figure yet obtained by direct measurement

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1. For details of the original paper see p.149, n.3. The second paper, with the same title, appeared in J. Phys., lxxxix (1819), 423-455.

2. Ibid., 428n.

3. Ibid., 440-441 and 'Nouveaux thermomètres métalliques des M. M. Bréguet', Ann. Chim. Phys., v (1817), 312-315.

on a thermometer and one in fair agreement with their own predicted figure. Turning to Gay-Lussac's more recent strictures on the absolute zero, which they regarded as a no less essential part of their theory of heat, Clément and Desormes claimed that two errors had been made. First, since tinder ignited at a lower temperature in high pressure air, Gay-Lussac had overestimated the temperature changes occurring in the fire-piston. More seriously, he had neglected the dependence of the capacity of a gas on its pressure, so that there was no reason to suppose that the abstraction of a given quantity of heat at low pressure would produce the same cooling effect as on the identical gas at high pressure. In fact the temperature changes would be expected to be less in the former case, which led to the prophetic conclusion: 'Réaliser le zéro absolu de la chaleur, est chose aussi impossible, sans doute, que faire le vide d'air absolu...' The zero was none the less real and its existence was given further plausibility by the two additional determinations of its value which Clément and Desormes described. The first, based on the increase in the pressure of a gas with temperature, did not differ essentially from that derived from the expansion coefficient and yielded -266.66°C. In the second they calculated the zero from a knowledge of the change in capacity accompanying the conversion of ice to water and of the latent heat. The method was Irvine's, but the insertion of their own experimental figure of 0.72 for the specific heat of ice, instead of the usual 0.9, gave a figure in good agreement with all their others.

Gay-Lussac was quick to rise in his own defence, though again without

mentioning Clément and Desormes. In a paper which appeared in 1820,[1] he recalled how, about the time of the 1812 competition, he had repeated his earlier experiments on the compression and expension of a vacuum on a considerably larger scale. The results had been unchanged and had served merely to confirm his views, no doubt to the detriment of Clément and Desormes's chances. The whole question of the amounts of heat contained in various bodies was dismissed, not as unsolvable, but as one of little importance, which it most certainly was in any but Irvine's theory of heat.

In the face of this attack such Irvinists as remained were noticeably silent. There were still those, Mollet, Navier and de la Rive and Marcet, for example,[2] who advocated the application of evacuated receiver experiments to the determination of specific heats, but there is no evidence that any of them proposed the retention of the concept of the capacity of the void or, indeed, of any principles which might be considered Irvinist. Clément and Desormes themselves did not reply to Gay-Lussac, but in a lecture in 1825[3] we find Clément stating as obviously quite familiar facts that the quantity of heat in a body was proportional to its capacity and that the absorption of latent heat had the effect of increasing capacity

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1. J. L. Gay-Lussac, 'Sur le calorique du vide', Ann. Chim. Phys., xiii (1820), 304-308.

2. J. Mollet, 'De la constitution intime des gaz...', J. Phys., xc (1820), 113-130; C. L. M. H. Navier, Bull. Soc. Phil., (1820), 101; de la Rive and Marcet, Bib. Univ., xxii (1823), 230.

3. From J. H. Baudot's notes taken at a lecture on 19 Dec. 1825. The notes are those designated Clément, Lectures A, in n.7, p.202.

during a change of state. Since he made no mention of the capacity of the void, it seems possible that he had been at least partially persuaded by Gay-Lussac's arguments.

Even Dalton had to make concessions. Just how quickly he did so, however, is not clear, since his views on Delaroche and Bérard's results did not appear until 1827.[1] Even then he was reluctant to admit defeat and he had accepted Delaroche and Bérard's evidence as irrefutable only after a thorough repetition of their experiments, which had proved to his own satisfaction that the specific heat of air was indeed much lower than Crawford (and he) had earlier supposed. It was in his interpretation of the results that Dalton still held reservations and, incidentally, showed the weakness of his position. His claim that even Crawford had all along believed caloric to be combined with ponderable matter and that therefore Delaroche and Bérard had said nothing new must appear either as a particularly weak attempt to justify his own change of heart or as an indication of some serious misunderstanding of the essential points at issue. After all, Crawford had at no time suggested that heat in combination thereby became latent, a point which Dalton appears to have understood perfectly well in 1803.[2] On one point, however, there could be no denying that Dalton's opinion had changed and he had to admit that Delaroche and Bérard's experiments had shown conclusively that the total quantities of heat in

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1. Dalton, New System, ii. 268-271 and 282-288.

2. See p.75.

gases were not proportional to their specific heats. But even this concession was hedged about with reservations and Dalton was in fact retreating less than might appear at first sight. The reason for the breakdown of proportionality, he argued, was merely that the specific heats of gases varied with temperature, so that in the case of solids and liquids, where this variation did not seem to occur, there was as yet no reason to abandon Irvine's principle. If his method of determining the absolute zero had to be abandoned, as seemed likely, it was for this and not for any more fundamental reason.

In his reaction to Dulong and Petit's discovery of 1819 that the atomic heats of all metal elements were identical Dalton was still less cautious,[1] and this despite the support which the discovery gave to the atomic theory. The essence of his criticism was to cast doubt on the constancy of the atomic heats adopted by Dulong and Petit, yet he was quick to point out that the relationship might yet be proved to hold for gases and so, he supposed, be reconciled with those views on caloric theory and gases which he had expounded in 1806. This claim that he was in some sense a precursor of Dulong and Petit hardly bears examination, although it was taken seriously by one zealous biographer.[2] Its falsity should be obvious to anyone who reads Dulong and Petit's highly critical opinion of the Irvinist

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1. Dalton, On. cit., 280-281 and 293-297. On Dulong and Petit's work see pp.273-283.

2. W. C. Henry, Memoirs of the Life and Scientific Researches of John Dalton (London, 1854), p.60.

theory and in particular of Dalton's interpretation of it. With the very existence of caloric open to serious doubt in their minds Dulong and Petit were unlikely to find much of value in Dalton's highly speculative views on the sizes of gas particles and on caloric, when not even caloricts had taken them seriously. Moreover, in predicting that the 'atoms' of all gases had identical capacities Dalton had made no attempt to distinguish between elements and compounds, whereas Dulong and Petit were quite sure that the law for compounds, when found, would be different from that for elementary atoms. It was clearly not in Dalton's interest to emphasize such differences between his own work and that of Dulong and Petit but it also seems possible that he did not fully understand the work of the French scientists. At one point, for example, we find him in the ludicrous situation of criticizing them for adopting the Irvinist view that the specific heat of a substance was proportional to the quantity of heat which it contained![1]

Such muddled thinking reflects the hopelessness of the Irvinist position. When its leading exponent could produce nothing better than this confused defence, the cause was surely lost. We shall find certain elements of Irvine's theory surviving, notably in the work of Amedeo Avogadro, but the pattern for the future development of caloric theory was now firmly based on principles which during the 1820s were to become increasingly associated with the name of Laplace. It was he who gave caloric theory its

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1. Dalton, On. cit., 296.

most sophisticated form and it is in his work that we see the natural culmination of the important developments in early nineteenth-century physics which we have examined in Chapters 2 and 3. With the special status of gases beyond all doubt, with the Irvinists routed and with experimental data which gave every appearance of reliability at last available, Laplace could now confidently proceed to apply his powerful mathematical techniques to the elaboration of a caloric theory which, in terms of elegance and completeness, bore little resemblance to the versions which we have so far encountered.

CHAPTER 4

Laplace and the Caloric Theory

Laplace made the most lasting of his contributions to the study of sound in a short paper which he read to the Académie des Sciences in December 1816.[1] In it he first showed that the effect of taking into account the small temperature changes accompanying the passage of a sound wave was to multiply Newton's expression for the velocity of sound by a factor $\sqrt{c_p/c_v}$. By using quite independent data to obtain a value for the correction factor which brought his own theoretical figure for the velocity into good agreement with the experimental value, he then not only established the correctness of his treatment but also put the need for a clear distinction between c_p and c_v beyond doubt. The latter was no small achievement, since scholars for some thirty years had been groping to the realization that c_p and c_v were in some respect different without ever confirming, let alone quantifying, their belief. It seems appropriate, therefore, that we should preface our account of Laplace's paper with a brief review of this earlier work.

c or c_v?

In Chapter 1[2] we saw how in 1738 Cranford used the (now) inaccurate experimental data then available to him to determine a value for the ratio

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1. P. S. Laplace, 'Sur la vitesse du son dans l'air et dans l'eau', Ann. Chim. Phys., iii (1816), 238-241.

2. See pp.28-29.

c_p/c_v. Although his figure of 1.03 (for oxygen) had the merit of being the first ever obtained, its smallness inevitably led him to dismiss the distinction between the two possible definitions of specific heat as unimportant and so to refer to it in only the briefest fashion in the *Animal est*. This treatment by such a prominent authority could serve only to mislead and it must clearly be taken into account in understanding the fact that Dalton alone of the later Irvinists was to return to the problem. Otherwise it becomes even more difficult to explain why anyone who used changes in capacity to account for the heat evolved in the compression of a gas should have failed to realize that c_p must be greater than c_v. De Luc, Leslie and Murray[1] were among those who fell into this category but who made no reference to the distinction.

There were others too who could easily have made the discovery quite independently of Crawford and even without any knowledge of adiabatic phenomena. Lavoisier is the obvious example. Not only did he believe that volume was a factor which determined specific heat[2] but, more importantly, with Laplace he had also clearly distinguished the heat which caused expansion from that which caused heating.[3] Did it not follow from this that the amount of heat required to effect any temperature change was greater

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1. See pp.49-50 and 110-117.

2. Lavoisier, *Traité*, i. 17-19. For his later modification of this view see A. Leguin, *J. Phys.*, xxxvi (1790), 420.

3. See p.20.

when expansion as well as heating occurred than when the volume of the heated substance remained constant? The deduction seems a simple one, but Lavoisier and Laplace failed to make it and to appreciate that in their experiments on gases they had been measuring a quantity quite different from that determined by Crawford. Unfortunately their views on the two-fold function of specific heat were largely ignored, with only de Luc commenting on them explicitly and then merely to reject them.[1] It was all too easy to accept, with de Luc, that the specific heat added to a substance always brought about both phenomena simultaneously and this may well account for the fact that some authorities[2] who shared this opinion did not think it worthy of detailed comment. That Crawford's experiments provided an exception was not pointed out until 1812.[3]

The ways in which the two main versions of caloric theory could have led to an appreciation of the difference between c_p and c_v are well illustrated by the treatments of Dalton and Daily. Writing soon after the turn of the century, both men had the advantage of a full acquaintance with the adiabatic phenomena, which they invoked in support of their arguments.[4] This knowledge was particularly valuable to Dalton who, following Crawford,

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1. De Luc, Météorologie, i. 137-139. See also his Physique terrestre, i. 243.

2. See, for example, M. Landriani, J. Phys., xxvi (1785), 89-90 and Adam, Natural Philosophy (1st edn., 1794), i. 220.

3. See pp.190-191.

4. Daily, Traité (2nd edn., 1806), i. 93; Dalton, New System, i (pt.1), 6-7.

used it as evidence that specific heat was dependent upon volume. His comments date from 1803 and occur in the section of his New System which deals with thermometry.[1] He was concerned to show not so much that c_p for a gas was greater than c_v, a fact which he evidently expected to be readily accepted, but rather that c_p (unlike c_v) increased steadily with temperature, i.e. as the gas expanded. If a standard of specific heat were to be chosen, therefore, a body whose volume could be kept constant would have to be chosen and for this purpose only gases were practicable. There was no need for Dalton to estimate the difference between c_p and c_v, as Crawford had done, and instead he merely cited his own experiments with the air pump receiver as evidence that the variations in specific heat with volume were far from negligible.

When he wrote in 1806 Daily too had little to say on the matter of quantification but he paid rather more attention than Dalton to showing that c_p must be greater than c_v.[2] Although his view of the function of caloric in effecting expansion was precisely that associated with Lavoisier and Laplace, he had the important advantage of independent evidence in the form of the adiabatic phenomena that even the isothermal expansion of a gas necessitated the addition of heat. The difference between c_p and c_v was precisely this quantity of what he termed 'latent caloric' which was required solely to effect expansion.

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1. Dalton, Op. cit., 4-6.

2. Daily, Op. cit., 56-58.

Kelly, like Kelton, believed that the ratio c_p/c_v normally varied with temperature and that this was a consideration of some importance in thermometry. The ideal thermometric substance, he pointed out, was one in which the increase in its volume was proportional to that in its true temperature, i.e. in the 'tendre' of the calorie which it contained. But this condition could not hold unless the relative quantities of sensible and latent caloric which went to raise by the specific heat were themselves in proportion to each other. In an argument which probably owed a great deal to Laplace[1] Kelly maintained that only air fulfilled these requirements and so should be adopted as the standard thermometric substance.[2] It should be noted that Kelly, unlike Kelton, had no objection to the use of a constant-pressure instrument as a standard. For someone who was not an Irvinist, after all, it was not necessary to suppose that any increase occured in the capacity of a body which was expanding and in his references to 'calorique spécifique' Kelly evidently understood c_p rather than c_v. Referring to the two contributions to the total specific heat he commented:

> L'expérience ne sépare pas ces deux parties l'une de l'autre, et ainsi, lorsqu'on définit le calorique spécifique, celui qui est employé à élever la température des corps d'un nombre donné de degrés, on doit sous-entendre, dans la définition, la partie qui n'intervient que pour produire la dilatation, ce dernier effet étant une condition liée à l'élévation de température.[3]

So by 1806 there was no reason why any calorist, whichever version of

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1. See pp.73-75.
2. Kelly, Op. cit., 88, 160 and 167-168.
3. Ibid., 115.

the theory he adopted, should have ignored the distinction between c_p and c_v. Both pairs of contestants in the Institute's prize competition of 1.12 were aware of it[1] and Clausius and Bérard at least saw it as an important factor in the design of their apparatus, although they made no attempt to estimate the relative magnitudes of the two quantities.

This latter problem was to remain unsolved for yet another four years during which the only contribution was an unsuccessful attempt by Dulong to measure c_v experimentally.[2] The practical difficulties must have been daunting and it is significant that, when the solution eventually did come, from Laplace in 1816, no new experiments were called for.

Laplace's chief concern in the paper of 1.16 was to develop his now familiar explanation of the error in Newton's expression for the velocity of sound. Just how he introduced the factor $\sqrt{c_p/c_v}$ is not described but, as we are to judge from a paper which he wrote in 1821,[3] it seems likely that the first part of his argument was essentially that given in present-day text-books.[4] Thus he probably began by showing that in a gas of pressure p and density ρ the velocity was given by

$$v = \sqrt{\frac{dp}{d\rho}}.$$

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1. See pp.150-151 and 159.

2. See p.232.

3. Laplace, Connaissance des tems...pour l'an 1825 (Paris, 1822), pp.234-237.

4. E.g. C. A. Coulson, Waves (7th edn., Edinburgh & London, 1955), pp.86-89.

It was Laplace's great achievement, of course, to identify Newton's error at this stage and to show that $\frac{dP}{\Phi}$ in a sound wave was not $\frac{P}{\rho}$ but $\frac{c_p}{c_v} \cdot \frac{P}{\rho}$, so that v became $\sqrt{\frac{c_p}{c_v} \cdot \frac{P}{\rho}}$. In deriving this relationship he assumed not only that the difference between c_p and c_v represented the latent heat which was required to bring about expansion but also that it was this same heat which, by losing its latent state and becoming 'sensible', caused heating when the gas was rapidly compressed. A decrease in the volume of unit mass of gas from V_o to $(V_o - \Delta V)$ would therefore release an amount of heat $\frac{\Delta V}{\alpha V_o}\left[c_p - c_v\right.$ and, if all the heat were absorbed by the gas, would cause a rise in temperature of $\frac{\Delta V}{\alpha V_o}\left[\frac{c_p - c_v}{c_v}\right]$, where α was the temperature coefficient of expansion. The overall increase in pressure from P_o to $(P_o + \bar{\Delta} P)$ was then given by

$$\left[\frac{\Delta P}{\Delta V}\right]_a = \frac{P_o}{V_o} + \frac{P_o}{V_o}\left[\frac{c_p}{c_v} - 1\right]$$

$$= \frac{c_p}{c_v}\left[\frac{\Delta P}{\Delta V}\right]_i$$

where $\left[\frac{\Delta P}{\Delta V}\right]_i$ represented the pressure increment under isothermal conditions. Thus, since $\frac{dP}{dV} \propto \frac{dP}{d\rho}$, it followed simply that the velocity of sound was $\sqrt{\frac{c_p}{c_v} \cdot \frac{1}{\rho}}$. It was clearly essential to suppose that all the heat liberated in compression did in fact go to heating the gas, but Laplace was confident that the vibrations constituting the sound wave occurred so quickly that there was no time for this heat to escape before it was re-absorbed in the succeeding period of rarefaction.

The next stage was to calculate $^{c}p/c_{v}$. In the absence of any reliable experimental data for c_v Laplace used an ingenious though fallacious argument to deduce the ratio from Delaroche and Bérard's results. Again his account of his reasoning was cryptic, although he admitted to making one additional assumption, namely that the amount of heat in any given mass of air at a constant pressure was proportional to its volume at different temperatures. An attempted reconstruction of his argument suggests that he considered a fixed mass of air undergoing two identical temperature changes, first at constant pressure and then at constant volume (see Fig. 1).

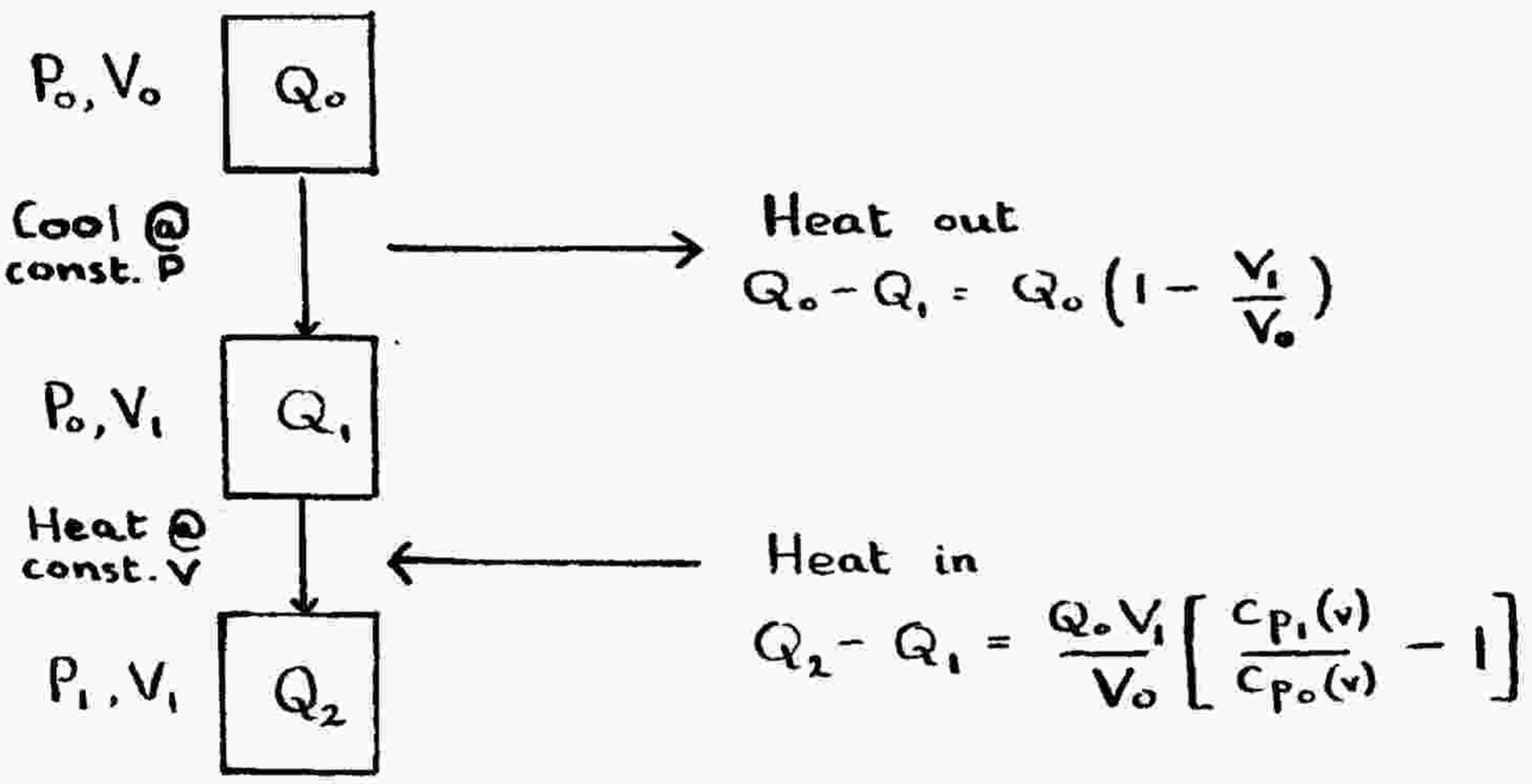

Fig. 1

The effect of allowing the air to cool at pressure P_0, so that its volume decreased from V_0 to V_1, was that it lost an amount of heat ($\omega_0 - \omega_1$) or, by Laplace's assumption, $\omega_0\left[1 - \frac{V_1}{V_0}\right]$, where ω_0 and ω_1 represented the total heat content of the air before and after the cooling. If the air was now supposed to be heated at constant volume until the temperature returned

to its original value and the pressure increased to P_1, where $P_1 = \frac{P_o V_o}{V_1}$ by Boyle's law, an amount of heat $(c_{p_1} - c_1)$ would be added to the gas. Now it could be shown from Laplace's initial premise that the quantities c_1 and c_2 were proportional, respectively, to the volume specific heats at the gas temperature and after the heating, $c_{p_o}(v)$ and $c_p(v)$ say. To get the data we now consider the two masses of air x and y illustrated in Figure 1. Letting unit volume specific heats at their pressures P_x and P_y equal to $c_{p_x}(v)$ and $c_{p_y}(v)$, so that the

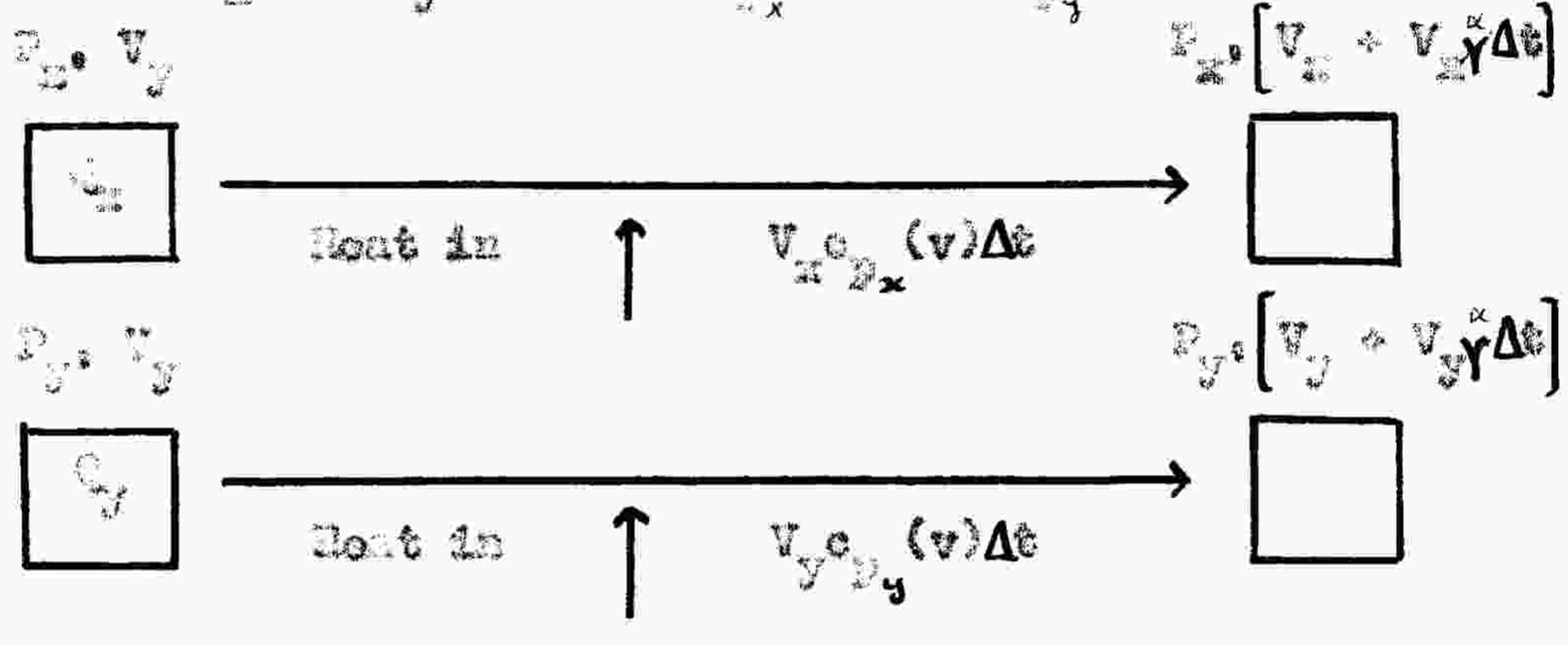

Fig. 1

additional heat required to raise the temperature of each of them at constant pressure by Δt would be $V_x c_{p_x}(v)\Delta t$ and $V_y c_{p_y}(v)\Delta t$, Laplace could argue that

$$\frac{V_x c_{p_x}(v)\Delta t}{V_x}, \frac{V_x \alpha \Delta t}{V_x} \approx \frac{V_y c_{p_y}(v)\Delta t}{V_y}, \frac{V_y \alpha \Delta t}{V_y}$$

and

$$\frac{V_y}{V_x} = \frac{c_{p_y}(\gamma)}{c_{p_x}(\gamma)}.$$

In other words, the quantity of heat in unit volume of any gas was proportional to its volume specific heat at that pressure.

To return now to the main argument of Figure 1, we can see that the heat gained by the gas in the constant-volume process was $\omega_1 \left[\frac{c_{p_1}(v)}{c_{p_o}(v)} - 1\right]$ or $\omega_o \frac{V_1}{V_o}\left[\frac{c_{p_1}(v)}{c_{p_o}(v)} - 1\right]$. One fact which could have raised problems at this point, namely that the ratio between the volume specific heats should have equalled that between the specific heats by weight for any change such as this in which the density remained constant, was happily ignored by Laplace. He seems now to have argued that, since the temperature changes in the two processes had been identical and had occurred respectively at constant pressure and at constant volume, the ratio c_p/c_v equalled the ratio of the quantities of heat lost and gained by the gas,

$$\underline{\text{i.e.}} \quad c_p/c_v = \frac{\omega_o\left[1 - V_{1/V_o}\right]}{\omega_o \frac{V_1}{V_o}\left[\frac{c_{p_1}(v)}{c_{p_o}(v)} - 1\right]}$$

$$= \left[\frac{\omega_{1/P_o} - 1}{\frac{c_{p_1}(v)}{c_{p_o}(v)} - 1}\right]$$

which, on inserting Delaroche and Bérard's results, yielded 3/2 for the ratio. We have already noted at least one weakness in the argument. Equally serious was Laplace's failure to observe that the pressure varied during

the rise in temperature so that c_v in his final expression was really a constant-volume specific heat for a mean pressure between P_o and P_1, while his c_p was a constant-pressure specific heat for heating at P_o. Moreover, his justification for using Delaroche and Bérard's results was doubtful since the ratio of 1.24 : 1.00 between the specific heats of air at 1.36 and 1.00 atmospheres had been determined for equal volumes of gas over the same range of temperature. These conditions did not of course hold in the second process, where the pressure increment was the result of an increase in temperature.

The remarkable agreement between Laplace's figure for c_p/c_v and the present accepted value of 1.40 was the result of pure coincidence, errors in his argument being largely compensated for by those in Delaroche and Bérard's data. But Laplace's reasoning, although faulty, was not quite so haphazard as would appear from a recent article by Dr. Bernard Finn.[1] As we have seen, Laplace made just one not unreasonable assumption and it is unnecessary to suppose, with Finn,[2] that he also assumed the quantity of calorie in unit volume of a gas to be proportional to its pressure. That it was proportional to $c_p(v)$, on the other hand, certainly was important, but this was a simple deduction from his initial premise and not, as Finn has it, yet another assumption. Lastly, Finn's claim that Laplace did not think it important or even realize that he was using constant-pressure

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1. Finn, Isis, lv (1964), 7-19.

2. Ibid., 15.

specific heats is surely wrong. We should recall that he supposed the caloric content to be proportional to volume only for a gas expanding at constant pressure so that it was essential to use c_p and not c_v in the argument outlined in Figure 2.

Laplace must have been highly satisfied, for the velocity of sound calculated with $c_p/c_v = 1.5$, 345.35 m per sec, was in striking agreement with the currently accepted experimental value of 337.18 m per sec. Moreover, the agreement had been attained with the minimum of speculation concerning the nature and properties of heat. Indeed, it might well have seemed that caloric theory had not been furthered by Laplace's paper, but an important foundation had been laid for the detailed elaboration of the theory which he was to begin some five years later.

Laplace

There is no difficulty in following the final stages in the development of Laplace's caloric theory of gases. Between September 1821 and April 1823 Laplace inserted accounts of his work on the subject in many of the leading French scientific journals, especially in the Connaissance des Tems, as well as in the fifth volume of the Mécanique Céleste. An examination of these papers will show that, despite the shortness of this period of activity, the theory was still undergoing important changes.

In analyzing the phenomena of gases Laplace leant heavily on his earlier work on gravitation which had appeared in volume 1 of his Mécanique Céleste as early as 1799.[1] In a paper which he read to the Académie des

1. See especially Laplace, Mécanique Céleste (Paris, 1799), i. 47-49 and 130-144.

Sciences on 10 September 1821[1] he applied his already familiar expressions for the forces between spherical bodies to the repulsion which he supposed to exist between the particles of a gas. For one case, of course, the force was gravitational and attractive, falling off in inverse proportion to the square of the distance r, while in the other it was repulsive and decreased as 1/r, but the necessary changes were easily made. One further modification, that the repulsive force was effective over only a very short range, was also required, if the predicted behaviour of gases was to agree with that observed, but here again there was little difficulty. The assumption and the backing of Newton himself and such short-range forces had already been successfully applied by Laplace in his work on capillary action,[2] as well as by his pupil Biot in the study of refraction.[3] Indeed, a comment which Laplace made either in December 1821 or early in 1822 suggests a clear intellectual lineage for his theory of heat and brings out its relationship to a far more general scheme of scientific investigation. Referring to the laws and phenomena of gases, he said:

> Ces lois et ces phénomènes sont ainsi ramenés à des forces attractives et répulsives qui ne sont sensibles qu'à des distances imperceptibles. Dans ma théorie de l'action capillaire, j'ai ramené à de semblables forces, tous les effets de la capillarité. J'ose espérer que cette nouvelle extension de la théorie de ces forces intéressera les

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1. P. S. Laplace, 'Sur l'attraction des sphères, et sur la répulsion des fluides élastiques' Connaissance des Tems...pour l'an 1824 (Paris, 1821), 320-343. Cited hereafter as Connaissance 1824.

2. Laplace, Mécanique Céleste, iv (1805), supplément.

3. See p.226.

démontrer. Lorsque tous les phénomènes terrestres en dépendent, comme les phénomènes célestes dépendent de la gravitation universelle. Cette théorie me paraît devoir être maintenant le principal objet de recherches dans la Philosophie mathématique: il me semble même utile de l'introduire dans les démonstrations de la Mécanique, en abandonnant les considérations abstraites de lignes sans masses, flexibles ou inflexibles. Quelques essais m'ont fait voir qu'en se rapprochant ainsi de la nature, on peut donner à ces démonstrations autant de simplicité et beaucoup plus de clarté que par les méthodes suivies jusqu'à ce jour.[1]

By applying these principles to the consideration of the equilibrium of a spherical shell taken at random inside a gas, Laplace showed that the pressure p of the gas must be proportional to $\rho^2 c^2$, where ρ represented its density and c the quantity of heat contained in each of its particles.[2] There were several grounds for objection in the argument. In particular, the all important assumption which he made at the outset, that the force between any two particles was proportional to c^2, was presented as self-evident, although in fact it was quite novel and without independent justification. A second equally original result followed from the same basic physical picture.[3] Constancy of temperature, Laplace maintained, was the result of a dynamic equilibrium, with the particles of a gas both radiating and absorbing caloric at an equal rate. Postulating the simplest of mechanisms for this process, he argued that radiation from any given particle was not spontaneous but resulted from the detachment of some of the particle's own caloric by incident radiant caloric (rayons caloriques), the density of

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1. Laplace, Connaissance 1825 (Paris, 1822), 323 and J. Phys., xciv, 70 (issue for Feb. 1822).

2. Laplace, Connaissance 1824, 328-334.

3. Ibid., 334-335.

which (t), was a function, and hence also a true measure, of temperature. Of the incident caloric a fraction q, determined by the nature of the gas, would be absorbed, while the quantity detached would be proportional both to c and to the total density of caloric in the gas, ρc. From these quite gratuitous assumptions it followed simply that

$$\rho c^2 = q^{\prime\prime}(t) \qquad \ldots(1).$$

Most consequences of the treatment only served to confirm its correctness. The laws of Boyle and Gay-Lussac, and Dalton's law of partial pressures could be readily predicted and it could be shown that the volume of a gas expanding at constant pressure must be proportional to $^{\prime\prime}$ (t),[1] a clear endorsement of Laplace's earlier support for the air thermometer. The obvious next step, of assuming $^{\prime\prime}(t)$ to be proportional to the (absolute) temperature u, was not taken in this paper but it appeared very soon afterwards.[2] One deduction, however, must have caused concern. From (1) it followed that a doubling of density at constant temperature would cause c to decrease by a factor $\sqrt{2}$,[3] so that heating was inevitable whenever compression took place in a container impermeable to heat. Although such a prediction confirmed, at least qualitatively, his explanation of the error in Newton's expression for the velocity of sound, it was clear to Laplace, for reasons which we shall examine below, that the amount of heat which he now thought to be expelled in compression was too great to account for the

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1. Ibid., 339.

2. Laplace, Ann. Chim. Phys., xviii (1821), 274.

3. For Laplace's opinion on this point in 1803 see pp.134-135.

discrepancy accurately.[1] His arbitrary solution, that the alternate compressions and rarefactions occurred slowly enough for there to be some heat exchange with the surroundings, could hardly have convinced even Laplace himself and three months later he had abandoned it. Thus by December 1821[2] he was arguing that there was in fact no heat exchange during the passage of a sound wave and that the heat 'expelled' in excess of that required to reconcile the theoretical and experimental figures for the velocity of sound remained attached to the particles of the gas, but merely became latent and so ceased to contribute to the inter-particle force. No modification in the expressions for P and ρ (t) was required, although c now represented not the total quantity of heat in a particle of gas but only that part of it which was 'free', so that a new term i had to be introduced to represent the quantity of latent heat. The form of the expression for the velocity of sound, i.e. for $\sqrt{\frac{dP}{d\rho}}$, which he now derived,[3] $\sqrt{\frac{2P}{\rho}(1 - C)}$, where P and ρ represented the pressure and density of the undisturbed gas and $C = -\frac{\rho}{c}\frac{dc}{d\rho}$, was similarly influenced in no way by the change. That this, under the condition $\frac{dc}{d\rho}$ and hence also $C = 0$, would yield far too high a value for the velocity is obvious and, as we mentioned above, this was evidently recognized by Laplace even in his paper of September.

The precise determination of C, which was so essential if Laplace's

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1. Laplace, Connaissance 1824, 336.

2. Laplace, Connaissance 1825, 223. Also Ibid., 302-305.

3. Ibid., 224-226.

analysis was to be proved correct, was impossible by any known direct method, but a simple argument showed that $(1 - C) = \frac{1}{2} c_p / c_v$ and so reduced the expression to that already derived in 1816. To do this Laplace assumed that the total heat content of a particle, $(c + i)$ or ω, say, was a function of ρ (i.e. $\rho^2 c^2$), ρ and the absolute temperature of the gas. From the supposition that ρ and the temperature remained constant, it followed that in a sound wave

$$d\rho \left(\frac{\partial \omega}{\partial \rho}\right)_\rho + d\rho \left(\frac{\partial \omega}{\partial \rho}\right)_\rho = 0 \qquad \ldots(2)$$

where partial differentials are introduced for clarity, although they were not in use when Laplace wrote. Hence $(1 - C)$ became equal to $-\frac{\rho}{2P} \cdot \frac{(d\omega/d\rho)_P}{(d\omega/d\rho)_\rho}$, which to anyone unfamilier with the interconvertibility of heat and work was itself equal to $\frac{1}{2} c_p / c_v$ or, to return to our earlier notation, $\frac{1}{2}\gamma$. In this way the determination of $(1 - C)$, a quantity intimately related to Laplace's speculations on the state of caloric in bodies, was reduced to that of γ, a quantity which it was now possible to measure by experiment far more reliably than in 1816 and quite independently of any physical explanations of pressure and radiation.

The necessary experimental advance had been made, albeit unwittingly, by Clément and Desormes, for although they themselves had not been concerned to determine γ, their work provided all the data required for the calculation. Naturally Laplace could not accept Clément and Desormes's explanation

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1. Ibid., 302-304.

of the temperature changes occurring in their experiments. Instead he argued that opening the stop-cock of a vessel in which the pressure had been slightly reduced caused the gas already in the vessel to be compressed and so heated.[1] In fact, provided the initial pressure is only slightly below that of the gas entering, this explanation is a good approximation to the truth and such conditions were certainly fulfilled in the experiments of Clément and Desormes. Laplace's expression for γ in terms of quantities given by Clément and Desormes was therefore correct, within those limitations, and his result of 1.35 was close to the true figure for air of 1.40. Further similar experiments conducted by Gay-Lussac and J. J. Welter during 1822, probably at Laplace's instigation,[2] only served to confirm the essential correctness of the method. The new experiments were preferable in several respects but above all in the reduction which was effected in the time for which the stop-cock was open and so also in heat loss, and they not surprisingly yielded values of 1.37244 and, a little later, of 1.3748 which brought the predicted figure for the velocity of sound into rather better agreement with experiment. That the agreement was still not perfect was almost certainly the motive for the experimental re-determination of the velocity which Laplace persuaded the Bureau des Longitudes to undertake, but the new measurements, made in June 1822[3] by a distinguished group under

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1. Laplace, Connaissance 1825, 304-306.

2. Ibid., 306. For the dating of these experiments see Ibid., 372; also Laplace, J. Phys., xciv (1822), 89 and Gay-Lussac and Welter, Ann. Chim. Phys., xix (1822), 436-437.

3. D. F. J. Arago, Ann. Chim. Phys., xx (1822), 210-223.

rago, only served to make the discrepancy slightly greater.

The additional observation by Gay-Lussac and Welter that γ remained very nearly constant over a wide range of temperature and pressure was an important one. It led to the conclusion, for example, that the velocity of sound should be independent of altitude, a fact which measurements made at Quito by a group of French and Spanish academicians in 1740 had already shown to be true. Unfortunately it also encouraged Laplace to make one quite erroneous prediction.[1] When the condition γ = constant was introduced into the relationship $\gamma = -\frac{(\partial v/\partial \rho)_p}{(\partial v/\partial p)_\rho} \cdot \frac{\rho}{p}$ and integration performed,

it followed that q must be a function of $\frac{p}{\rho^\gamma}$ or, where $p = k'u$, of $ku^{(\frac{1}{\gamma} - 1)}$. k was here an unknown constant. By postulating the simplest possible relationship between q and $p^{(\frac{1}{\gamma} - 1)}$, proportionality, Laplace could show that

$$q = Mku^{(\frac{1}{\gamma} - 1)^2} \qquad \ldots(3)$$

where M was another constant, and hence also that $q \propto u$ for heating at constant pressure. This last result he saw as strong confirmation for his work, for it was essentially no more than he had assumed to be true in 1816, and in a similar type of argument conducted before the results of Gay-Lussac and Welter became available he had begun with it as his basic assumption.[3]

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1. Laplace, Connaissance 1825, 307-308.

2. A slightly different form of this equation appeared in Laplace, Mecanique Celeste (Paris, 1825), v. 12b.

3. Laplace, Bull. Soc. Phil., (1821), 170-171.

It was now a simple step from equation (3) to the prediction that the ratio between the volume specific heats of any gas measured at two different pressures P_0 and P_1 was given by

$$\frac{c_{p_1}(v)}{c_{p_0}(v)} = \left[\frac{p_1}{p_0}\right]^{\frac{1}{\gamma}} \qquad \ldots(4)$$

Unfortunately Delaroche and Bérard's results only confirmed this false relationship. Indeed, their insertion in the equation yielded a good value of 1.425 for γ, different, it should be noted, from the value which Laplace had derived from the same experimental data in 1816.[1] In fact it is clear that he had now abandoned this earlier method of calculation, although he had adopted an argument very similar to it in a paper published late in 1821 in which, as five years earlier, he had shown $\gamma = 1.5$[2] and it may well have been this method which he was using in December 1821 when he gave an approximate figure of 0.3 for $(1 - c)$.[3] But the least reason for supposing this to be the case is that it would remove the need for the complex reconstruction of Laplace's reasoning which one recent commentator[4] has devised and of which no hint is to be found in any other Laplacian writings. In any case it is clear that Laplace

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1. See p.184.
2. Laplace, Op. cit.
3. Laplace Connaissance 1825, 226.
4. Finn, Isis, lv (1964), 16.

...w placed greater confidence in experiments of the Clément and Desormes type than in those of Delaroche and Bérard.[1]

The definitive version of Laplace's views appeared as Book XII of the fifth volume of the Mécanique céleste.[2] It is unnecessary to examine the work in detail, since it consisted almost entirely of the papers which had already been published in the Connaissance des Temps.[3] There were minor modifications of course. For example, it was now assumed from the outset that the calorie of a body existed in two states and no mention was made of his application of Delaroche and Bérard's results to the determination of γ. Such changes inevitably gave the caloric theory of gases the appearance of even greater consistency and rigour, so that the question of why this work, backed by the authority of Laplace and published in his greatest book, exerted so little influence becomes all the more difficult to answer. It seems that any explanation must take account of the more general decline of Laplacian science which we shall examine in Chapter 6, but some attempt to assess the merits of the theory considered in isolation will not be out of place here.

It was clearly a striking achievement to devise a physical picture of the state of caloric in gases from which the laws of Boyle, Gay-Lussac and

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1. For his scepticism towards Delaroche and Bérard's results see Laplace, Connaissance 1825, 226.

2. Laplace, Mécanique Céleste, v. 57-144.

3. His short papers in Connaissance 1825, 371-372 and 386-387 did not appear, however.

...lton could be predicted, but Laplace's initial assumptions concerning the ...pendence of and $\Pi(t)$ on ρ and σ were by no means beyond objection. ...he precise form which they took had clearly been determined by the re... ...irement that the deductions made from them should agree with the observed ...ws and had no basis either in Laplace's earlier thought or in the work ...f any contemporary calorist. The ad hoc nature of the assumptions is ...rought out well in an important modification which Laplace made early in ...s development of his theory. In his first paper, in September 1821,[1] he ...d shown that the main gas laws could be predicted if it was assumed that ...ere was an attractive force between the ponderable 'molecule' at the centre ...f any gas particle and the caloric attached to other molecules. This ...ttractive force was supposed to be far smaller than the inter-particle ...epulsion and so to be overcome by it, but it seemed reasonable to expect ...hat it existed and to take it into account in calculation. Only two ...onths later,[2] however, after detecting an error in his earlier argument ...nd so realizing that the gas laws were not in fact predicted on this basis, ...e denied outright the existence of any attractive force. In short, there ...as nothing inviolate about his initial premises. They were designed first ...nd foremost to 'save the phenomena' and only by the false relationship ...xpressed in equation (4) was anything resembling truly independent con... ...irmation possible. Even the derivation of the requisite correction factor

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1. Laplace, Connaissance 1824, 338-342.

2. Laplace, Connaissance 1825, 223.

$\sqrt{c_p/c_v}$ depended not on the more speculative parts of the theory but on the principle, which was then virtually beyond dispute, that it was a function of P and ρ only. Nevertheless Laplace used the determinations of γ which were now available to extend his knowledge of the state of caloric in bodies.[1] Was not (1 - c) equal to $\gamma/2$ and so also to 0.6074? And did not this in turn give a definite figure for $\frac{P}{c} \cdot \frac{dc}{d\rho}$? For Laplace this was sufficient proof that the quantity c in a gas undergoing adiabatic compression decreased with increasing density. The question whether the caloric thus 'expelled' was radiated or became latent was essentially a separate issue, although Laplace now had no hesitation in claiming that his determination of c not only proved that $\frac{dc}{d\rho} < 0$ but also, since dc = -di in conditions such that there was not heat loss, that di was too finite. He concluded: 'Ainsi l'existence d'une chaleur latente i, et son accroissement par la pression, sont des résultats de l'observation.'[2] The statement was bold, to say the least, although it did have the additional support of Delaroche and Bérard's paper of 1812, as Laplace pointed out.

How the mechanisms which Laplace devised to account for the behaviour of gases were viewed by his contemporaries is difficult to ascertain, but the very scarcity of comment[3] is surely significant. Even such a close

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1. Ibid., 308-309 and 318-319.

2. Ibid., 319.

3. For a particularly detailed criticism see J. Herapath, Phil. Mag., lxii (1823), 61-66 and 136-139. Herapath later attacked Poisson in the footnotes to his translation of some of Poisson's work on caloric theory (ibid., 329-338). See also W. Whewell, A History of the Inductive Sciences (London, 1837), ii. 530-533.

disciple as Poisson avoided using the mechanisms when, in 1823, he took up some of the problems which Laplace had raised.[1] Like his master, Poisson used Clément and Desormes's data to determine the correction factor to be applied to Newton's expression for the velocity of sound, inserting then in a result which he had already given in 1807,[2] namely

$$v = \sqrt{g\ln\left(1 + \frac{\varpi\,\omega}{(1+\varpi)\Gamma}\right)}.$$

In the first place he used the data simply to calculate the increment in temperature caused by a fractional decrease in volume Γ, but he also showed that his correction factor was equal to $\sqrt{c_p/c_v}$.[3] The argument was simple. He imagined a gas being heated at constant pressure from a temperature $(\theta - n)$ to θ and then compressed, without heat loss, back to its original volume. Finally, in a third stage, the gas regained its initial conditions by cooling at constant volume from its temperature after compression, $(\theta + \omega)$, to $(\theta - n)$. Since the initial and final conditions were the same and since also the heat content of the gas remained unchanged during the second stage, Poisson could equate the amounts of heat gained and lost in the first and third stages respectively.

Thus $$c_p n = c_v(n + \omega)$$

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1. S. D. Poisson, 'Sur la vitesse du son', Connaissance 1826 (Paris, 1825), 257-277.

2. Poisson, J. de. pol/tech., vii (1808),

3. Poisson, Connaissance 1826, 262-263.

and, where $n = \frac{\Gamma(1+\omega)}{\quad}$,

$$c_p/c_v = 1 + \frac{n\omega}{(1+\omega)\Gamma}.$$

By substituting $\frac{d\rho}{\rho}$ for Γ and $d\omega$ for ω, it was now a simple matter to derive the familiar relationships for adiabatic volume change,

$$\theta + 266.7 = 266.7\left[\frac{V}{v}\right]^{\gamma-1} \qquad \ldots(5)$$

where V and v are the volumes of a gas at 0°C and θ°C respectively and where the only error arose from Gay-Lussac's figure for the expansion coefficient of gases. From this the other relationships

$$p v^\gamma = \text{constant} \qquad \ldots(6)$$

and $$T^\gamma\, p^{1-\gamma} = \text{constant} \qquad \ldots(7)$$

follow immediately. It is hard to believe that Laplace himself would not have seen how these important equations could be derived from (2),[1] but he never gave them explicitly and Poisson must therefore retain at least some credit for their discovery.

Later in the same year, in August, Poisson published a further extension of Laplace's views on heat.[2] Again he avoided detailed discussion of the state of caloric in bodies, merely assuming that the amount of heat

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1. Laplace came particularly close to them in Connaissance 1825, 307.

2. S. D. Poisson, 'Sur la chaleur des gaz et des vapeurs', Ann. Chim. Phys., xxiii (1823), 337-352.

in a gas in excess of that present at some standard temperature and pressure was given by $q = f(P,\rho)$. This assumption, similar to that already made by Laplace, led first to an expression identical in form to equation (2), though with Poisson's q replacing θ, to equations (4), (5) and (6) and then to the relationship

$$q = A + B(266.7 + \theta)\rho^{\left(\frac{1}{\gamma}-1\right)} \quad 1$$

where A and B were constants. Expressions for the specific heats by weight, $\frac{1}{\gamma}-1$ and $\frac{1}{\gamma}B\frac{1}{\gamma}-1$ for c_p and c_v respectively, were also given and the magnitude of B was determined by inserting Delaroche and Bérard's data.

Throughout these two papers there is strong evidence that Poisson leant heavily on Laplace. Most of his results had already been obtained by Laplace or could have been derived by him without difficulty. Even Poisson's treatment of the quantity of heat in water vapour,[2] which led to the erroneous result that γ for steam was 1.073, was an obvious extension of a passage which had appeared in the Mécanique Céleste.[3] Poisson's greatest contribution, then, was rather to free Laplace's work of its more suspect elements, merely by picking up the argument at the stage $q = f(P,\rho)$.

In doing so he was showing in a most effective manner just how irrelevant much of Laplace's theory was, so that even to a reader convinced of the physical reality of caloric Poisson's must have seemed undeniably the more fruitful approach.

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1. Cf. Laplace, Mécanique Céleste, v. 120.
2. Poisson, Op. cit., 342-348.
3. Laplace, Op. cit., v. 139-140.

Sadi Carnot

Any addition to the mass of literature relating to Sadi Carnot must necessarily be made with caution. Carnot's contributions to the theory of heat-engines have received the well deserved attention not only of numerous historians but also of the writers of our modern text-books on thermodynamics. Yet problems remain and it is in an attempt to remove certain specific and limited gaps in our understanding of Carnot that this account will seek to relate his contributions in the field of physical theory to the caloric theory of gases, to the work of those of his contemporaries who accepted the theory and to the experimental data which supported it.

That Carnot was working in a period of intense activity and interest in power technology in France is well known. The concern with engines, especially steam-engines, took both a practical and theoretical form, with, on the one hand, the Académie des Sciences sponsoring an investigation into the safety measures to be adopted in high-pressure engines in 1823[1] and, on the other, some of the most talented mathematical minds of the day tackling the related theoretical problems. In 1818, for example, A. T. Petit had shown, erroneously of course, that in an ideal heat-engine the use of air as the working substance in place of steam would effect a four-fold increase in the motive power obtainable from a given quantity of heat.[2]

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1. See pp. 203-214.

2. A. T. Petit, Ann. Chim. Phys., viii (1818), 294.

Other writers were unconvinced and in August 1819[1] Clément and Desormes presented a paper before the Académie des Sciences in which they appear to have pointed out certain errors in Petit's treatment.[2] Unfortunately this joint paper, although it was read by Clément,[3] was evidently thought unworthy of publication by the referees, Fourier, Arago, Thenard and Gay-Lussac. No trace of it has been found and all we have is a brief summary which appeared in the bulletin of the Société Philomathique for August 1819. The original paper was nevertheless known to the civil engineer C. L. M. H. Navier[4] and also to Carnot, who read it in manuscript[5] and who, like Navier, rejected Petit's argument.[6]

Clément and Desormes's approach to the familiar problem of determining the effect or 'mechanical power' (puissance mécanique) produced by a given quantity of heat acting on steam and on various gases was based on a simple thought experiment (see Note 3).[7] They imagined steam, for example, being

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1. J. B. Desormes and N. Clément, 'Mémoire sur la théorie des machines à feu', Bull. Soc. Phil., (1819), 115-118.

2. Navier, Ann. Chim. Phys., xvii (1821), 357.

3. Proc. Verb., vi. 430 and 441 (16 and 23 Aug. 1819).

4. Navier, Op. cit.

5. Carnot, Réflexions (Blanchard reprint, 1953), p.93n.

6. Ibid., p.95n.

7. This account is based on the paper referred to in n.1 above and on two sets of notes taken by students at Clément's lectures. The relevant lectures in the first set (cited hereafter as Clément, Lectures A) are dated and cover the period January 1825 to March 1827. The second set (Clément, Lectures B) is undated, but appears to have been taken in 1827. For the dating and location of the notes see Bibliography.

[illegible]

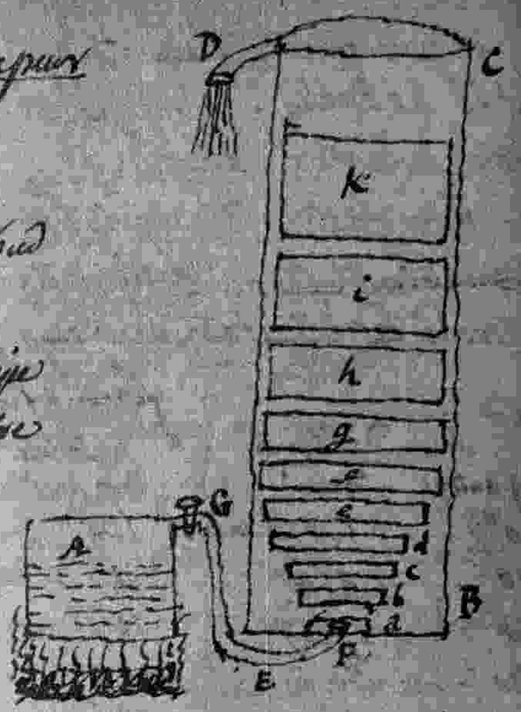
Plan of Jeremy's Lobe for the theoretical determination of the "subjective power" of a discourse

Plan of Jeremy's Lobe, from a book of notes taken by Dumont at lectures by Etienne Dumont c.1827 (on the building see p. 40). The book is now in the Library of the École Nationale Supérieure des Beaux-Arts, Paris, and the pages are reproduced by courtesy of the Librarian.

mesure de la force mécanique de la vapeur

BC est un vase cylindrique très étroit ; nous le supposerons pour notre exemple de 10 dm. de manière que rempli d'eau de fond soit pressé par le poids de 10 atmosphères.

A est une chaudière où le feu développe de la vapeur qui acquiert une force expansive dépendante de sa température. Si on ouvrait le robinet G servant à boucher le canal EF de communication avec le fond du vase BC, l'eau de ce vase se précipiterait de tout son poids dans la chaudière en refoulant les vapeurs K les absorbant ; mais si la température a été élevée à 182° centigrades, comme il est prouvé que la force expansive de la vapeur est de 10 atm. il y aura équilibre entre ces deux forces K le robinet ouvert ne produira rien. pour peu que la vapeur acquiert un excès de température, elle pénétrera dans le vase, et occupera au fond un espace 2 qui dépend du volume de la vapeur sous la pression de 10 atmosph.



Supposons qu'on ait laissé entrer par le conduit EF 1 kil. de vapeur, comme on sait que sous cette pression K cette température le volume de cette vapeur sera 0,262 de mètre cube (V. la table ci après), espace très peu occupé au fond du vase. il faut encore admettre que cette vapeur n'est pas refroidie par l'eau du vase, et par conséquent qu'elle a cette température de 182° ; on peut supposer cette supposition, qui n'est faite que pour arriver au moyen d'explication, en imaginant la vapeur contenue dans une enveloppe flexible, mais imperméable à la chaleur.

maintenant que ce volume 2 de 0,^{mc}262 est au fond du cylindre il a du chasser en D une portion de l'eau qu'elle remplissait en entier il a soulevé toute la colonne K a chassé un volume d'eau égal au sien il a donc développé une force mesurée par ce volume multiplié par la hauteur totale du vase, ou 10^{km} × 0,262 = = production ?!

C'est le nombre qui est dû à 182° dans la colonne des puissances mécaniques, K qui est formée des produits des nombres de la colonne des volumes multipliés par les hauteurs que le cylindre doit avoir pour produire une pression égale à celle que la température a développée dans 1 kil de vapeur.

mais ce volume 2 est plus léger que l'eau il montera donc en b, puis en a, en d, en e, ... et comme à chaque fois il porte une moindre colonne de liquide, il est moins pressé, K par là on voit, il spread un rôle croissant, que la figure exprime. à chaque augmentation de volume une nouvelle quantité d'eau s'échappe en D du cylindre, en sorte que quand la vapeur a été par l'étroite en 2, elle continue de développer de la force, K cette force due à l'expansion de la vapeur est ce qu'on nomme détente.

pour mesurer cette détente, il faut remarquer que à mesure que la vapeur se dilate, elle se refroidit : en sorte que en 2, elle aura plus que des degrés qui dans notre table décroit de 5 en 5. Et il est utile de supposer encore que la température de l'eau du cylindre est décroissante selon la même loi, pour que la vapeur reste dans l'état desiré, ou que les parois de l'enveloppe flexible qui la soutient, se dilate sans permettre la transmission de la chaleur.

on calculera donc de 5 en 5 degrés quel est l'accroissement de volume que prend la vapeur sous la pression correspondante, K on multipliera par la hauteur du vase qui l'enfermait où elle se trouve alors dans le vase. ces produits sous le titre d'expansion seront placés dans une colonne.

Enfin lorsque la vapeur est arrivée au haut du cylindre, la quantité d'eau élevée en totalité est la somme de la puissance développée en 2 sous le titre de production, plus tous les effets successifs de l'expansion, ou la somme de tous les nombres de cette dernière colonne cette somme opérée sur ce à chaque terme successif, est inscrite dans la colonne Détente. (Voyez la page qui suit la table)

formed at the bottom of a tall container full of water. The production of the steam, supposed to be contained in a bubble impermeable to water and to heat and to be at a pressure equal to that exerted by the column of water in the vessel, would cause some water to overflow. Hence an amount of mechanical power equal to the product of the height of the vessel and the mass of water expelled would be expended. As the bubble of steam then rose in the vessel, experiencing an ever decreasing pressure, it would expand still further, expelling more water and giving rise to additional mechanical power. The mechanical power produced in the first stage, which Clément later termed the process of 'production',[1] was easily calculated from the readily available tables of vapour pressure, but the calculation of that produced in the second part, the 'détente', required the further acceptance of a 'law'[2] which Clément and Desormes announced earlier in their 1819 paper. By experiments involving an ice-calorimeter they had been able to show, to their own satisfaction at least,[3] that the quantity of heat in unit mass of any given saturated vapour was always the same, being independent both of its temperature and pressure. In the process of 'détente', therefore, the expanding steam would remain saturated, so that its pressure and

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1. Clément, Lectures A and B, passim.

2. On earlier versions of the 'law' proposed by Watt and Hachette see Dickinson, Lectures, i. 190 and N. Clément-Desormes, Bull. Soc. Phil., (1826), 53.

3. Though not to that of Carnot, at least by 1827, (see the manuscript reproduced in M. A. Gabbey and J. M. Merival, Rev. Hist. Sci., xix (1966), 156) or to that of Clapeyron (see Clapeyron, J. de. Polytech., xiv (1834), 153). On the former document see p.212, n.1.

volume at any point, the two quantities required in calculating the mechanical power, could be determined from the vapour pressure tables. In the analogous calculation for gases Clément and Desormes applied their recently published data on specific heats to the principle that the magnitude of the temperature change occurring during adiabatic expansion was determined by a change in specific heat, but the result of their comparison between gases and steam considered as working substances is not known. All we can say is that by 1825[1] Clément was firmly convinced of the superiority of steam.

Of the originality of most of Carnot's work there can be no doubt but, if anyone did influence him in the years immediately preceding the publication of his Réflexions sur la puissance motrice du feu in 1824, this man may well have been Clément. Hippolyte Carnot records[2] that, in the later 1820s at least, the two men were close friends and that Carnot was a frequent visitor to the Conservatoire des Arts et Métiers, where since November 1819 Clément had held the newly established chair of applied chemistry. Carnot, as we have mentioned, had read the paper of Clément and Desormes in its original form by 1824 and the clear distinction which he made early in the Réflexions[3] between the 'motive power' (puissance motrice) produced during the formation of steam in the cylinder of an engine and that produced during its (adiabatic) expansion may well owe something

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1. Clément, Lectures A (lecture of 27 Jan. 1825).

2. H. Carnot, 'Notice biographique sur Sadi Carnot', pp.76-77, in the new edition of the Réflexions published in Paris in 1878.

3. Carnot, Réflexions, pp.17-18.

either to this reading or to a personal contact with Clément. Carnot, of course, added a third stage, condensation, the effect of which was to reduce the net motive power available, and it is significant in emphasizing the similarity between his work and that of Clément that in Clément's lectures of 1827[1] this third stage was introduced without any other modification being called for. It is also possible that the distinction between the first two parts of the cycle was suggested by a rather similar distinction already made by Watt[2] between the stages in the expansion stroke before and after the introduction of steam. Watt's treatment, however, differed in the important respect that it made no mention of the cooling which necessarily accompanied the second of these stages. Thus the credit for perceiving that under idealized conditions the expansion stroke could be considered as consisting of an isothermal phase followed by an adiabatic phase must remain with Clément. A final point of interest in this connection is that Clément was among the few contemporaries of Carnot who read the Réflexions. In January 1825[3] he brought the book to the notice of his pupils, referring to it as 'un ouvrage fort remarquable' and to Carnot as

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1. Clément, Lectures d, passim.

2. See John Robison's article 'Steam' in Encyc. Brit. (3rd edn., 1797), xvii. 765-766, which Carnot had read (Réflexions, p.105n). Watt and Buchotte are mentioned as possible sources for the Carnot cycle by . . . Kuhn in Isis, lii (1961), 573n and in the Actes du IXe Congrès International d'Histoire des Sciences, 1959 (Barcelona & Paris, 1960), pp.533-534. Buchotte's views in fact seem even further from Carnot's than Watt's.

3. Clément, Lectures A (lecture of 20 Jan. 1825).

'un des auditeurs de ce cours', but it was only in the respect already mentioned, the subsequent introduction of a condensation stage, that the lectures reflected Carnot's influence.

We turn now to examine the way in which Carnot applied the fundamental new concepts of the Réflexions to the theoretical study of the thermal properties of gases. Here the closed cycle of operations proved a powerful tool, although errors inevitably arose from Carnot's assumption that the motive power produced in the cycle resulted from the 'fall' of caloric between two temperatures (rather than from its conversion into work). Among those of his results which were correct, at least for a perfect gas, one of the most important was the conclusion that the difference between the volume specific heats at constant pressure and at constant volume must be the same for all gases, under similar conditions of pressure etc. The demonstration[1] depended entirely on the fundamental principle that the motive power produced in a Carnot cycle was not affected by the nature of the working substance, so that, if equal volumes of two gases at the same temperature and pressure were put through the same cycle of operations, they would yield identical quantities of power. If now it were supposed that the cycle operated between two temperatures which were so nearly equal that the contribution to the motive power of the two adiabatic stages could be neglected, it would follow, since Carnot's was the most efficient possible cycle, that equal volumes of all gases would absorb the same quantity of caloric when

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1. Carnot, Réflexions, pp.41-42.

expanded isothermally by the same amount and at the same temperature. Since this quantity of caloric represented the part of $c_p(v)$ which went to effect the volume change during heating, Carnot could then argue that $[c_p(v) - c_v(v)]$ must be the same for all gases. He could even qualify the difference by considering the heating of two identical samples of air, in one case at constant pressure and in the other at constant volume. Temperature increments of one degree, he argued, could be effected either by adding the appropriate quantities of heat, which would be proportional respectively to c_p and c_v, or in each case by a different two-stage process. For the heating at constant pressure the volume of the air could first be reduced adiabatically from V to $\left[V - \frac{V}{116}\right]$ and hence, as Poisson had shown,[1] heated by one degree. It could then be expanded isothermally, absorbing heat until its volume became $\left[V + \frac{V}{267}\right]$, the value which it would have had if it had been heated directly. For the temperature change at constant volume the first stage of the indirect process would be the same but in the second stage the isothermal expansion would be from $\left[V - \frac{V}{116}\right]$ to V. Now it was fundamental to any calorist that the quantity of heat absorbed by the air should be the same whether the direct or the indirect, two-stage process was followed, so that Carnot naturally though falsely assumed that the quantities of heat absorbed during the stages of isothermal expansion were respectively c_p and c_v in each of the two cases. By making the further assumption that these quantities of heat were pro-

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1. Loc. cit. pp. 91-92.

portional to the changes in volume, he could then show that

$$\frac{c_p}{c_v} = \frac{\frac{1}{267} + \frac{1}{116}}{\frac{1}{116}} \approx \frac{1.0}{0.7}$$

and hence that $c_v(v)$ for any gas could be found by subtracting 0.3 from Delaroche and Bérard's values of $c_p(v)$, on the scale where $c_p(v)$ for air was unity.

In this case Carnot was fortunate that his erroneous assumptions had not led him too far astray. But elsewhere in the Réflexions the inadequacy both of the caloric theory and of the experimental data on which he based his argument become very apparent to the modern reader. There are two obvious illustrations. In the first,[1] his proof that the difference between the specific heats of a gas measured at any given temperature but at two different densities ρ_1 and ρ_2 was proportional to $\log \rho_1/\rho_2$, Carnot was misled entirely by his assumption that the heat gained by a gas in passing from one state to another was independent of the path taken. Unfortunately, of course, the belief that variations with density occurred at all was supported by Delaroche and Bérard's results and Carnot was even able to drew up a table of specific heats at different densities[2] on the basis of their single observation on the matter. In the second illustration, his investigation of the dependence on temperature of the motive power pro-

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1. Carnot, Op. cit., pp.56-62.

2. Ibid., p.61.

duced by a given 'fall' of caloric,[1] he relied still more heavily on Delaroche and Bérard, despite his obvious doubts on the dependability of their work.[2] He considered equal masses of air being taken through two cycles working between temperatures 100°C and (100 - h)°C and between 1°C and (1 - h)°C respectively. By applying the limitation that h was very small he was able to ignore the stages of adiabatic expansion and compression, so that the net gain in motive power became simply the difference between that produced by the gas during isothermal expansion and that lost in compressing it isothermally back to its original volume. Provided the processes of expansion were conducted between the same limits of volume in each of the two cycles, the quantities of motive power produced would thus be independent of the temperature at which the cycle operated. This was not the case, however, for the quantities of caloric which underwent the 'fall' in temperature h, as Carnot proceeded to show. He argued that the temperature of a sample of air at 1°C could be raised to 100°C with any desired accompanying increase in volume in two ways. It could be heated to 100°C at constant volume and then expanded isothermally or, alternatively, the isothermal expansion could be effected at 1°C and the air could then be heated to 100°C. Once again he made the crucial mistake of supposing that the quantities of heat absorbed in the two processes were equal. Thus, by accepting Delaroche and Bérard's data as evidence that the quantity of heat

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1. Ibid., pp.66-79.
2. Ibid., p.73.

required to bri g about the rise in temperature increased with decreasing pressure, he was able to conclude that the quantity of heat absorbed during an isothermal expansion between any two given volumes was greater at higher temperatures and hence, as he put it, that 'La chute du calorique produit plus de puissance motrice dans les degrés inférieurs que dans les degrés supérieurs'.[1] In this case, the conclusion, an important one in the theory of heat-engines, happened to be correct, with the effects of the two caloric errors in Carnot's argument cancelling each other out. But in other cases he was less fortunate. We have already noted his erroneous conclusion concerning the dependence of variations in specific heat on changes in density and it was in part this same error which led him to another false relationship, this time between the volume and temperature of a gas undergoing adiabatic volume changes. Again we see how he was misled by the caloric theory, for he argued that the rise in temperature during an adiabatic compression could be determined by considering the process in two stages, isothermal compression followed by the absorption by the gas of the heat expelled in the first stage, the volume of the gas in this second stage being kept constant. He had already shown,[3] by an unexceptionable argument which involved none of the erroneous tenets of caloric theory, that the amount of heat evolved during the isothermal compression of a gas

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1. Ibid., p.76.
2. Ibid., pp.62-68.
3. Ibid., pp.52-53. See also Ibid., pp.73-76n.

from volume V_1 to V_2 at any given temperature was $\left[A + B\log\frac{V_2}{V_1}\right]$, where A and B were unknown constants. The expression, as we see, reduces easily to the correct one, $K \log\frac{V_2}{V_1}$, with K here being a function of temperature only. By now using this expression in conjunction with that for the specific heat of the gas at volume V_2, which also had the form $\left[A' + B' \log\frac{V_2}{V_1}\right]$, Carnot could deduce that the rise in temperature during the adiabatic compression from V_1 to V_2 was $\left[\frac{A + B \log V_2/V_1}{A' + B' \log V_2/V_1}\right]$, an expression differing considerably from Poisson's.[1] Unfortunately Carnot made no comment on the discrepancy and it is not absolutely certain that he even knew of Poisson's derivation in 1824, although he appears to have read another of his papers in the same volume of the Annales de Chimie et de Physique in which the $TV^{\gamma-1}$ = constant relationship was announced.[2]

Carnot's manuscript notes[3] indicate that he had abandoned the caloric theory before his death in 1832 and that he had substituted a vibrational theory in which motive power was only gained if a corresponding amount of heat was consumed. Unfortunately we have no evidence that Carnot ever investigated the full implications of his new theory and the only complete

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1. See p.199 Cf. also Poisson's expression in Bull. Soc. Phil., (1820), 97-101.

2. Carnot, Op. cit., p.43n.

3. Ibid., pp.125-151.

paper which was written by him after 1824[1] concerns an attempt to derive an expression for the motive power produced by steam in an engine operating between temperatures which differed by an appreciable amount, as opposed to the 'fall' of only 1 deg C used in the Réflexions.[2] The most important change which this entailed was that the motive power produced during the stage of adiabatic expansion now had to be calculated. Clément, in fact, had already done this for particular cases[3] but the derivation of a general expression, although it depended wholly on the correctness of Clément and Desormes's law and probably leant heavily on Clément's treatment, was something new. When, in a lecture on 8 March 1827, Clément dictated Carnot's result, without any explanation, a student wrote:

> La formule algébrique n'est ici que comme sujet d'exercice pour ceux qui voudront l'employer; toutefois, le Professeur avoue qu'il n'en a jamais fait usage; il préfère le calcul arithmétique. Elle lui a été donnée, dit-il, par un mathématicien distingué.[4]

Few people were impressed by Carnot and after a single (highly favourable) review of the Réflexions[5] ten years elapsed before the French engineer

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1. H. A. Gabbey and J. M. Merivel, 'Un manuscrit inédit de Sadi Carnot', Rev. Hist. Sci., xix (1966), 151-166. Gabbey and Merivel are unable to date the manuscript but believe that it probably antedates the Réflexions. However, a reference in Clément's lectures (see this page) suggests that it was written early in 1827. This dating is also more consistent with the contents.

2. Carnot, Op. cit., pp.62-86.

3. e.g. in Clément, Lectures A (lecture for 24 Jan. 1825). See also Plate 3 and Desormes and Clement, Bull. Soc. Phil., (1819), 117.

4. Clément, Lectures A (lecture for 8 Mar. 1827).

5. C. M. Girard, Revue encyclopédique, xxiii (1824), 411-414.

Émile Clapeyron again drew attention to his work.[1] In a lengthy paper Clapeyron sought to give Carnot's results the analytical form which they did not have in the Réflexions and he also introduced the now familiar indicator diagram to illustrate the argument. Throughout he adhered to the basic principles of caloric theory. For him, as for Laplace, Poisson and Carnot, the amount of caloric in a gas, φ, was a function only of pressure and volume, so that the heat gained or lost in any change of conditions was given by

$$d\varphi = \left(\frac{\partial \varphi}{\partial V}\right)_P dV + \left(\frac{\partial \varphi}{\partial P}\right)_V dP \quad \ldots(1)$$

From this Clapeyron was able to derive the equation which was fundamental to the whole paper, namely that for a perfect gas φ was equal to $R(B - C \log P)$[2] where B and C were unknown functions of temperature. Invoking unspecified experimental evidence, presumably Dulong's,[4] Clapeyron deduced that B must be the same for all elementary gases at least. C, on the other hand, was certainly independent of the nature of the gas, for it could be shown from the Carnot cycle that the greatest quantity of motive power obtainable from a given quantity of heat 'falling' through dt degrees was dt/C. C was in fact proportional to the absolute temperature T, but Clapeyron knew only

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1. B. P. Clapeyron, 'Mémoire sur la puissance motrice de la chaleur', J. de. polytech., xiv (1834), 153-190.

2. Ibid., 166.

3. Ibid., 167.

4. See p.208.

that it was some function of temperature, although he was able to show, by an argument which involved the acceptance of Delaroche and Bérnard's results, that it increased very slowly as a gas was heated.[1] So once again the derivation of this perfectly correct result depended principally on the false assumption and evidence that the specific heat of a gas was influenced by changes in its volume.[2] The rest of the paper was devoted largely to showing how Carnot's results could be derived from equation (1), but there are other points of interest, notably the first announcement[3] of the famous Clapeyron (or Clausius-Clapeyron) equation.

It should now be clear that Carnot occupies a somewhat isolated place in our story. Certainly the basic principles of his caloric theory and the experimental evidence which he used in expounding it would have been accepted by all caloricists in the 1820s, but there is too much in Carnot's work which distinguishes him from Laplace and Poisson for us to accept him as a Laplacian. His background, as has been recently pointed out,[4] was firmly in the traditions of power technology and his association with Clément only emphasizes the fact. Thus, despite the contributions which he made to the study of the thermal properties of gases, Carnot had no close contact with any major theoretical school and he stands virtually independent both of the

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1. Clapeyron, Op. cit., 182.

2. Although Clapeyron gave other supporting evidence (Ibid., 183-185).

3. Ibid., 171-173.

4. D. S. L. Cardwell, 'Power technologies and the advance of science, 1700-1825', Technology and Culture, vi (1965), 188-207.

first caloricists and of those, such as Dulong, who were already beginning to attack the caloric theory.

Other Work

With Carnot and Clapeyron we come to the end of our consideration of the work of the great French caloricists. It is true that even after Laplace's death Poisson continued to work in the context of caloric theory but, when his Théorie Mathématique de la Chaleur appeared in 1835 it was a relic of a bygone age and was seen as such by his contemporaries.[1] By the 1830s the prevailing attitude towards the nature of heat was one of agnosticism, with caloric no more than, at best, a useful aid to thought. Indeed, when we consider the isolation in which Laplace and Poisson worked even in the early 1820s, it seems likely that this same attitude was widespread in the previous decade also. There were no Laplacian disciples to develop the theory further and most of those who did pursue the theoretical study of heat in terms of caloric were, like Carnot, of little standing in the scientific community. Navier is a notable exception here, but his paper on the temperature variations accompanying rapid changes in the volume of a gas, first published in July 1820,[2] was hardly worthy of his already considerable reputation. Taking it as a basic experimental fact that the specific heat of a gas varied with its density and making certain other assumptions

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1. See pp.310-311.

2. C. L. M. H. Navier, 'Sur la variation de température qui accompagne les changemens de volume des gaz', Bull. Soc. Phil., (1820), 97-101.

which were still less justified, Navier showed that for any given gas the rise in temperature - t occurring during adiabatic compression was proportional to $\log c_1/c_2$, where c_1 and c_2 represented the gas's specific heat before and after the compression. His examination of the results of both Clément and Desormes and of Delaroche and Bérard led him also to the empirical relationship for the specific heat of air at any pressure h:

$$c = 0.76 \sqrt{\frac{1}{h} + 0.42},$$

where c = unity at h = 0.76 m of mercury, and hence to the conclusion that, even for $h = \infty$, Δt could not exceed 360 deg C, a result which few, and certainly not Gay-Lussac for example,[1] would have accepted. There was no limit, on the other hand, to the degree of cold obtainable, as Gay-Lussac had recently been suggesting.[2] The eclecticism of Navier's attitude to the existing experimental evidence and theories emphasizes his independence of the leading caloriste. In the study of heat Navier was no more than an interested amateur and he can hardly have been surprised, or greatly distressed, that his results, despite his attempt to apply them to the familiar problem of the economy of heat-engines,[3] were ignored. Laplace, after all, was the professional in the field of caloric theory and even he hardly obtained a hearing.

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1. See p.167.

2. Ibid.

3. C. L. M. H. Navier, 'Note sur l'action mécanique des combustibles', Ann. Chim. Phys., xvii (1821), 357-372.

If we were to assess the merits of scientific contributions in terms of their bulk alone, there could be no doubt that two of the most important writers on heat in the 1820s were the Scotsman James (later Sir James) Ivory and Henry Meikle. Ivory's concern with the subject arose from his work on astronomical refraction, for his acceptance of an explanation for the decrease in atmospheric temperature with altitude similar to Darwin's[1] led him naturally to an interest in the relationship between the temperature, volume and pressure of air expanding adiabatically. When Poisson's expressions became known he adopted them readily, first with $\gamma = 4/3$[2] and later with $\gamma = 11/8$.[3] His numerous papers on this and related topics which followed contained little that was original, although the clarity with which he expounded Laplace's distinction between the latent heat required to effect expansion and the sensible or free heat which went to increase temperature is noteworthy.[4]

Between 1827 and 1829 Ivory's view on heat brought him into an acrimonious dispute with Meikle.[5] Like Ivory, Meikle accepted Poisson's expre-

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1. J. Ivory, Phil. Mag., lviii (1821), 25.

2. Ivory, Phil. Mag., lxvi (1825), 9.

3. Ivory, Phil. Mag., [2] i (1827), 93.

4. See, for example, Phil. Mag., lxvi (1825), 4-6; Ibid., [2] i (1827), 90-93; Ibid., 168-170; Ibid., [2] iv (1828), 322-326; Ibid., [2] v (1829), 105-106.

5. H. Meikle, Edin. New Phil. J., iii (1827), 149-157; Quart. J. Sci., [2] iv (1828), 124-135 and 315-319; Ibid., [2] v (1828), 57n, 58-59 and 62; Ibid., 109-113. Ivory, Phil. Mag., [2] iv (1828), 321-326; Ibid., [2] v (1829), 104-106.

sions relating to adiabatic volume change, although as a result of experiments of his own,[1] he supposed γ to be 4/3. Yet there was much in the earlier caloricists' work which he rejected. He could not agree, for example, that the addition of equal quantities of heat to an air thermometer caused equal increments of volume[2] and he showed[3] by a perfectly sound argument that a necessary consequence of Gay-Lussac and Welter's demonstration that γ was independent of pressure and temperature was that the specific heat of a gas must be unaffected by changes in volume, although he did not deny the variation with temperature.

One of the few points of agreement between Ivory and Meikle is found in their acceptance of $\sqrt{\gamma}$ as the correction factor to be applied to Newton's expression for the velocity of sound. In this they were merely reflecting the mood of the time, for Laplace's solution of the discrepancy between theory and experiment had won general approval. There were critics of course. Notable among these was John Herapath, an early exponent of the kinetic theory of gases, who in 1830,[4] following an earlier vigorous attack[5] on the work of Laplace and Poisson on the caloric theory of gases, managed

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1. Meikle, Edin. New Phil. J., vi (1828), 28.

2. See especially Meikle, Edin. New Phil. J., 1 (1826), 332-336.

3. Ibid., 339-340; Ann. Phil., [2] xii (1826), 367-369; Quart. J. Sci., [2] v (1829), 65-67.

4. J. Herapath, 'On the velocity of sound and variation of temperature and pressure in the atmosphere', Quart. J. Sci., [2] vii (1830), 167-175.

5. Herapath, Phil. Mag., lxii (1823), 61-66, 136-139 and 328-338n.

to remove the discrepancy by the simple device of inserting an unexplained[1] factor $\sqrt{2}$ under the square root sign in Newton's expression. Herapath's views, not surprisingly, attracted little attention and nearly twenty years passed before Laplace's identification of Newton's error once again became an important issue. The causes of this revival of interest were James Challis, Plumian Professor of astronomy and experimental philosophy at Cambridge, and Richard Potter, professor of natural philosophy and astronomy at University College, London, both of whom[2] put forward the extraordinary criticism that, since rarefaction as well as compression occurred in a sound wave, a diminution in the velocity of sound was quite as likely by Laplace's argument as an increment. The response to this naive suggestion and to the alternative solutions which the two men proposed were swift and crushing, with the Astronomer Royal, G. B. Airy, replying to Challis in 1842 and Professor J. T. Stoker, William Hamilton, the Rev. Samuel Haughton, Fellow of Trinity College, Dublin, and Auguste Arthur Prevais, professor of physics at the École Polytechnique all rising in immediate defence of Laplace[3] when Potter's views were published in 1851.

The authority of this response only emphasizes how widely Laplace's

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1. Explained later in J. Herapath, Mathematical Physics (London, 1847), ii. 63.

2. J. Challis, Phil. Mag., [3] xxxii (1848), 283-284 and R. Potter, Phil. Mag., [4] i (1851), 151.

3. G. B. Airy, Phil. Mag., [3] xxxii (1848), 339-343; G. G. Stokes, Phil. Mag., [4] i (1851), 305-317; W. J. M. Rankine, Ibid., 225-227; W. Haughton, Ibid., 332-334; A. Prevais, Ann. Chim. Phys., [3] xxxiv (1852), 82-89.

work on sound had become accepted and how successfully it survived the development of the new science of thermodynamics and the final, definitive rejection of caloric. That the $\sqrt{\gamma}$ factor should have been generally accepted by caloricts was not surprising, since Laplace's derivation of it in 1816 had involved only limited assumptions concerning the properties of caloric and ones to which no one could have seriously objected. The really suspect parts of Laplace's caloric theory, on the other hand, the 1816 determination of γ and the speculative treatment developed after 1821, could be, and for the most part were, rejected quite independently. With the advent of thermodynamics the situation underwent little change. The cause ascribed to the production of heat in the compression of a gas was now different, of course, but the fact that it did occur and that it affected the velocity of sound was not in serious doubt and even the correction factor was seen to the right one.[1] Laplace was fortunate that the erroneous view of the adiabatic compression process as equivalent to an isothermal compression followed by heating at constant volume which he adopted in 1816 was a good approximation to the truth for the small changes in density which occur in sound waves and in this respect he must be contrasted with Carnot, who was led into serious error by similar basic assumptions. The correction factor has therefore undergone no modification since it was first derived by Laplace and it remains a solitary reminder in modern physics text-books that the theory of heat must be numbered among the most important interests of this great mathematical physicist.

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1. J. P. Joule, Phil. Mag., [3] xxxi (1847), 114-115.

CHAPTER 5

The Caloric Theory of Amedeo Avogadro

If we now went straight on to examine the process of the decline of caloric theory, our narrative would have continuity and every appearance of completeness. However, in doing so we should not only be ignoring one of the most elaborate of all the treatments of the theory but we should also be missing a much needed opportunity of increasing our understanding of its author, the Italian Amedeo Avogadro. As the originator of the celebrated hypothesis that, under similar conditions of temperature and pressure, equal volumes of all gases contain equal numbers of molecules, Avogadro is familiar enough, but of his other activities all too little is known. In his work on caloric theory in particular he appears in a somewhat unaccustomed light, not as the chemist of profound insight whose views were misunderstood in his lifetime, but as a physicist clinging to a discredited theory of heat. His voluminous writings on the theory, which we shall be examining in this chapter, can have done little to enhance his stature in the scientific community and it seems that this factor should at least be born in mind in any attempt to account for the neglect of his gas hypothesis between 1811, when it was first proposed, and 1860 when it was finally acclaimed at the Karlsruhe congress four years after his death.

It is in order to illustrate the outdated character of much of Avogadro's thought that we begin with an attempt to identify the research tradition in which he was working.

Affinity for Light

In Chapter 4 we saw that one of the main principles underlying Laplace's work in physics was his attempt to extend the concepts established in his treatment of gravitational forces from the celestial to the molecular scale. In chemistry too a similar approach was being attempted in the first few years of the nineteenth century by Laplace's close friend Berthollet. Since Avogadro's early scientific work was conducted in the years when these two men were at the height of their powers and when French influence in Italy, if only for political reasons, was considerable, it is not surprising to find that his treatment of specific heats as being determined by a characteristic attractive power between a particle of ponderable matter and the surrounding caloric owed much, both in detail and general conception, to the views on affinity developed in Berthollet's Essai de Statique Chimique of 1803.[1] One of Berthollet's greatest innovations in the study of affinities had been to take specific account of the masses of the reactants in a chemical reaction. He had emphasized his belief in the gravitational nature of chemical forces by putting the 'chemical action' of a substance, i.e. the measure of its tendency to combine chemically with another given substance, proportional to its own mass multiplied by its characteristic affinity for the second substance. Although earlier writers, notably Bergman,[2] had already suggested that the mechanism of chemical

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1. See especially Berthollet, Statique Chimique, i. 1-22.

2. Bergman, Opuscula, iii. 291-294.

affinity was gravitational, the explicit distinction between the effects of mass and affinity was quite original and its influence was soon to be felt not only in chemistry but also in attempts to extend the new principles to embrace imponderable matter, in the first instance light particles. This important extension was first made by Biot and Arago in their experimental work on the refractive powers of gases which they announced to the Institute in 1806.[1] Since it is not difficult to find close parallels with Avogadro's work in this paper and since here also the debt to Berthollet and Laplace was made explicit by the authors' profuse acknowledgements,[2] it is a significant document for our purpose. Avogadro was familiar with it[3] and probably owed much to the treatment of the forces between ponderable and imponderable matter which it contained.

The application of what were essentially Newtonian principles to light was not new. Newton himself treated refraction as the result of a 'refracting force' between the transparent material and light[4] and, in 1750, G. L. Le Sage had even advocated the inclusion of light in a table of affinities.[5] Nevertheless, to early nineteenth-century writers it must

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1. J. B. Biot and F. J. Arago, 'Mémoire sur les affinités des corps pour la lumière et particulièrement sur les forces réfringentes des différens gaz', Mém. Inst. Fr., vii (1806), 301-387.

2. Ibid., 304.

3. Ibid., pp.242-243.

4. Newton, Opticks (4th edn., London, 1730), pp.245-251.

5. G. L. Le Sage, Essai de Chymie Méchanique (Geneva, n.d.), pp.50-52. For other work on similar lines see H. Metzger, Newton, Stahl, Boerhaave et la Doctrine Chimique (Paris 1930), pp.68-82.

have been the 1806 paper which represented the modern approach to the problem, especially since it had the backing of such great names.

The instigator of the experiments was Laplace, who had elaborated Newton's treatment of refraction in terms of attractive forces in the fourth volume of his Mécanique céleste, published in 1805.[1] It was he who persuaded the Institute to organize the experimental work and he was no doubt instrumental in arranging for the appointment of Biot, who in turn engaged Arago as his assistant. As would be expected at a time when the materiality of light was in little doubt, least of all for such a close disciple of Laplace as Biot, the results were given in terms of refractive power (p) and not of refractive index (i). Laplace had retained Newton's concept of a refracting force, $(i^2 - 1)$, as the measure of the force of attraction which a body exerted on incident particles of light, the magnitude of the force being proportional to the increase in the square of the velocity of these particles, which was supposed to occur in accordance with the normal laws of dynamics. Since the force, a gravitational one, was thought to vary in proportion to the density of the material, the refracting force divided by the density, $\left[\frac{i^2 - 1}{\rho}\right]$, yielded the refractive power the quantity more closely related to the true nature of the substance, and characteristic of it alone. The distinction between the effects of mass and innate affinity was thus already implied in this procedure. Newton himself had obtained a continuous range of refractive powers for some twenty different substances

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1. Laplace, Mécanique céleste, iv. 231-237.

and had tentatively attributed the variations to varying quantities of what he termed 'sulphureous oily particles', but the powers of gases other than air had not been investigated. By 1806 the need to rectify this omission had become pressing. Quite apart from the fact that the experimental re-examination of refraction in gases would provide data for Laplace's immediate problem, atmospheric refraction, and even dispersion, the study of gases in general had now acquired a new significance, as we saw in Chapter 7. Biot and Arago fully shared the prevailing contemporary belief that in gases the laws of nature would appear in their simplest form[1] and there can be little doubt that this provided an important incentive for their work.

But the chief significance of the paper lies in the obvious debt which Biot and Arago owed to the principles of chemical affinity recently established by Berthollet. For anyone working under the influence of Berthollet's chemistry tables of affinity must have represented the most promising means of accounting for and systematizing the properties of matter. The new tables which Berthollet envisaged were intended to go much further than their eighteenth-century counterparts,[2] which provided merely a rule-of-thumb method of predicting the course of a reaction and which lacked any sound theoretical basis. He considered that chemical affinity for a substance such as oxygen, what he termed a 'dominant affinity', would

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1. See p.21.

2. On these see A. N. Duncan, 'Some theoretical aspects of eighteenth-century tables of affinity', Ann. Sci., xviii (1962), 177-194 and 217-232.

account for and allow prediction of a far wider range of properties than those governing the immediate chemical reaction.[1] And 'affinity' for light might be even more revealing, as Biot and Arago commented in a passage which emphasizes their interest in what were essentially chemical problems. They wrote:

> ...l'action des corps sur la lumière ne s'exerçant d'une manière sensible qu'à de très-petites distances, l'intensité de cette action est nécessairement liée à la nature des particules des corps et à leur arrangement, c'est-à-dire à leurs propriétés les plus intimes; de sorte que le physicien qui observe les pouvoirs réfringens des substances pour les comparer entre eux, agit absolument comme le chimiste qui présente successivement une même base à tous les acides, ou un même acide à tous les alcalis, pour déterminer leurs forces respectives et leur degré de saturation. Dans nos expériences, la substance que nous présentons à tous les corps est la lumière, et nous évaluons l'action qu'ils exercent sur elle par leur pouvoir réfringent, c'est-à-dire par l'accroissement de force vive que l'action de leurs particules tend à lui imprimer...Ainsi, la diversité des vîtesses imprimées à la lumière, indiquée par la différence des pouvoirs réfringens, offre une serie très-étendue où tous les corps peuvent se ranger à de grands intervalles, et qui peut par conséquent servir soit pour distinguer et caractériser leur nature, soit pour suivre en quelque façon leurs traces, et reconnoître leur présence dans les combinaisons.[2]

The mere fact that the eight gases examined were found to have widely differing refractive powers was sufficient evidence that the first of the two aims mentioned in the last sentence of this quotation had been attained. The effect of a chemical reaction on the characteristic affinities was more problematical, however, but it seemed likely that there was some connection between the high refractive power of ammonia, for example, and

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1. Berthollet, Statique Chimique, i. 61 and ii. 3-6.

2. Biot and Arago, Op. cit., 325-328.

the fact that one of its constituent elements was hydrogen, which had a power higher than that of any other gas. Berthollet, whose work had been purely qualitative, had offered no solution of the analogous problem for ponderable matter, except in so far as he believed it reasonable to suppose that a property so closely linked to the essential nature of a substance as affinity was somehow conserved.[1] Yet the substance would retain only that part of its affinity, and hence of its characteristic properties, which was not neutralized by the effect of the other reactant. This was as far as Berthollet could go, since there were too many unaccountable factors, such as the effect of the change in volume during a reaction, for the matter to be treated quantitatively. Affinities for light, on the other hand, were subject to no such difficulties, at least in the opinion of Biot and Arago. They maintained[2] that the smallness (ténuité) of the light particles by comparison with the distance between the particles of ponderable matter would diminish any effect which a change in volume in a reaction might have, so that the refractive power of a compound would be determined in a predictable way by those of its constituents, except in cases where very great decreases in volume occurred. Moreover, they had no qualms about extending Berthollet's principles of affinity, with necessary modifications, to imponderable matter. It was assumed that each substance

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1. Berthollet, Op. cit., i. 300-332. See also his Recherches sur les Lois de l'Affinité (Paris, an IX), 62-69.

2. Biot and Arago, Op. cit., 329-330.

had a characteristic affinity for light independent of its affinity for other substances, so that the contributions of the various elements making up a compound would be unaffected by the chemical reaction. Also, since it was axiomatic that the attractive force exerted by any given body was proportional to its mass, it followed that the respective contributions of the reactants to the refractive power of the resulting compound would be proportional to the weights in which they combined. On this basis it was possible to establish a conservation law in which the refractive powers of reactants and compound were intimately related. The law[1] was expressed as follows:

$$px + p'x' + p''x'' + \ldots = P \qquad \ldots(1)$$

where x, x', x''...were the masses of the various elements of refractive power p, p', p''... which combined to form unit mass of a compound of refractive power P. In the case of air, a mixture, the refractive power calculated from those of its constituent gases was within 0.6% of the observed value. The calculated and experimental values for ammonia, a compound in the formation of which a comparatively small decrease in volume occurred, showed even closer agreement, so close in fact as to suggest that such observations might be used in the determination of the composition of compounds by weight. In the case of water, the only other compound for which a test was possible, the discrepancy of over 10% was serious, but this was readily dismissed as the effect of the large decrease in volume,

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1. Ibid., 330n.

an explanation which was sanctioned by Berthollet's own views on the effect of volume changes on affinity.[1]

Largely because of the lack of precise data concerning the composition of compounds, Biot and Arago's treatment, supported by results for only one gaseous compound, was far from vindicated and, although J. B. J. Delambre's contribution to the Institute's History for 1806 contained a glowing account of their work and of its importance in many branches of science,[2] the promise of the optical method of investigating the properties of matter was never fulfilled. When Arago and Petit re-examined the matter in 1815[3] they could find no justification for a simple relationship of the type expressed in equation (1) and they cast grave doubts on the corpuscular theory as a whole. The sequel is well known. The growing popularity of the wave theory, despite the opposition of such influential figures as Laplace and Biot, was soon to put a decisive end to work on ponderable matter based on the search for characteristic affinities for light.

Affinity for Heat

The situation regarding the theory of heat was rather different. For all its apparent inadequacy, there was no obvious alternative to caloric theory which had the stature of the wave theory of light and it is therefore

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1. Berthollet, Statique Chimique, i. 312.

2. J. B. J. Delambre, 'Analyse des travaux de la Classe...partie mathématique', pp.9-11, in Mém. Inst. Fr., vii (1806).

3. D. F. J. Arago and A. T. Petit, Ann. Chim. Phys., i (1816), 1-9.

not surprising to find that problems analogous to those treated by Biot and Arago were being tackled in terms of caloric even after 1815, with specific heat replacing refractive power as the significant observable quantity. We have already seen[1] that the prediction of the specific heat of a compound from those of its constituent elements was possible in the Irvinist version of caloric theory, but even here the solution was not simple, if only because it required a knowledge of the heat evolved in the relevant reaction. For someone holding the rival 'Laplacian' view the problem was even more complex, of course, but the conviction that the specific heat of a compound and those of its constituents were somehow related was present among these caloricts also. Delaroche and Bérard, for example, concluded their prize-winning memoir:

> Il ne faut pas croire cependant qu'il n'existe aucune relation entre la chaleur spécifique des composés et celles de leurs élémens; trop de faits attestent cette relation pour qu'on puisse la nier. L'eau présente à cet égard le plus grand écart qui soit bien constaté, et cependant il ne va qu'à 1/3 de la chaleur spécifique de ce fluide; en général, on peut dire que les composans communiquent au composé leur chaleur spécifique. Cela s'observe d'une manière bien marquée dans les combinaisons de l'hydrogène, celui de tous les corps dont la chaleur spécifique est la plus considérable; les composés qu'il forme ont une chaleur spécifique beaucoup plus grande que celle des autres substances: de là vient la grande chaleur spécifique de l'eau, du gaz oléfiant et des substances végétales et animales.[2]

But in the absence of any knowledge concerning either the relative quantities of the two types of caloric in a body or of their relationship with the only observable quantity, specific heat, the problem remained unsolved and

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1. See p.154.

2. Delaroche and Bérard, Ann. Chim., lxxxv (1813), 175-176.

even Laplace's definitive version of the caloric theory of gases was to throw no light on the problem.

The deduction of some quantity which would characterize substances and allow a meaningful classification of them was another problem which was attracting attention, although the approaches were very different from that which Biot and Arago had adopted in 1806. In 1815 Arago and Petit, having abandoned the corpuscular theory of light, did not even mention this application of studies of refraction and in the same year A. M. Ampère pointed out the inadequacy of Berthollet's somewhat similar proposals for the classification of elements,[1] based on affinity for oxygen, a quantity which Ampère considered to have no significance. In rejecting the uniqueness of oxygen, which he believed Lavoisier had overemphasized, he stressed the need for a 'natural' classification which would emphasize analogies by grouping together similar substances, suggest the best procedure for further investigation of their properties and allow the prediction of the properties of a compound in terms of those of its constituents. Affinities could not provide the answer and Ampère's classification was to be based on purely observable chemical properties only. In the search for a system of classification, specific heats were not overlooked, but the only reliable data, those of Delaroche and Bérard, appeared to be quite unrelated to such properties as acidity or basicity. Biot himself

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1. A. M. Ampère, 'Essai d'une classification naturelle pour les corps simples', Ann. Chim. Phys., i (1816), 295-308 and 373-394, and ii (1816), 5-32 and 105-125.

seems to have looked in vain for some correlation and he suggested in 1816 that his failure might be due to the fact that specific heats had normally been measured at constant pressure and so included the heat required both to raise the temperature and to cause expansion. He commented:

> tant que ces deux effets ne seront pas séparés par l'expérience, les chaleurs spécifiques, telles qu'on les observe, seront des résultats composés; et peut-être est-ce cette composition qui jusqu'à présent empêche d'y découvrir aucune relation évidente avec la nature chimique des corps.[1]

According to Biot,[2] Dulong was at this time engaged on measuring the specific heats of vapours at constant volume and it seems at least possible that the experiments were being conducted with the end in view which Biot saw, for he showed great familiarity with Dulong's work. But the failure of the very difficult experiments was only to be expected and the results were never published. Thus, despite this work and despite Crawford's crude attempts some forty years earlier, it was not until 1890[3] that the direct measurement of specific heats at constant volume became a practical possibility. Why Biot looked to specific heats for help in this problem is not clear and there is no definite evidence that he saw any special analogy with his work on refractive power. In 1816, however, he was still greatly influenced by Laplace and Berthollet, as his praise for their work in the Traité de Physique[4] and his dedication of the book to Berthollet

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1. Biot, Traité de Physique, iv. 728.
2. Ibid., 728-730.
3. J. Joly, Proc. Roy. Soc., xlviii (1890), 440-441.
4. Biot, Op. cit., passim but especially i. pp. i-ii and xxiii-xxiv.

emphasize. Moreover, his professed agnosticism towards the nature of heat scarcely conceals a preference for the material theory, which he felt was supported by the analogies between heat and light revealed by recent work on radiation.[1] So it is quite conceivable that Biot did expect the correlation with chemical properties which he had observed for refractive powers to be repeated somehow in terms of specific heats but, in the absence of any developed theory of affinity for caloric, he would have had difficulty in taking the matter further. And this is to say nothing of his own doubts whether it really was affinity that retained caloric in bodies in any case.[2]

Such, then, was the state of the problem which Avogadro first tackled in 1816. In understanding his approach it seems important to begin by emphasizing his isolation, especially from Paris. He had few contacts, even in Italy, and very rarely travelled abroad.[3] Hence he was not influenced by the growing crisis in the Laplacian programme for physics and he had none of the scepticism towards imponderable fluids felt by certain younger French scientists even before 1820. On the other hand, even though he was a calorist, he was in no way committed to the Laplacian version of the theory, which had still to reach its highest stage of development despite the notable and effective victory which it had already won over its Irvinist

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1. Ibid., iv. 611-617. Biot's views on caloric are a little clearer in his biographical sketch of Petit (Ann. Chim. Phys., xvi (1821), 334).

2. Biot, Traité de Physique, iv. 730.

3. See I. Guareschi's introduction to Opere Scelte di Amedeo Avogadro (Turin, 1911).

rival. Thus Avogadro was able to devise a caloric theory which borrowed something from both the main versions of caloric theory. His isolation was important in other ways also, for it allowed him to continue to use Berthollet's increasingly unpopular theory of affinities and to apply his gas hypothesis effectively and with every confidence. These were opportunities denied to contemporary French scientists, working as they were in a more tightly defined context of acceptable theories and results.

Like Dalton, Avogadro believed that gases were composed of particles of ponderable matter each surrounded by a sphere of caloric which was retained by an attractive force between it and the particle. It was this force, he maintained, which determined the quantity of caloric in any given molecule and he thus differed from Dalton, for whom the quantity of caloric was the same in all molecules under similar conditions of temperature and pressure, irrespective of the magnitude of the force. For Dalton also, and in particular for his second theory of mixed gases, it had been fundamental that the size of a gas molecule was determined by its chemical nature and here again Avogadro differed. Since he accepted, like Dalton, that adjacent gas molecules were in contact, it followed from his hypothesis that they must be of the same size in all gases and he naturally enough showed an interest in Dalton's diffusion problem when he first announced the hypothesis in 1811.[1] The immediate inspiration for his views was Gay-Lussac's law of combining volumes, which Dalton could not accept.[2] Despite

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1. Avogadro, J. Phys., lxxiii (1811), 58-76.

2. Dalton, New System (1810), i (pt.2). 555-560.

he independent derivation of a somewhat different version of the hypothesis by Ampère in 1814,[1] there were few contemporaries who accepted Avogadro's view of gas structure and such acceptance as there was was only partial. Berzelius, for example, considered the number of gas molecules per unit volume to be identical in elementary gases only[2] and the same may well be true of Dulong and Petit.[3] And we can be sure that none of these men, all of whom rejected caloric theory before 1820, would have entertained Avogadro's views on molecule size. This latter comment undoubtedly applies to Joseph Mollet who, in 1817,[4] expounded the view that equal volumes of all gases did contain equal numbers of molecules, as Avogadro had said, but that the sizes of the molecules varied according to the nature of the gas. His molecules, of course, did not touch one another.

To Avogadro's view of gas structure provided him with a unique tool for the development of caloric theory. In fact, he did not examine the implications of his hypothesis for the theory of heat in his 1811 paper nor in the supplement to it written in 1814,[5] but once the implications could be examined in conjunction with Delaroche and Bérard's results some very pertinent conclusions could be drawn. Avogadro described them in the obscure journal Bibliotega Italiana, published in Milan, in December

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1. A. M. Ampère, Ann. Chim., xc (1814), 43-86.

2. J. J. Berzelius, Essai sur la Théorie des Proportions Chimiques... (Paris, 1819), pp.52-54.

3. ce p.247.

4. J. Mollet, J. Phys., xc (1820), 113-130.

5. Avogadro, J. Phys., lxxviii (1814), 131-156.

1816 and January 1817.[1] He argued that, by his hypothesis, the volume specific heats of all gases would represent the quantities of heat which identical numbers of molecules must receive in order that their temperature should rise by one degree. The possibility that a readily observable thermal property might thus be used for the examination of matter on the molecular scale was attractive and one which Avogadro's views on caloric and the constitution of gases alone made practicable. By introducing the additional assumption that the quantity of caloric required to produce a given temperature increment in unit volume of any gas was determined solely by the characteristic 'attractive power' (potere attrattivo) of the molecules and assuming also that it was this quantity and not specific heat which was conserved in a chemical reaction, Avogadro was able to set up a conservation law for attractive power. Unfortunately his determination of the power from the one observable quantity, specific heat, was open to serious objection. It was based on the quite unjustified assumption that the attractive power of an individual molecule was proportional to some integral power n of the volume (or, for Avogadro, molecular) specific heat. n, of course, was unknown and the small number of the gases whose specific heats had been measured made any determination of its magnitude extremely suspect. Yet Avogadro showed every confidence in his method. By reading 'molecule' for volume in the data concerning the volumes in which gases were known to combine chemi-

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1. A. Avogadro, 'Memoria sul calore specifico de' gaz composti parragonato a quello de' loro gaz componenti', Biblioteca Italiana, iv (1816), 473-491 and v (1817), 73-87.

cally, and by using Delaroche and Bérard's results, he was able to derive several equations expressing the conservation of attractive power in a reaction. His first example concerned the formation of one volume of carbon dioxide from one volume of carbon monoxide and half a volume of oxygen. In molecular terms he could thus write:

1 molecule of carbon monoxide	+	$\frac{1}{2}$ molecule of oxygen	⟶	1 molecule of carbon dioxide
$(1.0340)^n$	+	$\frac{1}{2}(0.9765)^n$	=	$(1.2583)^n$

giving n = 1.088.

The only other reaction in which values of specific heat were available for both the reactants and the resulting compound was:

1 molecule of nitrogen	+	$\frac{1}{2}$ molecule of oxygen	⟶	1 molecule of nitrous oxide
$(1.0356)^n$	+	$\frac{1}{2}(0.9765)^n$	=	$(1.3503)^n$

giving n = 1.333.

Even in this equation the specific heat for nitrogen was not an experimental one but was calculated from the specific heat of air treated as a mixture of oxygen and nitrogen. The other reactions which he used involved the undetermined volume specific heat of carbon vapour, but Avogadro easily eliminated the unknown quantity and made further determinations of n from the following three equations, all of which are imaginary. x throughout is the unknown specific heat.

1) $\frac{1}{2}$ volume of carbon vapour	+	1 volume of oxygen	⟶	1 volume of carbon dioxide
$\frac{1}{2}x^n$	+	$(0.9765)^n$	=	$(1.2583)^n$

ii)	1 volume of carbon vapour	+	2 volumes of hydrogen	⟶		1 volume of ethylene
	x^m	+	$2\ (0.9033)^m$	=		$(1.5530)^m$
iii)	$\frac{1}{2}$ volume of carbon vapour	+	$\frac{1}{2}$ volume of oxygen	⟶		1 volume of carbon monoxide
	$\frac{1}{2}\ x^m$	+	$\frac{1}{2}\ (0.9705)^m$	=		$(1.0340)^m$

By taking in turn equations i) and ii), i) and iii) and ii) and iii), values for m of 2.012, 1.983 and 1.991 were obtained. Since now the mean of all his values for m was 2.001 when the repeated figure of 1.983 was neglected, Avogadro confidently and, in view of the wide discrepancies between the values, very really assumed that m was exactly 2. Hence the general equation representing the conservation of attractive power for caloric became:

$$c^2 = n'c'^2 + n''c''^2 + n'''c'''^2 + \ldots \qquad \ldots(2)$$

where c was the volume specific heat of the resulting compound and c', c'', c''' ... those of the constituent gases. n', n'', n''' ... were the respective numbers of molecules of these gases which combined to form one molecule of the compound.

When Delaroche and Bérard's results for oxygen, hydrogen and carbon monoxide and Avogadro's own calculated value for nitrogen were inserted, equation (2) yielded theoretical specific heats for a wide range of compounds in the gaseous state. For many of these no experimental data were available and, even where comparisons were possible, agreement between the calculated and observed values were poor, the discrepancy for nitrous oxide being over 10%. (See Table 4, col. 2). Avogadro nevertheless considered the

calculated specific heats to lie within the limits of experimental error.

Avogadro's debt to the important movement which sought to extend the principles of gravitational attraction first to chemistry and then to the study of light is nowhere more apparent than in his interpretation of the attractive power for caloric which he had now determined. He made no reference to this earlier work but, in stating as self-evident that the attractive power of a molecule was 'necessarily' proportional to the product of the mass of the molecule and its characteristic affinity for caloric, Avogadro was evidently assuming a close analogy between the mechanism which retained caloric around a molecule and that which, according to Berthollet, governed the chemical combination between two substances. The extension from the molar to the molecular scale appears to have required no justification. The gas hypothesis made the derivation of the affinity particularly simple, since the mass of a molecule could be taken as proportional to the density of the gas and division of the attractive powers by the known densities thus yielded the affinities listed in Table 4, column 4.

The subject of affinities for caloric would never have assumed the importance which it was to have for Avogadro if he had not immediately observed a point of obvious though apparently unexpected significance in the table. The order in which the substances appeared suggested some remarkable analogies with his earlier work on chemical affinities, which had been conducted without reference to specific heats. In 1809 he had published an important paper[1] describing his early views on chemical combination,

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1. Avogadro, J. Phys., lxix (1809), 142-143.

in which he used the concept of an antagonistic force between acids and alkalis to explain the tendency of substances to combine. Alkalinity and acidity were not absolute properties of matter but were relative, so that the same substance A might be at once acidic with respect to B and alkaline with respect to C. A's behaviour, in fact, could be predicted by means of a single table of affinities in which it would act as the 'acid' component in a reaction with all substances below it but would be alkaline with respect to any above it. In order of decreasing acidity, the table would be headed by oxygen, followed by carbon and the acids, then by water and the neutral salts and lastly by the alkalis and hydrogen. Avogadro found support for his views in Davy's recent and much publicized attempt to identify the strength of chemical affinity with the degree of electrical heterogeneity,[1] although he was not convinced that the mechanism of affinity was in fact electrical. Neither he nor Davy had drawn up complete tables but the existence of some analogy between Avogadro's own proposed table and those already established by Volta and Pfaff from purely electrical considerations was an intriguing possibility. Volta, for example, working in terms of the contact theory of electricity (which Davy had adopted by 1807), had given a series on which the distance between two metals was a measure of the degree to which they assumed electricity of the opposite

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1. H. Davy, 'The Bakerian Lecture, on some chemical agencies of electricity', Phil. Trans., xcvii (1807), 1-56. This work won the lesser of two prizes for 'galvanism' offered by Napoleon.

sign on contact,[1] the presence of a conducting liquid being necessary without being thought to be the seat of the galvanic phenomenon. Davy's references to Volta suggest that he would have adopted distance apart on this series as a measure of chemical affinity.

Avogadro's view of the matter was not entirely novel, although he made no mention of his precursors. Already, in 1793, J. W. Ritter[2] had pointed out the resemblance between Volta's series and Gren's table of affinities for oxygen.[3] Although Avogadro specifically rejected Lavoisier's view of the uniqueness of oxygen as the principle of acidity, maintaining than an even more electro-positive substance may yet be found, with respect to which oxygen itself would be alkaline, his series too was essentially one of affinity for oxygen. The term 'oxygenicity' (oxigénicité, ossigenicità) was introduced as a measure of proximity on the series to oxygen and chemical affinity was to be measured by the difference between the oxygenicities of two reactants.

So it was the similarity between the table of affinities for caloric derived in 1816 and the degrees of oxygenicity suggested seven years earlier, though as yet undetermined, which caught Avogadro's attention. The order of increasing affinity for caloric, with one or two exceptions, resembled

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1. A. Volta, Neues Journal der Physik ed. F. A. C. Gren, ii (1795), 142.

2. This information is taken from J. R. Partington, A History of Chemistry (London, 1964), iv. 19. The source for Ritter's comment cited by Partington has not yet been traced.

3. F. A. C. Gren, Principles of Modern Chemistry (London, 1800), ii. 442. A copy of the original German edition of 1796 has not yet been found.

lent of increasing affinity for oxygen, i.e. of decreasing acidity, with the affinity between hydrogen and caloric being greatest of all. Since even oxygen itself had affinity for caloric, it followed, as he put it in 1825 in a comment which emphasizes his belief that affinities for oxygen and for caloric were of the same nature, that caloric was 'la sostanza ossigenica per eccellenza'.[1]

We have already noted[2] the interest which was being shown during the early years of the nineteenth century in the possibility that the two imponderables, light and caloric, might be essentially identical, being merely modifications of one and the same fluid. For Avogadro it was an obvious extension of this idea to suppose that affinity for caloric and refractive power might be connected and in 1817[3] he was able to establish a relationship between the two quantities. A comparison of his own values for affinities with Biot and Arago's refractive powers showed that the relationship was not one of proportionality, but the variations could nevertheless be accounted for on the assumption that light was merely caloric in rapid motion. Those molecules with a large affinity would attract a large quantity of caloric about them and, since the caloric particles were mutually repulsive, this accumulation would tend to diminish the resultant attractive power of the molecules for light particles and so act against the

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1. Avogadro, Giornale di Fisica, Decade II, viii (1825), 9.
2. See pp.102-104.
3. Avogadro, Mem. Soc. Ital., xvii (1820), 155-173.

effect of the high affinity, without entirely counteracting it. Hence affinity for caloric would be expected to show greater variation from substance to substance than would affinity for light and this agreed with the observations.

From results relating to five gases for which adequate data were available Avogadro derived the following purely empirical equation involving refractive power P and affinity for caloric A:

$$P = kA + (1 - k)\sqrt{A} \qquad \ldots(3)$$

where k, a constant, was found to be 0.4193 by insertion of the relevant figures for hydrogen. Equation (3) thus became:

$$P = 0.4193A + 0.5807\sqrt{A} \qquad \ldots(4)$$

By inserting the known affinities for caloric, other refractive powers could now be deduced and compared with Biot and Arago's results. In the absence of any but the most rudimentary physical picture of the nature and behaviour of the imponderable fluid, Avogadro was under no restriction concerning the form of the equation. There was no conservation principle to be expressed and, with no limit on its complexity, the equation could always be made to accommodate any new data. Such a 'trial and error' approach could hardly fail to give good agreement, although ethylene, for which the theoretical and experimental refractive powers would have been in serious disagreement, was significantly omitted.

In 1819 Avogadro was elected a Fellow of the Reale Accademia delle Scienze at Turin and he proceeded to expound his views in the lengthy memoirs which he now began to submit regularly to the Accademia. Nearly

all his contributions for several years to come were in some way derived from his work on affinity, although its genuine relevance to certain topics is hard to accept. Perhaps most extravagant of all was his attempt, in 1824, to relate the density of solids and liquids to the mass of their molecules and to their affinity for caloric.[1] Although he succeeded in incorporating all three relevant quantities in a single equation, he could not even attempt a theoretical explanation of the connection between them. Understandably, he took this topic no further and he concentrated instead on establishing the relationship between chemical affinity and affinities for light and heat. Of the existence of this relationship, we note, he was still in no doubt.

In 1824 and 1825 Avogadro's views became even better known through the series of summaries of all his earlier papers on affinity which he published in Configliachi and Brugnatelli's Giornale di Fisica,[2] but it was two particularly long memoirs on the subject, read before the Turin Academy in 1823 and published in French,[3] which first attracted attention in France, being reviewed in Baron Férussac's Bulletin des Sciences for August 1825 by a contributor who signed himself 'S'.[4] An examination of

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1. Avogadro, Mem. Accad. Sci. Torino, xxx (1826), 81-154 and xxxi (1827), 1-94.

2. Giornale di Fisica, Decade II, vii (1824), 427-437; Ibid., Decade II, viii (1825), 1-9, 108-117, 160-164 and 313-330.

3. Avogadro, Mem. Accad. Sci. Torino, xxviii (1824), 1-122 and xxix (1825), 79-162.

4. 'S', Bull. de Férussac, iv (1825), 101-103.

the list of editors printed in the journal suggests that this was the mathematician Jacques Frédéric Laigey, chairman of the editorial board for the physics section. It may well have been at this time that Dulong first became aware of the work, for he sat on the same distinguished board together with Ampère, Fresnel and Poisson. The reception in France was unlikely to be favourable. Quite apart from his unconvincing reasoning, too many basic tenets of Avogadro's treatment were unacceptable. By 1825 the physical reality of caloric was in serious doubt, so that speculative attempts to account for its behaviour in terms of affinity, a property which was itself largely discredited in the theory of both refraction and chemical reaction, were particularly suspect. Even those who remained calorists, Laplace, Poisson and Carnot, for example, would have found little of interest in Avogadro's views, since affinity played no major part in their versions of the theory. The rejection of the other important basis for the work, Avogadro's gas hypothesis, was perhaps less central, for it had enjoyed some slight measure of acceptance by 1825, as we have seen.

Laigey's review was predictably unenthusiastic, but he conceded that the three sorts of affinity considered by Avogadro were somehow related. After a critical description of Avogadro's work, he concluded:

> En résumé, nous croyons, avec M. Avogadro, qu'il y a une dépendance mutuelle entre l'affinité des corps pour le calorique, leur pouvoir réfringent, et leur capacité de saturation; reste encore, après toutes ses recherches, à trouver le lien qui les unit.[1]

At about the time of the review, Dulong was himself engaged in the

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1. Ibid., 107.

vain search for some law relating the refractive powers of substances which would be analogous to the Dulong and Petit law for specific heats. Although he retained the material theory of light to the point of interpreting his readings in terms of refractive power, he dismissed Avogadro's work on the subject as 'une longue suite de travaux purement spéculatifs'.[1] Not surprisingly, his experiments showed that equation (3) was grossly in error, a fact which Avogadro promptly denied in typically vigorous fashion.[2] Dulong's scepticism is interesting since it represents the attitude of a leading contemporary scientist, and in particular of one who was far from unsympathetic either to Avogadro's gas hypothesis[3] or to the concept of affinity as applied in refraction. Dulong, moreover, shared Avogadro's interest in the search for some relationship between the properties of a compound and those of its constituents and he pursued the search not only in his work on refractive powers but also in his study of heat.[4] Despite all this, Avogadro would seem to have been a figure of no great consequence in Dulong's opinion.

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1. P. L. Dulong, Ann. Chim. Phys., xxi (1826), 177.

2. A. Avogadro, 'Comparaison des observations de Mr Dulong...avec les formules de la relation entre les pouvoirs et les affinités pour le calorique déduites des chaleurs spécifiques', Mem. Accad. Sci. Torino, xxxiii (1829), 49-111. However, in this paper Dulong did recalculate the affinities on the basis of Dulong's data.

3. In his paper on refraction (Ann. Chim. Phys., xxxi (1826), 174) Dulong explicitly supported the view that all gases, under similar conditions of temperature and pressure, contained equal numbers of particles. He was almost certainly referring to both elementary and compound gases. See also p.247.

4. See pp.205-207, 290 and 297-298.

If Avogadro's treatment was suspect by virtue of his speculative reasoning, the experimental results on which it was based were hardly less so by 1825. Despite their early acclaim and their retention by the great French calorists of the 1820s, Delaroche and Bérard's values for the specific heats of gases were increasingly seen as unreliable. In particular there was a growing belief that the volume specific heats of at least the elementary gases were equal and hence that the small differences which had been so fundamental to Avogadro's system of affinities did not really exist. Even by 1819 the belief almost certainly had the support of Dulong and Petit, who can hardly have failed to notice that a consequence of their conviction that the equality of the atomic heats of elementary substances held for gases as well as for metals[1] was that the volume specific heats of the elementary gases were equal. Although this result in turn implied, for Dulong and Petit at least, that the number of particles in unit volume was the same in these gases, Avogadro's confidence in Delaroche and Bérard's results was undiminished and in 1825[2] he rejected not only the validity of the extension from metals to gases which Dulong and Petit proposed but also the exactness of the law even as applied to metallic elements. He likewise rejected the results of W. T. Haycraft, who had shown experimentally in 1823 that the volume specific heats of oxygen, nitrogen, hydrogen and also carbon dioxide were equal, and a little later the somewhat similar

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1. A. T. Petit and P. L. Dulong, Ann. Chim. Phys., x (1819), 406-407.

2. Avogadro, Giornale di Fisica, Decade II, viii (1825), 432-438. See also Ibid., ln.

results of de la Rive and Marcet were also dismissed as unreliable.[1] Avogadro thus set himself in opposition to the weight of experimental evidence as well as to the latest theoretical developments.

Yet he was unmoved either by these difficulties or by direct criticism. He replied to Baigey by reiterating his beliefs in the Giornale[2] and to Dulong by making minor concessions of a purely numerical nature.[3] His article in Férussac's Bulletin for February 1827,[4] in which for the first time he presented his views on affinity in a French journal, thus showed few changes, the treatment being that which he had described to the Turin Academy in 1823. He used the same value for k which he had used then[5] and gave the same table of affinities, based on values deduced both from Biot and Arago's refractive powers and from Delaroche and Bérard's specific heats.

One serious difficulty which was not removed even in these highly developed versions of his theory arose from the considerable variations between the affinities of compounds which, when tested chemically, appeared to be neutral. The affinities of such compounds varied from 1.300 to 2.4893. (on scale of Table 4, col.7) and between these limits lay certain acids

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1. Avogadro, Mem. Accad. Sci. Torino, xxiv (1830), 201n. In this paper, read on 7 Dec. 1820, he rejected the results announced by de la Rive and Marcet in 1827. In Bull. de Férussac, xii (1829), 47-48n he also rejected their revised version of 1829. On the work of Mayeraft and of de la Rive and Marcet see p.245, n.2.

2. Avogrado, Giornale di Fisica, Decade II, viii (1825), 432-438.

3. See

4. Avogrado, Bull. de Férussac, vii (1827), 129-142.

5. k = 0.5412, slightly different from the figure used in 1817.

and alkalis. To answer the difficulty Avogadro invoked a distinction between true and apparent neutrality which he had made as early as 1811.[1] Although all known chemical tests would indicate neutrality, he argued, the compounds in question were neutral only by virtue of the fact that any change in the proportions of their constituent elements in accordance with the law of definite proportions, interpreted on the basis of Daltonian atomic theory, would displace the compound on the electrochemical series away from the fixed point of true neutrality. This true neutrality was at 1.7035, the mean of the affinities of the apparently neutral compounds with affinities between those of the last acid, at 1.6725, and the first alkali, at 1.7281. The scale of the numerical values in the table could of course be readily modified, to give the affinity of oxygen as unity for example, (they were then 'nombres affinitaires'), or, more significantly, in a way which brought out the connection between affinity for caloric and what he termed 'neutralizing power' (pouvoir neutralisant), as measured by the distance from the point of true neutrality, with the value zero for this point and -1.0000 and +10.0222 for oxygen (electro-negative) and hydrogen (electro-positive) respectively.

So it was that Avogadro's treatment of affinities attained its most extravagant form. What had begun as a chance observation of some ill-defined similarities between chemical affinities and a hypothetical thermal property, deduced with an obvious debt to Berthollet's chemistry, had now yielded a table of affinities for caloric which Avogadro took to be a definitive version of the electro-chemical series. Such was his confidence

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1. Avogadro, J. Phys., lxxiii (1811), 74-75.

in his system that the very dubious initial assumptions on which it was based were no longer seen by him as matters for discussion and justification for linking together chemical affinity and affinities for heat and light was for him, if not for his contemporaries, unnecessary.

Avogadro's New Approach

Despite this confidence, which Avogadro felt as late as February 1827, the days were already numbered for his elaborate system. A paper read in December of the following year[1] indicated an important change of approach. In it he described a method of determining neutralising powers simply from the composition of neutral compounds by using an additive relationship of the form

$$ap + bq = 0$$

where a, b were the proportions by weight of the constituent elements and p, q their neutralising powers, that of the compound being zero. For more complex compounds additional terms would be required and the derivation of a table of powers on the basis of an arbitrary value for a chosen element, in this case oxygen, was far from easy. But the significance lies not so much in the results as in Avogadro's assertion that, for all its imperfections, such a table was the standard and would hold good whether the treatment in terms of affinities for caloric was valid or not.[2] In

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1. A. Avogadro, 'Mémoire sur les pouvoirs neutralisans des différens corps simples déduits de leurs proportions en poids dans les composés neutres qui en sont formés', Mem. Accad. Sci. Torino, xxxiv (1830), 146-216.

2. Ibid., 161.

deducing those affinities he now also abandoned the values derived from refractive power, finally acknowledging that Dulong's data had shown equation (3) to be false, at least for certain gases. He maintained, moreover, that a comparison between the powers determined by purely chemical considerations and those deduced from specific heats suggested but did not prove a connection between the two.

After the initial neglect and then the unfavourable reaction in France, the final blow came with a new and particularly effective attack on Delaroche and Bérard's data. The critic was Dulong, who in 1828 confirmed experimentally that the volume specific heats of all elementary gases were identical.[1] Avogadro would perhaps have remained unmoved by the new evidence had he not recognized that the relationship expressed in equation (3), if not the theoretical justification for it in terms of affinities, could still be salvaged. Thus in March 1830[2] he at last felt able to take the important step of rejecting Delaroche and Bérard's data.

An interesting modification which he made at the same time was the substitution of constant-volume specific heats for those measured at constant pressure. In his work on affinity for caloric he had assumed from the outset that the effect on the specific heat of allowing expansion to take place during heating was the same for all gases. But Dulong's dis-

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1. See pp. 287-290 for Dulong's somewhat indirect approach to the problem.

2. Avogadro, Bull. de Férussac, xiii (1830), 211.

3. Avogadro, Biblioteca Italiana, v (1817), 73.

covery that γ varied appreciably with the nature of the gas, being consistently lower for compound gases than for elementary gases, made this view untenable. A choice between c_p and c_v had to be made and Avogadro came down in favour of c_v, though only, it seems,[1] because this yielded a closer approximation to the relationship expressed in equation (2).

A test of the equation was possible for the following four reactions, in the first three of which the volume relationships are imaginary and erroneous. The volume specific heat of all elementary gases is unity throughout:

i) 1 volume of oxygen + $\frac{1}{2}$ volume of carbon vapour ⟶ 1 volume of carbon dioxide

$1^2 + \frac{1}{2}(1)^2 = [c_v(v) \text{ of } CO_2]^2$

giving for the volume specific heat of carbon dioxide 1.225 (experimental value 1.243).

ii) $\frac{1}{2}$ volume of oxygen + $\frac{1}{2}$ volume of carbon vapour ⟶ 1 volume of carbon monoxide

$\frac{1}{2}(1)^2 + \frac{1}{2}(1)^2 = [c_v(v) \text{ of } CO]^2$

giving for $c_v(v)$ of carbon monoxide 1.00 (experimental value 0.994).

iii) 1 volume of carbon vapour + 2 volumes of hydrogen ⟶ 1 volume of ethylene

$1^2 + 2(1)^2 = [c_v(v) \text{ of } C_2H_4]^2$

giving for $c_v(v)$ of ethylene 1.732 (experimental value 1.754).

iv) $\frac{1}{2}$ volume of oxygen + 1 volume of nitrogen ⟶ 1 volume of nitrous oxide

$\frac{1}{2}(1)^2 + 1^2 = [c_v(v) \text{ of } N_2O]^2$

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1. Avogadro, Bull. de Férussac, xiii (1830), 213.

giving $c_v(v)$ of nitrous oxide 1.225 (experimental value 1.227).

Although Avogadro had every reason to be satisfied with the way in which his equation accommodated Dulong's new data, the theoretical implications of the relationship had to be abandoned, together with the elaborate system of affinities which was derived from them. Since the specific heats of equal volumes of all elementary gases, and hence of their individual molecules, were identical, they could no longer be interpreted as indicating a characteristic attractive power of the molecule for caloric. Avogadro accepted this conclusion, maintaining that affinity was not the factor which determined specific heat, although he did not reject the concept of affinity entirely. Any correlation between specific heat and chemical affinity was now out of the question and equation (2) assumed the status of a purely empirical relationship in which the quantities represented by the square of the volume specific heats had no theoretical significance. The tables of affinities based on specific heats and those derived from optical data were never revived.

The gas hypothesis could only be strengthened by the shedding of such unexpect extensions and by being reconciled with both Dulong and Petit's law and the latest experimental data. So long as Avogadro persisted in his support of Delaroche and Bérard's results, to the necessary exclusion of the Dulong and Petit law for gases, he was alienating support for the gas hypothesis. Such influential chemists as Gmelin[1] and Berzelius, who, like

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1. See pp.318-324.

Dulong and Petit, were led to at least a partial belief in the hypothesis, could have found little that was convincing in the system of affinities, the establishment of which constituted most of Avogadro's scientific output at the time. So to contemporaries the hypothesis must have appeared least convincing in the hands of the author himself. It is ironical, and possibly even significant for our understanding of the neglect of the hypothesis, that the paper in which Avogadro abandoned affinities and brought his work into line with more acceptable principles was the last in which he dealt specifically with gases. It was thus by his subsequent attempts to extend equation (2) to solids and liquids[1] that he became most widely known, while the significance of his work in relation to gases was largely ignored.

Although equation (2) had assumed a purely empirical status, Avogadro's new view of specific heats had some theoretical implications, since he now felt that specific heats reflected the physical constitution of the particles of matter and not their chemical nature. The well known implication of his gas hypothesis, that the whole or 'integrant' molecules of elementary gases could be subdivided into two or more 'partial' molecules, had not previously been relevant, for affinity had been ascribed to whole molecules only. But the existence of partial molecules now became very central, since Avogadro argued that it was the number of these in a given volume and not their chemical nature which alone determined specific

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1. See pp.256-258.

lent. That the number of partial molecules rather than the number of integrant molecules was the crucial factor was demonstrated by the differences between the volume specific heats of elementary and compound gases. In gases of both types the number of integrant molecules in unit volume was the same, according to Avogadro, and it was only the number of partial molecules which varied and hence caused the specific heats to vary. If further evidence was needed, it was found in the second of the four equations listed above, that expressing the volume composition of carbon monoxide. Since the reaction involved no change in the number of partial molecules per unit volume, the volume specific heat of carbon monoxide would be expected to equal that of the elementary gases and this had in fact been shown to be the case. And the argument could go further, for equation (2) could be made to yield an explicit relationship between specific heat and the internal structure of the molecules. It followed from Avogadro's hypothesis that the number of partial molecules in unit volume of any gas, compound or elementary, was proportional to the number in each integrant molecule, so that volume specific heat depended solely on what we should now term the atomicity of the molecule. The realization that the physical structure of substances rather than their chemical properties determined specific heats represented an important change which has re-appeared since in a more modern form; for the dependence on atomicity (among other factors) also emerges from the principle of the equipartition of energy applied to the kinetic theory of gases. But the form of equation (2), to say nothing of the uncertainty of some molecular compositions, did not allow Avogadro

to approach even approximately to the later predictions. Instead equation (2) led to the quite erroneous consequence that the molecular (or volume) specific heat of a compound would be proportional to the square of the number of elementary integrant molecules which combined to form one molecule of it, on a scale where the specific heat of an elementary integrant molecule was unity. With the possible exception of Dulong[1] Avogadro's contemporaries appear to have ignored his bold interpretation of specific heats in atomic terms. There was simply too much in his work which was suspect and, in any case, the doubts concerning the physical reality of atoms which were to be expressed so forcibly during the 1830s[2] were probably already being felt.

Avogadro's subsequent work on specific heats is of less concern to us, since it dealt exclusively with solids and liquids. But his two contributions to the Annales de Chimie et de Physique in 1833 and 1834,[3] the first of his papers on specific heats to appear in this leading French journal, were the ones which attracted most attention in France.[4] The object of the papers was to extend the relationship between the specific heat of a compound and those of the elements composing it and, hence also, the dependence of spe-

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1. See the letter quoted on p.297. See also pp.318-319.

2. On these see pp.320-326.

3. A. Avogadro, 'Mémoire sur les chaleurs spécifiques des corps solides et liquides', Ann. Chim. Phys., lv (1833), 80-111, and 'Nouvelles recherches...', Ann. Chim. Phys., lvii (1834), 113-140.

4. Being almost certainly the source of Regnault's knowledge of Avogadro's work, for example. See A. V. Regnault, Ann. Chim. Phys., [3] i (1841), 129-130.

cific heat on molecular structure, both of which he had already established for gases, to matter in other states. The possibility of making such an extension had became of increasing interest since the original theoretical implications of his work had been abandoned. In his early paper of 1811 he had claimed that, although the attraction of a molecule for caloric could not be altered by a change of state, the square-law relating specific heat and attractive power need not hold also for solids and liquids.[1] By 1830, however, when specific heat had been related to the physical structure of the molecule rather than to its innate affinity, there was no reason why some extension should not be sought. Although Avogadro at first doubted whether the relationship was the same for matter in all three states,[2] he quickly changed h s mind and in 1832[3] we find him attempting to establish that the specific heat of one molecule of a solid or liquid compound was determined in exactly the same way as that of a gas, by the 'constituent number' (numero costitutivo) or the number of elementary integrant molecules composing it. To support the extension of his principles he introduced some novel ideas. For example, it now became necessary to assume that the molecule of water vapour split up into four parts when it passed into the solid or liquid state and the atomic weights of many elements, in particular those proposed by Berzelius, also required modification. It

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1. Avogadro, Biblioteca Italiana, v (1817), 77.

2. Avogadro, Bull. de Férussac, xiii (1830), 215.

3. Avogadro, Mem. Soc. Ital., xx, fasc. 2° delle memorie di fisica (n.s., 1333?), 451-536.

seems clear that chemists were being asked to change too many of their established principles in order to accommodate a theory of specific heats which none of them had ever seriously entertained.

Avogadro's views had changed little when he stated them for the last time in the third volume of his text-book Fisica de' Corpi Ponderabili in 1840.[1] However, in this work, distinguished primarily by its extraordinary size but read with appreciation by Faraday,[2] he declined to commit himself to any particular theory of heat. This new and more rigorous attitude, which reflected the general mood of the time, finally precluded any arguments in terms of affinities for caloric and henceforth it was only with chemical affinity that Avogadro showed any concern.[3]

The text of the Fisica, though it was never translated, and the papers which appeared in the Annales in 1833 and 1834 were the versions of his work which were most readily available in the period after 1830 when interest in specific heats was revived by the experiments of F. E. Neumann and Regnault.[4] Such sources can have conveyed little impression of the true origins of Avogadro's views and it is therefore not surprising that these

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1. A. Avogadro, Fisica de' Corpi Ponderabili (Turin, 1840), iii. 203-226.

2. Faraday to Avogadro, 10 Aug. 1842, in Avogadro, Opere Scelte, p.cxxxix.

3. See, for example, his attempts to relate chemical affinity with atomic and molecular volumes in Mem. Accad. Sci. Torino, [2] viii (1846), 129-193 and 293-532; Ibid., [2] xi (1850), 231-355; Ibid., [2] xii (1852) 39-122.

4. See p.324-325 and 334-336.

origins have almost completel, disappeared from the historical record. In any case, writers of the 1830s and 1840s would surely have dismissed the work on affinities for caloric as hopelessly wrong even if they had known of it. For the historian, however, the work has obvious significance, since it represents the interpretation of caloric theory adopted by a scientist of considerable distinction, working largely in isolation but under tenuous French influences. These unusual conditions, as we have seen, allowed Avogadro to retain such concepts as affinity between ponderable and imponderable matter long after they had ceased to be major research interests in France, the country of their origin. Moreover, and it is this which prevents us from dismissing Avogadro lightly, it was not simply a question of his retaining them, for by 1837 he had developed them to a degree of sophistication which they had never had in France. The result was a notable technical achievement, but it is tempting to wonder how much more Avogadro might have accomplished had he been in a position to detect earlier than he did that the nature of his fundamental beliefs was dissociating him increasingly from the main trends in European thought and hence ensuring his comparative, if not total, neglect.

CHAPTER 6

The Decline of Laplacian Influence

The history of the decline of caloric theory in France must constitute first and foremost a study of the growing inadequacy of a theory, but it is perhaps equally instructive when viewed rather as just one case-history in the decline of a whole orthodoxy in scientific thought based on principles which we can broadly describe as Laplacian. In this caloric was by no means the only victim and, if we are to place the work on the thermal properties of gases after 1815 in anything more than a narrow 'internalist' context, we must therefore bear in mind that the changing attitudes to the nature of light and to the atomic theory were now even closer to the scientific conciousness of the time than the study of heat and gases. With the decline of caloric theory the work on gases inevitably lost the special significance with which it had been invested by the caloricists and it will be the chief problem of this chapter to discover how the research tradition was kept alive in the quarter of a century before Victor Regnault revived it in the 1840s.

The Beginnings of Revolt

The really serious cracks in the Laplacian orthodoxy began to appear quite suddenly after 1815. The assailants, among them Jean Baptiste Joseph Fourier, Dominique François Jean Arago, Pierre Louis Dulong, Augustin Jean Fresnel and Alexis Thérèse Petit, were men who for various reasons had

previously exerted only a modest influence on science. Their rise to prominence is therefore as significant as the views which they held and in attempting to account for it we must clearly look beyond purely intellectual factors. Above all, it is tempting to seek some correlation between the rise of these men and the momentous political events associated with the downfall of Napoleon and the Bourbon restoration. In fact, no direct correlation appears to exist and the political beliefs of the men we have mentioned were as varied as their motives for attacking the existing scientific theories. Among the most prominent supporters of the wave theory of light, for example, Fresnel was a royalist[1] and Arago an opponent of the Bourbons who almost lost his post at the <u>École Polytechnique</u> for his views in 1815.[2] Fourier had accompanied Napoleon to Egypt and had been a distinguished Secretary of the Institute of Egypt, but his attitude to Napoleon during the Hundred Days was equivocal[3] and in 1815 he earned the displeasure of both Napoleon and the royalist party in rapid succession. Of the others,

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1. Arago, <u>Oeuvres Complètes</u> (2nd edn.), i. 116.

2. <u>Ibid.</u>, iii. 62-63. Here (in a biographical sketch of Gay-Lussac, read at a public meeting of the <u>Académie</u> on 20 Dec. 1852) Arago recounts how in the <u>Conseil d'Instruction</u> of the <u>École Polytechnique</u> the professor of literature tried to have an unnamed professor removed from his post for his political views. A footnote added on p.62 identifies the victim of this attack as Arago himself. E. Blanc and L. Delhoume in <u>Le Vie Mouvant et Noble de Gay-Lussac</u> (Paris, 1950), 29n, state that the professor concerned was Dulong, but there seems to be no evidence for their conclusion. Dulong was not treated unfavourably by the royalists (see p.262).

3. D. F. J. Arago, 'Éloge historique de Joseph Fourier', <u>Mém. Acad. Roi.</u>, xlv (1838), pp.cxxiv-cxxxi.

ulong and Petit appear to have taken little interest in politics and they certainly did not suffer at the restoration of monarchy. Petit was made a professor at the École Polytechnique by the new government[1] and Dulong was elected to the Académie des Sciences by royal decree, although he angrily declined the honour.[2] Nevertheless the events of 1815 are not entirely without significance, for it was they which created the opening for Petit[3] and which, however indirectly, brought Fourier and Fresnel into the circle of Parisian scientists after several years of provincial obscurity.[4]

Probably the most striking characteristic of the men who led the move away from Laplacian science was their youth. Fourier alone was over thirty in 1815, so that it would have been surprising had they offered any serious opposition to established scientific principles much before that date. As we should expect, there is little evidence of even individual dissent before 1815, for the members of the new generation were good Laplacians by training. All were products of the École Polytechnique, with the obvious exception of Fourier, who taught there at its inception; yet, significantly, their ties with the great (though now ageing) figures of Laplace and Berthollet

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1. A. Fourcy, Histoire de l'École Polytechnique (Paris, 1828), pp.330-332.

2. From a recollection by Boutou de Villardière, once Dulong's laboratory assistant, quoted by Girardin in J. Girardin and J. Laurens, Eulogie de Louen (Rouen, 1854), pp.34-35.

3. See p.265.

4. See Arago, 'Éloge de Fourier', pp.cxxix-cxxx and Émile Verdet in Œuvres complètes d'Augustin Fresnel (Paris, 1866), i. pp.xxix-xxxv.

were not those of close disciples. Either they were not members of the Arcueil circle or, as in the case of Dulong and Arago, they joined at a comparatively late stage.

In view of the positivistic nature of much later French science, notably Fourier's, it might seem that in this anti-Laplacian movement we have the first signs of a wholesale rejection of unobservable, hypothetical entities. In fact, this was by no means the case, since Fresnel, Arago, Dulong and Petit all had rival theories to oppose to those based on imponderable fluids. They naturally believed their own theories to be more rational but they did not abandon interest in the nature of heat and light and, as is shown by support which Dulong gave to the atomic theory, in the building blocks of matter.

Since our concern is primarily with the decline of caloric theory in this period, we must naturally single out Petit and Dulong for more detailed consideration. Petit[1] was perhaps the most gifted member of the new generation. After completing the entrance requirements for the École Polytechnique at the remarkably early age of 10, he came to the notice of J. N. P. Hachette, who invited him to a school in Paris run by teachers from the École. Here Petit filled in the time before reaching the statutory age for entry (16). He emerged from the École Polytechnique with extraordinary distinction in 1809, being placed 'hors de ligne', with the next student in the year designated 'first'. That his training in physics would have been firmly based

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1. For biographical details see J. B. Biot, 'Notice historique sur ... Petit', Ann. Chim. Phys., xvi (1821), 327-335.

on Laplacian principles seems clear from Hachette's Programmen d'un Cours de Physique of 1809. The chapter entitled 'Du Calorique'[1] is by Monge and, although the customary concession of mentioning both the material and vibrational theories of heat is made at the outset, only caloric theory is described in detail. And a thoroughly conventional view it is, including accounts of the 'latent-sensible' distinction and of the opinion which Laplace could so easily have held although there is no evidence that he ever did, that the particles of matter attracted caloric to themselves with a force proportional to their own mass as well as to their natural affinity. It is not surprising to find that in his contribution on light Hachette categorically asserts that light is an elastic fluid governed by the usual laws of molecular attraction and affinity.[2] The wave theory is not even mentioned. Throughout his life Petit seems to have been particularly close to Hachette, who was himself both intellectually and politically an ardent disciple of Monge (to the extent of losing his post at the École Polytechnique, with Monge, after the Bourbon restoration[3]) and who, during Petit's student days taught several courses with Monge.[4] One of these was on machines and was no doubt the origin of Petit's particular interest in this subject in later years.

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1. Hachette, Programmes, pp.54-72.

2. Ibid., p.74.

3. D. B. G., art. Hachette.

4. J. N. P. Hachette, Correspondance sur l'École Impériale Polytechnique (Paris, 1809), i. 464.

Petit's merit did not go unnoticed. In November 1811 the examiners of his doctoral thesis were amazed by the lucidity of his defence of the work, a study of capillary action treated in the Laplacian manner and with full and respectful acknowledgements to Laplace.[1] After short periods first as répétiteur in analysis at the École Polytechnique and, from 1810, as the first répétiteur in physics,[2] he replaced his professor, the now discredited revolutionary Hassenfratz, as assistant professor and later, in October 1815, as full professor of physics.[3]

When Petit himself came to teach, he was predictably committed to Laplacian orthodoxy. Some previously unpublished notes taken at his physics lectures in the winter of 1814-1815[4] show that he was wholeheartedly a caloricist in November and December 1814. The vibrational theory is not even mentioned and, instead, the supposed properties of caloric are described in some detail. Heat from friction and the compression of a gas are explained by the expulsion of caloric attendant on any decrease in volume, although Petit's account of adiabatic heating seems to indicate that his views were not highly developed. His comment 'si l'on diminue de moitié le volume du gaz il devrait y avoir la moitié de la chaleur dégagée' even suggests that he had adopted a view which Laplace had held in 1803.[5]

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1. A. T. Petit, J. Éc. Polytech., ix (1813), 1-40.

2. Hachette, Correspondence (Paris, 1813), i. 296.

3. Fourcy, École Polytechnique, p.331 and N. B. G., art. Hassenfratz.

4. The notes, taken by Auguste Comte, are in the Maison d'Auguste Comte, 10 rue Monsieur le Prince, Paris VIe.

5. See n.l 4.

but quickly rejected. Accounts of other physical phenomena, including both electricity and magnetism, are also given without question in terms of fluids and, although Petit did not cover light in these lectures, there seems little doubt that here too he would have supported the material theory.

Petit appears to have performed all his experimental work at the École Polytechnique. There is no evidence that he ever worked at Arcueil, although his two most important scientific contacts, Dulong and Arago, were members of Berthollet's circle. Yet the influence of Arcueil on neither of these men was strong, for they only joined the group when its greatest days were almost over[1] and soon they were to become distinguished for their dissent from Laplacian views.

Arago's election to the chair of analysis at the École Polytechnique would have brought him into contact with Petit as early as 1809 and the two men were already on good terms when, by his marriage in November 1814, Petit became Arago's brother-in-law. So it is not surprising to find that Petit was involved in Arago's championing of the wave theory of light after October 1815, when Fresnel's first paper on diffraction was deposited at the Institute, and that as early as December of that year he and Arago were already interpreting their experiments on refraction in gases in a manner which struck a telling blow against the corpuscular theory.[2] Even by the

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1. The names of both men appear in the list of members published in 1816 (Mém. Soc. Arcueil, iii (1817), p.vii) but not in that of 1809 (Mém. Soc. Arcueil, ii (1819), 449). They probably joined soon after the appearance of this earlier list. On Dulong see also p.269 fn. 2.1.

2. See p.229.

time they described their work, on 11 December 1815, they would have known of Fresnel's paper for less than two months, since it was only on 23 October that Arago had been nominated, with Poinsot, as the Institute's official referee for the paper. This is striking evidence of the impression which Fresnel made and thereafter Arago's confidence in the correctness of the wave theory never weakened. Early in 1816 he wrote in support of Fresnel in the Annales de Chimie et de Physique,[2] of which he was now joint editor, with Gay-Lussac, and he was presumably also responsible for the appearance of Fresnel's paper on diffraction in the same journal.[3] Further support came quickly. Ampère was an immediate convert to the new theory[4] and even one so thoroughly under Laplacian influence as Gay-Lussac was impressed when he and Arago met Thomas Young during a visit which they made to England in 1816.[5] But the victory was not easily won and even after his success in the prize competition set by the Académie for 1819 Fresnel still experienced the full weight of Laplacian opposition. It seems likely, for example, that Laplace, Biot and Poisson were chiefly responsible for the delay in publishing the prize-winning memoir until 1826 and for losing some of Fresnel's

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1. Proc. Verb., v. 562 (23 Oct. 1815).

2. Arago, Ann. Chim. Phys., i (1816), 199-202.

3. A. J. Fresnel, 'Mémoire sur la diffraction de la lumière...', Ann. Chim. Phys., i (1816), 239-281.

4. See e.g. M. Ampère to Bellanoe fils, 19 May 1816, in Correspondance du Grand Ampère, ed. L. de Launay (Paris, 1936), ii. 511.

5. e.g. F. J. Arago, 'Éloge historique de T. Young', Mém. Acad. Sci., xiii (1835), pp.cli-clv.

papers;[1] and all this despite the favourable opinion of the Secrétaire Perpétuel himself, Fourier, who in 1822 joined Ampère and Arago in giving a glowing report on a paper by Fresnel.[2] The bitterness of the dispute over the theories of light, with Biot and Arago the chief protagonists, reflects the fact that more than the immediate issue was at stake for French science and on account written some years later by G. B. I. T. Libri, who had strong sympathies for Laplace, shows how easily the dispute turned into a reaction against Laplacian science in general. Libri wrote:

> ...comme Laplace, qui voulait que l'on fût géomètre avant tout, avait semblé prendre parti contre M. Arago, on lui suscita des ennemis de toutes parts...on tendit la main à tous ceux qui attaquaient les résultats contenus dans la Mécanique céleste, et l'on remua toute la presse libérale pour la lancer contre nos anciennes gloires, qui, disait-on, n'étaient plus que de vieilles idoles qu'il fallait briser.[3]

Ampère, incidentally, was another who experienced the opposition of Laplace after 1820, in this case to his view that magnetism and electricity in motion were essentially identical.[4]

Petit's other main contact, Dulong,[5] was a less controversial figure

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1. For a somewhat speculative account see Whewell, History of the Inductive Sciences, ii. 403-411 and 435-439. Also Whewell, 'Comte and Positivism', Macmillan's Magazine, xiii (1866), 355-356.

2. J. B. J. Fourier, A. M. Ampère and D. F. J. Arago, 'Rapport...sur un Mémoire de Fresnel', Ann. Chim. Phys., xx (1822), 337-344.

3. [G. B. L. T. Libri], 'Lettres à un Américain sur l'état des sciences en France. I. L'Institut', Rev. Deux Mondes, 31 Mar. 1840, p.732. The author is identified in Rev. Deux Mondes. Table Générale 1831-1874 (Paris, 1875), p.83.

4. Ampère to Savy, 1825(?), in Ampère, Correspondance, ii. 660.

5. For biographical details see Girardin and Laurens, Eulogy de Rouen.

than Arago. He did not share the precocious brilliance which distinguished, say, Petit nor was his grounding in Laplacian science quite so thorough. He was orphaned at the age of four and his student days at the École Polytechnique were dogged by ill health. Within a year of his admission in 1801 he was granted a month's leave of absence on three occasions and he finally left without completing the course in October 1802.[1] He practised medicine for some years in Paris, but his excessive generosity to needy patients seems to have almost ruined him. In 1810 he was fortunate enough to be noticed by Berthollet, who invited him to Arcueil and arranged for his appointment as répétiteur to Thenard. With his future further assured by teaching posts at the École Normale in Paris and, from 1813, at the Alfort veterinary school, Dulong began to make his name as a chemist, working in accordance with Berthollet's principles and without reference to such controversial matters as the atomic theory. His association with Petit appears to have begun early in 1815, almost certainly as a result of the prize competition in physics announced by the First Class of the Institute on 9 January 1815.[2] Competitors were asked to measure the expansion of mercury in a thermometer between $0^{o}C$ and $200^{o}C$ and then to determine the rate at which a body cooled both in a vacuum and in various specified gases at different temperatures and pressures. It seems clear that the subject was set to answer problems arising from the competition of 1811 in which

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1. Details from Dulong's record card at the École Polytechnique.

2. See p.1 of the pamphlet cited in n.4, p.164.

Joseph Fourier had won the prize for his theoretical treatment of heat conduction in solids.[1] Although it was fundamental to his theory that the rate of flow of heat from a point inside a solid bar to another either inside or outside the bar was proportional to the difference of temperature between the points, Fourier had nevertheless emphasized that modifications would be simple should Newton's law of cooling, on which he based his assumption, be proved inexact. In fact, the approximate nature of the law for any but the smallest temperature differences had long been in little doubt,[2] so that a determination of its precise form became an obvious subject for further study now that Fourier's work had drawn new attention to the problem.

As the Institute's committee for the competitio evidently recognised, even a determination could not be made without some clear definition of temperature or, better still, the establishment of a rational temperature scale and it was presumably in an attempt to answer this, the first, part of the question set by the Institute that Petit and Dulong began some joint experiments in 1815. That they were only partially successful was inevitable,

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1. Fourier's paper appeared only in 1824 and 1826 in Mém. Acad. Sci., iv (1819-20), 185-556 and v (1821-2), 153-246. The delay is significant. For comments on the reserved praise of Laplace, Lagrange, Malus, Mndly and Legendre in 1811 see J. Herivaux in Oeuvres de Fourier (Paris, 1888), i. pp.vi-viii and Arago, 'Éloge de Fourier', pp.cxli-cxlii.

2. On this see Martine, Essays (1740), pp.233-247; J. C. P. Erxleben, Nov. Commentationes Societatis Reg. Scientarum Gottingensis, commentationes physicae et mathematicae classis, viii (1778), 74-95; Melton, New System, i (pt.1), 12 and 108-123; Delaroche, J. Phys., lxxv (1812), 201-228.

but the paper describing this early work which they read to the Institute in May 1815[1] is nevertheless of considerable interest since it shows clearly how they were first led to the subject for which they are now best known, namely specific heats. They realized that it was not enough merely to relate the expansion of the thermometric substance to the quantities of heat which it absorbed, for even if a substance were found which expanded regularly for the addition of equal amounts of heat, it could still not be assured that these equal increases in volume corresponded to the same temperature increment at all points on the scale. Only if the specific heat of the substance were shown to be independent of temperature was this conclusion justified. How Petit and Dulong thought that meaningful determinations of specific heat could be made <u>before</u> the establishment of a rational temperature scale is not clear, but it was the experimental and not the theoretical difficulties which they cited as their greatest obstacle. In particular, the measurement of specific heats at high temperatures appears to have presented certain insurmountable problems. No details of any experiments on specific heat were given and their work consisted of little more than a comparison between the expansion of mercury, air and a number of metals. It certainly did little to justify the strong preferences which they expressed for the gas thermometer as an ultimate standard.[2]

Owing to a number of unspecified interruptions, possibly connected

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1. Dulong and Petit, <u>Ann. Chim. Phys.</u>, 1i (1.16), 240-263.

2. <u>Ibid.</u>, 263.

with the political unrest of 1815[1] or with Petit's promotion at the École Polytechnique in October of that year, Petit and Dulong were unable to continue the experiments and in July 1816 they published their paper in its original form, having apparently given up any intention they might have had of entering for the competition. Fortunately no award was made and in March 1817[2] the identical subject was set again for 1818. This time Petit and Dulong produced a masterpiece[3] which won the prize and which was to be acclaimed as a model of experimental method by such varied authorities as Comte, Poisson, Lamé and Whewell.[4] Again they began with the problem of thermometry and again they came down in favour of the air thermometer, convinced that increments of temperature measured on this instrument, or indeed on any gas thermometer, were increments in the true temperature. This was little more than they had said in 1815, but they had now made undoubted progress with the specific heat problem, which was still important, even though the question of the temperature scale had been settled, if changes in the temperature of a cooling body were to be interpreted in

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1. On the effect of the unrest see J. Pinet, Histoire de l'École Polytechnique (Paris, 1887), pp.74-102 and Berthollet to Berzelius, 27 Aug. 1815, in Berzelius, Bref, 1. 54-55.

2. Ann. Chim. Phys., iv (1817), 302-303.

3. P. L. Dulong and A. T. Petit, 'Recherches sur la mesure des températures et sur les lois de la communication de la chaleur', Ann. Chim. Phys., vii (1818), 113-154, 224-264 and 337-367.

4. A. Comte, Cours de Philosophie Positive (Paris, 1835), ii. 534; S. D. Poisson, Theorie Mathematique de la Chaleur (Paris, 1835), p.6; G. Lamé, Cours de Physique (Paris, 1836), i. pp.i-ii; Whewell, History, i. 485.

terms of quantity of heat lost. Using a method of mixtures they managed to determine the specific heats of mercury and of several solids over a number of different temperature ranges up to 350°C. So accurate were the results obtained that the Dulong and Petit law might even have been deduced from them now in 1818, but the very fact that no such conclusion was drawn emphasizes that Petit and Dulong still regarded their work on specific heats as doing little more than provide a tool which could be applied in other problems such as cooling.

Dulong and Petit's law

In a year of intense activity following their victory Petit and Dulong used a refined method of cooling to extend their determinations of specific heats to new solid elements and to modify some but not all of their original values of 1818. Their train of thought during this year is not clear. Above all, there is little evidence to indicate that they were looking for a relationship of the type which emerged in April 1819 and which we now know as Dulong and Petit's law. That the discovery of the law was unexpected is further suggested by the nature of Petit and Dulong's interests in the period between 1815 and 1818 and, even more clearly, by an account written by the great French chemist Jean Baptiste Dumas in 1841. Dumas wrote:

> Le lundi 5 avril 1819, date mémorable, Petit...montrait, en confidence, à son beau-frère Arago,[2] un chiffon de papier, sur lequel se trouvaient inscrits les rapports selon lesquels les corps simples se combinent, et les quantités de chaleur exigées par chacun d'eux pour s'échauffer d'une manière égale sous le même poids. Au premier aspect, c'était le désordre; mais, en multipliant pour chacun de ces corps les deux

> chiffres l'un par l'autre, tous les produits se trouvaient égaux. Une heure après, l'illustre secrétaire perpétuel,[1] convaincu que Dulong, toujours hésitant, pourrait s'opposer à la divulgation de cette belle loi, en entretenait ses confrères, par une indiscrétion calculée.[4] Huit jours plus tard, les deux collaborateurs l'énonçaient devant l'Académie elle-même...[2]

So it was that on 12 April 1819 Dulong announced to the Académie the conclusion that 'les atomes de tous les corps simples ont exactement la même capacité pour la chaleur'.[3]

Dumas's recollection, written as it was over sixty years after the event, is inevitably suspect, the more so since Dumas, who was only eighteen at the time and working in Geneva, was presumably not present. In view of this we cannot completely ignore the somewhat different account given by Petit and Dulong themselves. Their paper of 12 April made no reference either to the unexpectedness of the discovery or to any debt to Arago. It implied rather[4] that they had been working all along in the belief that certain natural laws would emerge in their simplest form if only they could be related to the properties of individual atoms and not, for example, of equal weights or volumes. Written as an introduction to one of the most striking pieces of evidence yet obtained for the truth of the atomic theory, the story is a convincing one; but it was all too easy to write in this vein after the discovery had been made and it is clear that the

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1. Arago did not in fact become Secrétaire Perpétuel until 1830.

2. J. B. A. Dumas, 'Éloge historique de Henri-Victor Regnault', Mém. Acad. Sci., xlii (1863), p.xlviii.

3. A. T. Petit and P. L. Dulong, 'Sur quelques points importans de la théorie de la chaleur', Ann. Chim. Phys., x (1819), 405.

4. Ibid., 396.

accounts of neither Petit and Dulong nor of Dumas are wholly trustworthy. Nevertheless the weight of evidence seems to suggest that the discovery was unexpected and, if this was in fact the case, we should not be surprised that it was so long delayed. Even if Petit had collated specific heats and atomic weights in the way that Dumas describes, it would have been by no means obvious that the two quantities were related. The atomic weights in use at this time were deduced from the combining weights in chemical reactions, a method of great unreliability owing to the uncertainty surrounding the numbers of elementary atoms which combined to form any given 'compound atom'. The best available values, those published by the Swedish chemist J. J. Berzelius in 1818[1] after more than ten years of patient experiments, were derived in just this way. Although they formed the basis for the atomic weights which Petit and Dulong used in establishing their law, they were adopted without modification in the cases of only sulphur and platinum. For the other eleven elements treated, simple fractions of Berzelius's values were employed, so that the Dulong and Petit law, far from being obvious, was an extremely bold deduction from the existing evidence.

The paper of April 1819 constituted a major attack on Laplacian orthodoxy on two fronts - the nature of heat and the atomic theory. As

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1. Berzelius's atomic weights are most easily referred to in his Essai sur la Théorie des Proportions Chimiques (Paris, 1819), a translation of part of his Lärbok i Kemien (Stockholm, 1818), iii.

far as heat was concerned, both of the main versions of caloric theory were soundly rejected. Although they gave no details, Petit and Dulong had apparently shown[1] that the overall decrease in specific heat which had long been supposed to occur in exothermic reactions and which was an essential part of Irvinist doctrines, was by no means always observed. If this was indeed the case, it was in itself decisive evidence and Petit and Dulong had no hesitation in dismissing the views of Irvine and Crawford as being 'en opposition avec un trop grand nombre de faits pour pouvoir être adopté'.[2] Dalton's theoretical work on the specific heats of gases received similar treatment.[3] The alternative, 'Laplacian' version of caloric theory, on the other hand, was less easily disposed of. Here the absence of any apparent connection between heats of chemical reaction and changes in specific heat in no way invalidated the theory, but to Petit and Dulong the existence of caloric in two states was simply a 'supposition trop invraisemblable'.[4] Their conviction to this effect is striking in view of the small amount of evidence available and it clearly owed something to the fact that a more acceptable explanation was now to hand. The origin of this, though unacknowledged, was almost certainly Berzelius.

Berzelius was in France from 25 August 1816 until 10 July 1819. At

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1. Petit and Dulong, Op. cit., 408.
2. Ibid., 397.
3. Ibid., 397-398.
4. Ibid., 408.

Berthollet's instigation, he and Dulong worked together on the composition of water in the laboratory at Arcueil[1] and there the two men struck up an extremely close friendship ended only by Dulong's death in 1838. By the time they first met, in September 1813, Berzelius's opinions on the nature of heat had already undergone considerable changes. In his earliest work[2] he had shown a distinct preference for the caloric theory, but in some extensive and far from complimentary comments on Davy's Elements of Chemical Philosophy which he communicated to the author soon after the book appeared in 1812, he declared:

> Je suis intimement convaincu qu'il n'existe aucune hypothèse qui explique suffisamment les phénomenènes du calorique. Donc, plutôt que de tromper nos lecteurs par des apparences imparfaites, avouons notre ignorance à cet égard...[3]

By 1813 he was somewhat bolder and, after firmly rejecting the caloric theory as a means of accounting for the heat evolved in chemical reactions, he substituted the view, which Petit and Dulong were to adopt in the following April[4] and which Davy had already suggested,[5] that the heat was electrical in origin.[6] It was already well known that an electrical discharge could

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1. Dulong and Berzelius, Ann. Chim. Phys., xv (1820), 386-395.

2. Partington, History of Chemistry, iv. 165, states that Berzelius adopted the caloric theory in volume i of the first edition of his Lärbok i Kemien (Stockholm, 1808), but a copy of the latter work has not yet been traced. Also relevant is Berzelius, Ann. Chim., lxxxvi (1813), 158-171.

3. Berzelius, Pref, ii. 41.

4. Petit and Dulong, Op. cit., 411-412.

5. Davy, Phil. Trans., xcvii (1807), 42-44.

6. Berzelius, Essai, pp.61-63 and 72-73.

gave rise to heat even though no chemical reaction occurred and it was therefore a short step from Davy's demonstration that a piece of graphite was heated even in the absence of oxygen by being placed across the poles of a coil[1] to the view that it was an electrical discharge between the oppositely charged reactants entering into chemical combination which caused the emission of heat. If we are to appreciate the full seriousness of the blow dealt to caloric by the growth of the electrochemical theory, we must recall that, while the hypothesis of the electrical origin of heats of reaction did not in itself either exclude the material theory or imply the vibrational nature of heat, yet one of caloric's greatest strengths had been precisely that it provided such a convincing explanation of chemical heat. Once an alternative explanation was accepted, then the whole question of the nature of heat would become a completely open one again, with the material and vibrational theories fighting, so to speak, on equal terms. It was in July that this alternative first became well known in France, not only through Petit and Dulong but also by the publication in Paris of Berzelius's own views on the matter, which had previously been available only in Swedish.[2]

Petit and Dulong were careful to present their acceptance of the electrical origin of heats of reaction as no more than a highly probable

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1. Davy, Phil. Trans., xcix (1809), 71-72.

2. Cuvier's comments in Mém. Acad. Sci., iv (1810-20), pp.lxxxiii-lxxxvii indicate contemporary recognition of the importance of Berzelius's views.

conjecture, to the point of admitting that the emission of latent heat might still contribute to the overall effect. But private correspondence, as we might expect, tells us rather more. That Dulong at least had unreservedly abandoned the caloric theory by January 1820 is evident from the following comment in a letter to Berzelius:

> Nous avions déjà porté un coup funeste à la théorie chimique de la chaleur dans le mémoire que nous avons lu à l'Institut pendant votre séjour à Paris. - Les nouvelles expériences ne portent à regarder comme une vérité incontestable que tous les phénomènes qui n'ont point de rapport avec la chaleur rayonnante ne sont que le résultat des mouvements vibratoires des molécules matérielles elles-mêmes. Le calorique rayonnant se propagerait, d'après cette manière de voir, par les vibrations d'un fluide qui, avec une plus grande vitesse, produit sur nous la sensation de la lumière. Ainsi la pile voltaïque ne développerait le phénomène du feu qu'en excitant par le courant électrique les vibrations des particules matérielles. MM.Clément et Desormes ont publié un fait qui vient à l'appui de mon opinion dont je n'ai du reste parlé encore à personne. C'est qu'un même poids de vapeur d'eau, prise sous une force élastique quelconque et avec la température qui convient à cette force élastique, contient toujours la même quantité de chaleur. M.Despretz a trouvé qu'il en était de même pour les autres liquides. Or, je puis prouver qu'en faisant varier subitement le volume d'un gaz ou d'une vapeur, on produit par là des changements de température incomparablement plus grands que ceux qui résulteraient des quantités de chaleur développées ou absorbées, s'il n'y avait pas de chaleur engendrée par le mouvement. Rumford avait déjà employé à peu près le même mode de raisonnement pour soutenir son opinion, mais il avait pris pour sujet de ses observations les corps solides, ce qui rendait ses arguments beaucoup plus faciles à attaquer.[1]

In view of the evidence which had now confirmed Dulong's belief in the vibrational nature of heat is of considerable interest. The word 'engendrée', which Dulong underlined, suggests that he saw adiabatic heating as a conversion process, although there is no evidence that he even considered the

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1. Dulong to Berzelius, 15 Jan. 1820, in Berzelius, Lref, 1v. 13-14.

possibility of conservation. Unfortunately he nowhere enlarged on the conjectures contained in this letter, so that his attempt to use the adiabatic phenomena as evidence for the vibrational rather than for the material theory of heat could have been known to few contemporaries. Precisely how the applied Clément and Desormes's law was thus never made clear, but the following is a possible reconstruction of his argument.

It was an obvious consequence of the law for a calorist that the compression of a given mass of saturated vapour under perfectly adiabatic conditions would cause no change in the initial state of saturation. Since no condensation occurred, therefore, the vapour could be treated as a perfect gas and the volume of, say, unit mass of a saturated vapour at any temperature could hence be determined by applying the laws of Boyle and Gay-Lussac in conjunction with the well known tables relating saturated vapour pressure and temperature. From an argument conducted in this way[1] it followed, for example, that the adiabatic compression of a mass of steam at 0°C to one third of its original volume would require that the temperature should rise by roughly 20 deg C if the steam were to remain saturated and if no condensation were to occur. Now since Clément and Desormes's law predicted that the state of saturation would in fact remain unchanged in such a compression, it could be argued that a rise in temperature of roughly 20 deg C should be observed. Dulong was almost certainly aware that this predicted figure was far too small and it seems likely that it

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1. A similar argument appears in Carnot, Réflexions, 67-68n.

was this discrepancy which led him to look elsewhere for the source of the additional heat which would be observed in any actual compression. For him, as we have seen, the movement of the piston provided the answer, an answer which was convincing only in the context of a vibrational theory of heat.

The support which Dulong and Petit's law gave to the atomic theory dealt an equally telling blow at Laplacian science. The existence of a completely unexpected relationship between the familiar physical quantity specific heat and the individual atoms of matter was important evidence, especially in France, where even by 1819 the theory had made only modest headway. During the first decade and a half of the nineteenth-century Berthollet's system, teaching as it did that elements combined in varying and not fixed proportions by weight, had dominated French chemistry. There are many examples which illustrate this point but, to select just one, we might note in particular how in 1808 Gay-Lussac had interpreted his newly discovered law of combining volumes in terms not of the atomic theory, as we might have expected, but of Berthollet's chemistry.[1] Dulong's early work at Arcueil[2] thus posts a similar acceptance of established opinion and not until 1816 do we find any evidence of his dissent. In that year it became apparent that he had been deeply impressed by the atomic theory when he persuaded all the other members of the distinguished editorial board of the Annales de Chimie et de Physique to allow the publication of an extract from William Prout's

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1. Gay-Lussac, Mém. Soc. Arcueil, ii (1809), 231-233.

2. e.g. his 'Recherches sur la décomposition mutuelle des sels insolubles et des sels solubles'. Ann. Chim., lxxxii (1812), 273-308.

papers on the structure of atoms which had recently appeared in England.[1] Dulong himself prepared the extract.[2] It was in that year also that he described a classic example of what we now know as the law of multiple proportions for the various oxides of phosphorus[3] and, although he did not interpret it as such himself, it can hardly have escaped his notice that Berzelius almost simultaneously used his own work on the subject as strong evidence for the atomic theory.[4]

When Berzelius came to Paris, Dulong could therefore have required little further persuasion, although his adoption of the electrochemical theory may well date from this time. Any doubts he might still have retained were finally dispelled in 1819, as we know, but not only by the Dulong and Petit law. In November 1819 Berzelius, now back in Sweden, sent word to Dulong of Mitscherlich's discovery of isomorphism,[5] which Dulong immediately saw as yet another proof of the existence of atoms. After welcoming the news, he wrote to Berzelius:

> Je suis convaincu, nonobstant les objections de M. de Laplace et de quelques autres, que cette théorie [i.e. the atomic theory] est la conception la plus importante du siècle et que d'ici à une vingtaine d'années elle fera prendre à toutes les parties des sciences physiques une extension incalculable.[6]

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1. Dulong to Berzelius, 8 Jan. 1822, in Berzelius, Bref, iv. 36-37. Prout's paper had appeared in Ann. Phil., vi (1815), 321-330 and vii (1816), 111-113.

2. Ann. Chim. Phys., i (1816), 411-416.

3. Dulong, Ann. Chim. Phys., ii (1816) 141-150.

4. Berzelius, Ibid., 329-339.

5. Berzelius to Dulong, 5 Nov. 1819, in Berzelius, Bref, iv. 10-11.

6. Dulong to Berzelius, 15 Jan. 1820, Ibid., iv. 12.

.he prediction, as we shall see, was over optimistic.

.he Rôle of Gases

.etit's tragically early death from tuberculosis in 1820 was a serious blow to French science in general and to Dulong in particular. Yet despite the loss of his gifted colleague, Dulong still had fruitful years ahead of him. His research interests were henceforth concerned almost exclusively with gases, for reasons which are not hard to suggest. Above all, he appears to have been guided throughout by a conviction that the familiar, simple laws which were thought to govern the physical properties of gases were in some sense true while the corresponding ones for liquids and solids were only approximate, being vitiated by unknown factors. It was natural to suppose, therefore, that all the 'true' laws of nature, including those as yet undiscovered, would be observed most easily in gases. There were also external factors which brought Dulong increasingly into contact with matter in the gaseous state. Thus the stimulus for several months of experiments by him on animal heat appears to have come from the prize competition on the subject set by the Académie for 1823, although the paper which resulted[1] was never submitted. A far more absorbing undertaking was his work on the vapour pressure of steam.[2] A commission set up by the Académie at the govern-

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1. P. L. Dulong, 'Mémoire sur la chaleur animale', Ann. Chim. Phys., [3] i (1841), 440-455.

2. Dulong (et al.), Ann. Chim. Phys., xxvii (1824), 95-101 and xliii (1830), 74-111.

nent's request had recommended, among several safety measures for steam-engines working at more than two atmospheres, the insertion of a fusible metal plug in the boiler walls. Since the plug was intended to melt at a temperature slightly higher than that at which the engine normally operated, it was essential to have reliable data relating vapour pressure and temperature and once again the Government asked the Académie for assistance. The resulting commission was headed by Dulong, who with Arago seems to have borne the burden of the long and often dangerous experimental work. It was small consolation that the vapour pressure measurements extending up to twenty-four atmospheres which Dulong eventually set before the Académie in November 1829 remained standard until Regnault's still more comprehensive study in the 1840s. These results need not detain us here, but the accompanying experimental proof of the exactness of Boyle's law for air up to twenty-seven atmospheres is of some interest. Unfortunately bureaucratic opposition[1] prevented a more detailed investigation, which would have included an extension of measurements to other gases, but the result as it stood gave further authority to the view that the physical behaviour of gases was governed by simple laws. Above all, it did nothing to weaken Dulong's own conviction to this effect.

Despite the demanding nature of his work for the commission,[2] Dulong

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1. Dulong, Ann. Chim. Phys., xliii (1830), 92.

2. The wearisomeness of the experiments is suggested in the following: Dulong, On. cit., 111; Dulong to Berzelius, 10 Nov. 1825, in Berzelius, Lref, iv. 63; Berzelius to Dulong, 2 Feb. 1825, Ibid., iv. 93. Also relevant are the passage from a letter of Aug. 1828 quoted on p.291 and a letter from Dulong to an unnamed correspondent (file 2220, Library of the Institut de France, Paris) where Dulong speaks of giving up responsibility for the work. The letter is dated 4 Nov. 1828.

did not entirely neglect more theoretical problems. Indeed, his constant concern until his death in 1838 seems to have been to answer the many questions arising from the law which he and Petit had discovered so suddenly in 1819. New determinations of specific heat were obviously called for, but the experimental difficulties of such work, especially where gases were concerned, were only too well known and it may well have been this consideration which caused Dulong to seek his answers instead in terms of refractive power. This he did in 1825.[1] That one who had shown no reluctance to depart from Laplacian principles and who in the letter to Berzelius quoted on p.279 had already given evidence of support for the wave theory of light should have conducted such a study in the language of the corpuscular theory, using measurements of refractive index to calculate refractive power, becomes understandable once we appreciate Dulong's aims. He was seeking above all a way of investigating the properties of individual atoms or molecules from observations on the refraction of light and for this purpose the wave theory offered no quantity which had a significance comparable with that of refractive power. By quoting comments which he made on two quite separate occasions, we may summarize Dulong's aims as follows:

> [1] Je me suis proposé, en entreprenant ce travail, de rechercher si les molécules des corps simples exercent la même action sur la lumière, ce qui pouvait paraître probable, d'après la loi des capacités pour la chaleur.[2]

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1. P. L. Dulong, 'Recherches sur les pouvoirs réfringens des fluides élastiques', Ann. Chim. Phys., xxxi (1826), 154-181.

2. Dulong to Berzelius, 10 Nov. 1825, in Berzelius, Bref, iv. 63.

> [2] Il était probable même que l'on pénétrerait plus avant, par cette voie, dans la connaissance des modifications que l'acte de la combinaison peut imprimer aux molécules matérielles...[1]

the second sin was one which had so far eluded him in the case of heat. In 1819 he and Petit concluded from experiments which they had already conducted that there was a simple relationship between the capacity of a molecule of any compound and that of all elementary atoms.[2] Doubts concerning the true composition of compounds were a major difficulty, however, and the relationship had not been, and never was to be, divulged. By 1825 the problem must have appeared as intractable as ever and it was presumably with some feeling of frustration that Dulong now turned to refractive power. Here at least was a quantity which was more easily measurable than specific heat. Moreover, by determining it for different gases under similar conditions of temperature and pressure Dulong was convinced that he was obtaining a precise measure of the 'action' of the individual gas particles on light, for he believed that under such conditions the particles of all gases had the important property of being equally spaced.[3] Thus he accepted Avogadro's hypothesis and found in it yet another good reason for believing that the laws he was seeking would emerge most simply if he studied matter in the gaseous state. Just how great Dulong's hopes of success really were is not clear, but the results were undoubtedly disappointing. A complete

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1. Dulong, Op. cit., 155.
2. Petit and Dulong, Ann. Chim. Phys., x (1819), 407-408.
3. Dulong, Op. cit., 174.

analogy with the Dulong and Petit law for elements would have demanded proportionality between the refracting force and the density or atomic weight, but no relation of any sort emerged. And, needless to say, Dulong had to admit failure with his second problem also. Refraction, it seemed, was a phenomenon quite unrelated to specific heat and one which probably depended on the electrical state of the molecule rather than on its mass. Such a conclusion, as Dulong pointed out, accorded well with the wave theory, the truth of which was now in little doubt in his mind.[1]

Dulong was distressed by his failure. In October 1825, shortly after completing the work on refraction, he complained to Auguste de la Rive:

> oint de loi générale...rien que des lois approximatives. Que voulez-vous! je n'ai point de bonheur; tandis que Gay-Lussac, il suffit qu'il touche à un sujet pour trouver une loi.[2]

It is fortunate perhaps that he did not live to witness Regnault's systematic refutation of the gas laws in the 1840s. For Dulong, as we see, 'true' laws were essentially simple.

When in 1829 he turned again to specific heats[3] his problems were unchanged and the answers were hardly more satisfactory. The method, however, represented a distinct advance in so far as, although only indirectly, it did allow the determination of c_v, the quantity which he considered the

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1. Ibid., 160-161; see also Dulong to Berzelius, 10 Nov. 1825, in Berzelius, Bref, iv. 64.

2. From a recollection by de la Rive in Oeuvres de L. Verdet (Paris, 1872), i. pp.xxv-xxvi.

3. P. L. Dulong, 'Recherches sur la chaleur spécifique des fluides élastiques', Ann. Chim. Phys., xli (1829), 113-159.

more important for the theory of heat.[1] The principle was to determine the pitch of the fundamental notes sounded in a tube sixty cm in length when filled with various gases, a procedure made practicable by Dulong's considerable talent for music.[2] A simple calculation based on Laplace's expression for the velocity of sound allowed the calculation of γ for any gas. Where t' was the temperature of the gas and n' the frequency of the fundamental note obtained with the gas in the tube, t and n being the corresponding quantities for air, then

$$\frac{n}{n'} = \frac{\sqrt{1 + 0.00375t}\sqrt{\frac{\gamma_{air}}{\rho_{air}}}}{\sqrt{1 + 0.00375t'}\sqrt{\frac{\gamma_{gas}}{\rho_{gas}}}}$$

ρ_{air} and ρ_{gas} were the densities of air and the gas measured at the same temperature and pressure. The values of γ for oxygen (1.415) and hydrogen (1.407) were so similar to that for air (1.421), a figure already known from observations on the velocity of sound, that it was assumed that γ was the same for all elementary gases. This conclusion, taken in conjunction with the supposed identity of the volume specific heats of such gases (now seen as a consequence of Dulong and Petit's law), suggested a corollary, the vast importance of which Dulong did not appreciate. Consider the argument for air. If air were heated at constant pressure from $0^{\circ}C$ to $1^{\circ}C$, i.e. so as to absorb 1.421 units of heat on the scale where c_v for that volume of

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1. Ibid., 130.

2. Girardin and Laurens, Dulong de Rouen, p.10.

air was unity, it would expand by 1/267 of its initial volume. If now it were compressed to its original volume without loss of heat, it could be argued that the 0.421 units of heat, whose function had been solely to effect expansion, would be liberated and would raise the temperature of the air by 0.421 deg C. This same temperature change, in all cases (γ - 1) for a compression by 1/267, would of course be predicted for all elementary gases. For compound gases, however, γ and hence also the increase in temperature produced by the same fractional decrease in volume varied considerably. In fact, it was Dulong's observation that γ was smallest for those gases with the greatest volume specific heat which led him to investigate whether the magnitude of the temperature changes might be determined solely by capacity and whether the amounts of heat liberated in equal volumes of gases for any given compression might in fact be identical. Once this assumption was made, it was possible to calculate $c_p(v)$ for any gas relative to air simply from a knowledge of γ. In the case of carbon dioxide for example (γ = 1.337), a fractional decrease in volume of 1/267 would liberate $0.337 c_v(v)_{CO_2}$ units of heat, where $c_v(v)$ for air on the same scale was unity. Hence, on equating $0.337 c_v(v)_{CO_2}$ to 0.421, the heat liberated by a similar compression in air, we find 1.249 and 1.670 for the volume specific heats of carbon dioxide at constant volume and constant pressure respectively. Similar calculations for other gases allowed several comparisons to be made between the predicted specific heats and the experimental values of Delaroche and Bérard. The agreement between the two sets of figures was only moderate but for Dulong, who in any case had good reason to be sceptical towards Delaroche

and Gérard's work, it was sufficiently convincing for him to conclude that given decrease in volume did in fact release the same quantity of heat from equal volumes of all gases taken at the same temperature and pressure. Privately he referred to this conclusion as 'une loi très remarquable par sa simplicité et par ses nombreuses applications',[1] but he was unfortunately not able to appreciate fully the implications of his discovery. The all important next step of quantifying the compression process in terms of work done and hence of realizing that the work of compression was always the same when equal quantities of heat were produced was by no means an obvious one to take, especially for someone like Dulong who had no engineering background.

Despite its enormous significance to modern eyes, the paper was in many ways yet another failure. Above all, the recurring problem of relating the specific heat of a compound to its composition remained unanswered. Dulong merely stated that the results he had just obtained confirmed the relationship which he and Petit had tentatively established in 1819,[2] but that further progress depended on his obtaining new information concerning the contractions which occurred in chemical reactions between gases.

Dulong never fulfilled his promise that this topic and a study of the variation of specific heat with pressure would be the subject of a second memoir. His scientific career was in fact almost at an end, for overwork

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1. Dulong to Berzelius, 15 June 1828, in Berzelius, Bref, iv. 84. See also Dulong, Op. cit., 156.

2. Dulong, Op. cit., 158 and the letter cited in the last note. For the comments of Petit and Dulong in 1819 see their paper in Ann. Chim. Phys., x (1819), 407-408.

and ill health were already seriously hindering his research. In 1827 he was Vice-President and in the following year President of the Académie des Sciences and in addition there was always the burden of teaching and the work of the commission on vapour pressures. In 1829 he complained bitterly to Berzelius:

> Ma santé est, depuis deux ans surtout, dans un état déplorable... Il y a quatre ans que j'ai commencé un grand travail sur la chaleur. Je ne puis parvenir à le terminer...Ce sont les leçons qui me tuent.[1]

His teaching in chemistry at the Faculté des Sciences had now been taken over by Gay-Lussac to leave him free for the less taxing physics course, but by 1830 he had declined so seriously that his anxious colleagues persuaded him to give up the chair of physics at the École Polytechnique and become the first Director of Studies there.[2] The freedom from teaching duties effected an improvement in his health, but there would now be even less time for scientific work. To Berzelius he confided:

> ...quelque grand que soit pour moi cet avantage, c'est l'acheter trop cher que d'être obligé de renoncer à travailler pour la science. Je suis accablé d'une multitude de détails administratifs qui ne me laissent pas un instant disponible.[3]

Yet he held the post for the rest of his life and never carried out the threat which he made elsewhere in this letter to resume the physics chair should it become vacant, although the resignation of his successor in the

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1. Dulong to Berzelius, 10 Aug, 1828, in Berzelius, Bref, iv. 74.
2. Dulong to Berzelius, 20 June 1831, Ibid., iv. 100-101.
3. Ibid., 101.

chair. C. S. M. Pouillet, in 1832, gave him the opportunity of doing so. His health failed him yet again in July 1833 when he was obliged to relinquish the coveted position of Secrétaire Perpétuel of the Académie after holding office for only one year. Friedrich Wöhler, who met Dulong about this time, commented how 'Son état constant de maladie semble cependant fortement marquer de son empreinte toute sa personnalité...'.[1]

Dulong was not alone in his interest in the specific heats of gases during the 1820s and in his belief that Delaroche and Bérard had not said the last word on the matter. There were others, it seems, who were also influenced by the Dulong and Petit law. In 1823 W. T. Haycraft announced to the Royal Society of Edinburgh his conclusion that the volume specific heats of all gases were identical.[2] His apparatus consisted of two identical calorimeters filled with water, in each of which was immersed a spiral tube. Dry air heated to about 180°F was passed through the tube in one calorimeter while the gas under test, similarly heated and carefully dried, flowed through the other. By comparing the rises in temperature in the two calorimeters the specific heat at constant pressure of any gas relative to air could thus be determined. The heating effects of equal volumes of carbon dioxide and ethylene, the only compound gases used, were found to be the same as those of all the common elementary gases.

The apparatus of the two young Swiss physicists Auguste de la Rive and

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1. Berzelius, Bref, iv. 4.

2. W. T. Haycraft, 'On the specific heat of the gases', Edin. Trans., x (1824), 195-216.

François Marcet[1] was equally insensitive. In 1827 they rejected existing determinations made at constant pressure[2] and described their own simple method designed to yield the specific heat at constant volume. The gas was enclosed in a small glass vessel which could be exposed to a constant source of heat, either by direct immersion in hot water or by being suspended at the centre of an almost completely evacuated copper sphere which was itself immersed in the water. The specific heats of fourteen gases were deduced by comparing the increases in temperature indicated by a manometer fitted to the vessel, when it was exposed to the source of heat for equal intervals of time. Like Haycraft, de la Rive and Marcet concluded that the volume specific heats of all gases, elementary and compound, were identical. The apparatus lent itself readily to the determination of specific heats at pressures below atmospheric and, predictably enough, there emerged further evidence to support the well established myth that the specific heat of a given mass of gas increased with rarefaction. Observations on air, for example, showed that the decrease in volume specific heat accompanying a reduction in pressure to one third of atmospheric was only about 1%, and similar results were apparently obtained for hydrogen, ethylene and carbon dioxide. As good calorists, de la Rive and Marcet naturally had no reason to doubt the accuracy of their experiments and even the smallness of the change which they observed was quite predictable. They explained it as

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1. A. de la Rive and F. Marcet, 'Recherches sur la chaleur spécifique des gaz', Ann. Chim. Phys., xxxv (1827), 5-34.

2. On the reasons for this rejection see p.313.

follow[1]:

> ...si, d'un côté, le nombre des molécules matérielles à échauffer diminue par la rarefaction, d'un autre côté les interstices qui regnent entre elles, et que l'on suppose être pleins de calorique, augmenteront dans la même proportion. Enfin nous remarquerons que les variations de température qui ont lieu dans les changemens de volume des gaz, deviennent très faciles à expliquer, tandis que si la chaleur spécifique diminuait ou augmentait dans le même rapport que la pression, il faudroit recourir à une autre cause pour en rendre compte.

t is used to avoid the conviction that we are here face to face with yet another illustration of the effect which prior commitment to a theory can have on experimental work, if only in making the observer less critical of his apparatus. e are reminded all too clearly how Delaroche and Bérard drew a similar conclusion to the above on the basis of two sets of readings only.

Later experiments, in which a larger glass vessel and hence also larger quantities of gas were used, were announced in April 1823,[2] before the publication of Dulong's results. Although the observed decrease in volume specific heat for a reduction in pressure to one third of atmospheric had now risen to about 30, observations on air, carbon dioxide, nitrous oxide and hydrogen at various pressures gave no reason to modify the earlier general conclusions. In particular, the volume specific heats of all gases still appeared to be equal.

James John, professor of chemistry at the Royal College of Surgeons in Ireland, was presumably following a suggestion

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1. De la Rive and Marcet, Op. cit., 30.

2. De la Rive and Marcet, Ann. Chim. Phys., xli (1829), 70-92.

by Gay-Lussac in devising his ingenious method, although he made no acknowledgement. In 1815[1] Gay-Lussac had pointed out that, when a current of air passed over a thermometer, the bulb of which was wrapped with wet muslin, the temperature observed was a minimum when the latent heat absorbed by the liquid on the muslin in evaporating equalled the heat given up by the air in cooling to the temperature of the bulb. Thus, after corrections for such factors as radiant heat reaching the bulb, it was possible for the specific heat of the air at constant pressure and the latent heat of the liquid to be simply related. Between 1835 and 1837 Apjohn announced three sets of results obtained by various methods, but all based on this same principle.[2] Despite an obvious lack of consistency between the results he felt justified in rejecting the view that all gases had identical volume specific heats, even when this conclusion was restricted to elementary gases, and he declared furthermore that specific heat and atomic weight were unrelated.

A similar principle was used quite independently by the Utrecht physician, Alexander Karel Willem Suerman.[3] In 1829 he had outlined the theory in an essay on vapours which he submitted successfully for a prize competi-

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1. Gay-Lussac, Ann. Chim. Phys., xxi (1822), 82-92.

2. J. Apjohn, 'On the specific heats of the permanently elastic fluids', Notices of the Communications to the British Association...1835 (London, 1836), 30-32. Also Trans. R. Irish Acad., xviii (1838), 1-16.

3. Biographical details kindly supplied from the university records by Mev. Dr. J. Meijer of the Academisch Historisch Museum of the University of Leiden.

tion in physics at the University of Leiden[1] but it was not until June 1836 that he presented his work on the specific heats of gases for an honorary doctorate at Utrecht. His results,[2] which included a study of the variation of specific heats with pressure, were far more favourable to Dulong's views than were Apjohn's. Slight deviations from equality and even an unexpectedly high value for hydrogen, which Suerman believed he could explain away, did not rule out the possibility that elementary gases had identical volume specific heats, while the values for nitrous oxide and carbon dioxide, though not carbon monoxide, were appreciably higher.

As a result of new experiments de la Rive and Marcet were also in agreement with Dulong by 1835.[3] The principle of their method was to allow a small copper vessel containing heated terebene to cool at the centre of a large evacuated copper sphere. Gas could be passed through a spiral tube immersed in the terebene and, from a comparison of the rates of cooling observed both with and without the gas flowing, the amount of heat carried off by the gas could be calculated and interpreted to yield its specific heat at constant pressure. A letter from Dulong written in 1832 approving this procedure[4] shows that this was essentially the method which he himself

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1. Published in Annales Academiae Lugduno-Batavae, 1829-1830 (Leiden, 1831).

2. A. C. W. Suerman, 'Expériences sur la chaleur spécifique des gaz et de l'air à pressions différentes', Ann. Chim. Phys., lxiii (1836), 315-332.

3. De la Rive and Marcet, Ann. Chim. Phys., lxxv (1840), 113-144.

4. Ibid., 123-126.

was using at the time. Once de la Rive and Marcet accepted that compound gases had volume specific heats which were generally greater than those of elementary gases the problem of discovering the factors which determined specific heat became as important for them as it was for Dulong. They could as yet offer no solution but they promised to give the matter the closest attention.[1]

Dulong never lost interest in the problem despite his extreme disability. In the letter of 1832 mentioned above he wrote that he needed only one week free from other duties in order to complete his experiments on specific heat, but there is no evidence that the measurements were ever made. A letter to Alexandre Baudrimont written towards the end of 1834 gives a further indication of Dulong's activity and of his undiminished confidence in the efficacy of the study of gases in elucidating the structure of matter. He wrote:

> Depuis longtemps, j'ai pensé comme vous que les éléments des corps composés, au lieu de s'unir directement, comme les chimistes le supposent, pourraient bien se diviser en entrant en combinaison, et que les corps élémentaires pourraient être moléculaires comme les corps composés, et non pas simplement atomiques. C'est au moins ce qui résulterait d'expériences que j'ai entreprises anciennement avec Petit. Dans ce moment même je m'occupe à résoudre cette question, et j'en trouverai la solution d'une manière plus certaine que vous, parce que j'opère sur des corps pour lesquels j'ai un élément de moins à considérer, et cet élément est la cohésion qui vient troubler les résultats: j'opère sur des gaz où elle est presque nulle.[2]

The nature of the experiments Dulong was performing at this time is not

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1. Ibid., 119.

2. Girardin and Laurens, Dulong de Rouen, p.73.

stated, but the mention of Petit suggests that he may be referring to determinations of the specific heats of gases. Aided by the important concept of a polyatomic elementary molecule he may well have been attempting to predict specific heats in terms of atomicity. However, by the time of his death in July 1838 he had made little progress, although he still maintained that he needed only a few more days in order to complete the work.[1] In September of that year Arago, who had been entrusted with the task of inspecting Dulong's papers, announced to the Académie des Sciences two 'laws' which he had managed to deduce from a scrap of paper found in Dulong's study. In this he was aided by Cabart, Dulong's répétiteur, and Savary, who had been partially in Dulong's confidence over the work. The 'laws' were:

> Les gaz composés formés de gaz simples qui dans l'acte de leur réunion ne sont pas condensés, ont la même chaleur spécifique que les gaz simples.
>
> Les gaz composés dans la formation desquels il y a eu une même condensation des gaz constituants, ont des chaleurs spécifiques égales, quoique très différentes de celle des gaz simples.[2]

The very statement of these conclusions reflects the measure of Dulong's failure, for the fact that one who had always appeared as such an enthusiastic believer in the literal truth of the atomic theory should relate specific heat not to the composition of an atom or molecule but to purely observational volume relationships hardly represents success. It seems possible, moreover, that by 1838 Dulong had been influenced not only by

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1. Ibid., p.27, from a recollection by Girardin.
2. Comptes Rendus, vii (1838), 604 (17 Sep. 1838).

the difficulty of the task which he had set himself but also by a mood of scepticism which had come over French science, especially where the atomic theory was concerned.[1]

This can be no more than conjecture, since the absence of published papers by Dulong after 1830 makes the interpretation of these latter years of his life difficult. Yet one event, his sudden flirtation with the positivists about 1836, does suggest a growing disillusionment. The pessimistic philosophy of positivism appears to have attracted him at a period of great frustration and so to have overcome his undoubted independence of mind, which would not have allowed him to fall in readily with any philosophical movement and which had already been apparent in his relations with the Arcueil circle. In the hope of throwing light both on Dulong's philosophy of science in the mid-1830s and also on his standing in the scientific community, we shall examine his association with Comte in some detail.

Dulong and the Positivists

Positivism, in the form given it by August Comte, originated in France in the 1820s. While its principles can hardly be said to have dictated the course of French science in the second quarter of the nineteenth century, they nevertheless contained elements which appealed to some of the most prominent French scientists of the period and their acceptance, limited though it was, does seem to reflect important changes of attitude, even if

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1. On this see pp.320-328.

it did not cause them. Some clarification we follow here in the work of Dulong.

Since mathematics headed Comte's hierarchy of the sciences, as fulfilling most nearly the positivist ideals, it is not surprising to find that his models of scientific method were commonly taken from mathematics rather than from the comparatively 'backward' science of chemistry, to which the Dulong and Petit law belonged. Despite this and despite the fact that Fourier's analytical treatment of heat conduction in solids became a natural archetype for positive method from the beginning,[1] Comte did find much to admire in Dulong. He was generous in his praise of Dulong's purely physical work, in determination of a law of vapour pressures, for example, or the experiments conducted with Petit in 1818 and the accompanying examination of Newton's law of cooling.[2] Here Dulong had done all that the positive philosophy could have demanded, which was, as Comte put it, to:

> regarder tous les phénomènes comme assujettis à des lois naturelles invariables, dont la découverte précise et la réduction au moindre nombre possible sont le but de tous nos efforts, en considérant comme absolument inaccessible et vide de sens pour nous la recherche de ce qu'on appelle les causes, soit premières, soit finales.[3]

For Dulong and Petit law, however, barely belonged in this category. There can be little doubt that it suffered in Comte's eyes from forming part of

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1. Correspondance inédite d'Auguste Comte (Paris, 1903), i. 28, where, in a letter to Blainville dated 31 Mar. 1826, Comte expresses the hope that Fourier may be persuaded to attend his lectures on positivism. There are many examples of his high regard for Fourier in the Cours de Philosophie positive, but we may note especially the reference in Cours (Paris, 1830), i. 1-17.

2. Comte, Cours, ii. 534 and 544.

3. Ibid., i. 14.

the study of chemistry, a branch of science in which the theological and metaphysical phases of reasoning, which preceded the positive, had exerted a great influence, more so than on mathematics, astronomy and physics, for example, though less than on physiology.[1] The law also implied belief in the truth of the atomic theory, although this was less damning then might be concluded from a reading of the later positivists. Comte thought highly of Dalton and, although Dalton appeared on the Positive Calendar not with the chemists but with such engineers as Watt and Carnot, i.e. by virtue of his work on vapours, Comte could refer to his theory as:

> ...la célèbre théorie atomistique, qui a présidé jusqu'ici à tous les développements ultérieurs de la doctrine des proportions chimiques, et qui sert encore de base essentielle à son application journalière... le principe est tellement en harmonie avec l'ensemble des notions scientifiques de tous genres, qu'il se réduit presque à une heureuse généralisation directe des idées spontanément familières à tous les esprits qui cultivent les diverses parties de la philosophie naturelle; aussi en a-t-elle eu lieu sans obstacles.[2]

The substitution of a theory of chemical equivalents for the atomic theory would naturally be welcomed as more 'positive' but, as Comte pointed out, Dalton's attempt to do just this had effected a change merely in terminology and not in basic conception.[3]

Comte's attitude to chemistry was almost certainly not determined by his philosophical convictions alone, however. A most cursory examination of his writings, and in particular of his correspondence, indicates how

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1. _Ibid._, (Paris, 1830), iii. 7-11.
2. _Ibid._, iii. 142-143.
3. _Ibid._, iii. 149.

greatly his estimates of scientific worth were coloured by the state of his personal relationships,[1] which were themselves in turn influenced above all by the working of his extraordinary ambition, notably for the principal mathematical chair at the École Polytechnique.[2] It is therefore not surprising that his most laudatory references to Poinsot date from after 1835, when Poinsot appears first to have taken a genuine interest in Comte's principles. Poinsot had not been present at the first public exposition of the positivist philosophy in April 1826, which was terminated after only a few lectures by Comte's temporary insanity, nor at the repetition of the course in 1829.[3] Many scientists prominent at the Académie des Sciences and at the École Polytechnique, Fourier, Louis Poinsot and Henri Marie Ducrotay de Blainville attended both courses and Lavier, who sponsored Comte's entry to the École Polytechnique as répétiteur in 1832, was present in 1829. So Poinsot could hardly have been unaware of the new philosophy and he seems to have felt a positive antipathy towards Comte until the latter months of 1836. In November and December of that year he attended the lectures which Comte gave at the École Polytechnique while filling temporarily the chair of analysis and mechanics vacated by the death of Lavier. That the distinguished Director of Studies should follow the lectures of a mere répétiteur was a

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1. See, for example, the comments on his changing attitudes to Lamé and Duhamel on pp. 304-305.

2. Comte was an unsuccessful candidate for one of the chairs of analysis and mechanics on three occasions, in 1831, 1836 and 1840.

3. Comte, Cours, i. p.v.

notable event. Comte wrote in 1842:

> L'illustre Dulong...y avait personnellement suivi ces mémorables leçons qui m'avaient hautement conquis sa consciencieuse estime, malgré sa disposition antérieure à partager involontairement envers moi les préventions routinières de nos coteries scientifiques.[1]

...and even more eloquently in 1840:

> ...je n'oublierai jamais le zèle généreux avec lequel sa rare et scrupuleuse loyauté, surmontant sa modeste réserve habituelle, lui fit une loi de proclamer énergiquement les impressions favorables que cette épreuve décisive lui avait inspirées à mon égard, afin de regagner, par l'irrésistible ascendant de son esprit et de son caractère, les injustes et malveillantes insinuations auxquelles j'avais été en butte, un peu auparavant, au sein même de cette Académie.[2]

Dulong had already given evidence of some degree of sympathy when, on 19 September 1836, he specially requested that Comte's letter of candidature for Savior's chair at the <u>École Polytechnique</u> should be read out before the <u>Académie des Sciences</u>.[3] Comte had earlier solicited Dulong's support[4] and this mark of esteem greatly impressed him, as his numerous subsequent references to the incident attest.[5] But it proved of no avail and Comte

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1. <u>Ibid.</u> (Paris, 1842), vi. pp.xxiii-xxiv.

2. Comte, <u>Correspondance inédite</u> (Paris, 1904), iv. 203. On Dulong's attendance at these lectures see also <u>Ibid.</u>, 248-249 and Comte, <u>Cours</u>, vi. pp.xii-xiv.

3. <u>Comptes rendus</u>, iii (1836), 387-388.

4. Comte to Dulong, 31 Aug. 1836, in Comte, <u>Correspondance inédite</u>, iv. 162-163.

5. Comte to Blainville, 24 Sept. 1836, <u>Ibid.</u>, i. 42; Comte to Dubois, 29 Sep. 1836, <u>Ibid.</u>, iv. 191; also the document dated 4 Aug. 1840 in <u>Ibid.</u>, iv. 206. Comte frequently claimed that Dulong held him in high esteem. On this see, apart from the above references, Comte to Blainville, 27 July 1840, <u>Ibid.</u>, i. 49 and Comte to the Minister of War, 25 Jan. 1844, <u>Ibid.</u>, iv. 223.

who unsuccessful for the second time in five years.

So there can be little doubt that Comte's tributes to Dulong were inspired at least in part by gratitude for the furthering of his ambition. We can only speculate how much more prominent Dulong would have been in that part of the Cours de Philosophie Positive which dealt with chemistry had it been written after 1836 and not in the last months of 1835,[1] when, as we recall, Dulong was less well disposed to Comte. In particular, the Dulong and Petit law might well have figured prominently instead of being ignored.

Since evidence from Comte's mouth was so rarely disinterested, it is fortunate that we can document the high esteem in which Dulong was held by those subscribing to positivist ideals from another source, the Cours de Physique of Gabriel Lamé. Lamé was a contemporary of Comte, and also of C. M. J. Brunel, at the École Polytechnique, all three men having entered in the same promotion of 1814.[2] Both Lamé and Brunel were ardent disciples of Fourier and so by implication subscribed to the principles which Comte advocated. Comte's dismissal of Lamé as his inferior in 1832[3] can all too easily be attributed to their rivalry for the position of secrétaire perpétuel at the Académie des Sciences. In fact, he admired the work of both of his contemporaries, although again we must note the element of jealousy which

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1. On his dating see Louis, Cours, III. 5.

2. Launay, École Polytechnique, pp.452-453.

3. Comte to Blainville, 21 June 1832, in Comte, Correspondance inédite, I. 35-36.

disclosed his attitude towards Lamarck in 1833.[1] By 1843 his attitude to Lamé had changed considerably and he strongly advocated his election to the Académie des Sciences.[2] Since Lamé had then for several years defended principles against his detractors on the Council of the École Polytechnique, there is once again the inevitable personal element, but his tribute on the intellectual, scientific or, rather, philosophical level was now warm:

> ... car il nous paraîtra naturel, M.Lamé est celui dont l'esprit peut le plus s'ouvrir à de vraies inspirations philosophiques, et sentir le vrai prix scientifique ou logique, des raisons relatives aux plus éminentes parties de la philosophie naturelle.

Who did Lamé acknowledge as his own model in science? Not Fourier, as Comte's remarks might lead us to expect, but Petit and Dulong. In fact the entire preface to his Cours in 1836 was a tribute to the work of these two predecessors in the chair of physics at the École Polytechnique and it was to Dulong he strove to emulate. In a passage in which the use of the words 'métaphysique' and 'positif' emphasize the identity of his ideals with those of Comte, he declared:

> M.Petit et Dulon ont constamment cherché à dégager l'enseignement de ces théories incertaines et métaphysiques, de ces hypothèses vagues et désormais stériles, qui composaient presque toute la science avant que l'art de l'expérience fût assez perfectionné pour lui servir de guide certain. Leurs admirables travaux sur la thermométrie et les lois du refroidissement ont complétement reconstruit la théorie physique de la chaleur, en créant des instrumens précis et comparables, et en présentant une base irréprouvable aux raisonnemens mathématiques. Ils l'ont aussi parvenus, dans un ordre de recherches incomparablement plus difficile que tout autre, à des lois générales, qui par leur exactitude et leur fécondité ne le cèdent en rien aux plus belles lois

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1. Comte to Blainville, 17 Nov. 1833, Ibid., i. 37.

2. Comte to Blainville, 27 Jan. 1843. Ibid., i. 54-55.

de l'acoustique et de la lumière dont la découverte est due en grande partie à la perfection de nos organes, et à la précision géométrique des instruments dont ils empruntent le secours. On pouvait concevoir dès lors qu'il serait possible un jour de faire consister l'enseignement de la physique dans le seul exposé des procédés d'expérience et d'observation conduisant aux lois des phénomènes naturels, sans qu'il fut nécessaire d'énoncer aucune hypothèse préternaturée, et souvent nuisible, sur la cause primitive de ces phénomènes. C'est à cet état positif et rationnel qu'il importe de ramener la science.[1]

The positive principles were those which Petit and Dulong followed in their research, and which, according to Lamé, they had fulfilled so far as was possible in the contemporary state of science. Although the experiments on expansion and cooling represented the ideal procedure for Lamé, as they did for Kant, he showed interest in their law of specific heats, which he accepted as evidence in favour of the physical reality of atoms, despite the fact that its exactness was in serious doubt.[2]

The relationships which Dulong had with Comte and the praise from one so obviously familiar with orthodox positivist principles as Lamé can leave little doubt that his methods won the approval of many positivists. Although, at least until 1836, Dulong had shown himself a daring speculator, he had demonstrated convincingly how the effective experimental study of heat could proceed without reference to its nature. In this way he was effecting a change in attitude which complemented the similar and equally influential demonstration by Fourier in the mathematical field.

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1. Lamé, Cours de Physique. 1. pp.ii-iii.

2. Ibid., 1. 412-414.

The Decline of Laplacian Influence

'Intellectualist' factors were not alone in bringing about the decline of Laplacian science. Equally important were the changes in the scientific 'establishment' in which opponents of Laplace gradually gained high and influential office, particularly after 1816. To illustrate the importance of these changes, we might note how easy it became for Arago, as the newly appointed editor responsible for the physical sciences, to publicize Fresnel's views in the Annales de Chimie et de Physique from 1816 onwards. New elections to the Académie des Sciences also told against Laplacian interests. Arago, as it happened, had been elected (as a good Laplacian) as early as 1809, when he overwhelmingly defeated Poisson.[1] Ampère too had been elected in 1814, but it was after the Bourbon restoration that the changes became most marked. In 1816 an election for the chemistry section brought in Joseph Louis Proust, the well known exponent of the doctrine of fixed proportions in chemistry, who had been graciously proposed as the best candidate by Berthollet.[2] In 1823 Dulong was finally elected after two unsuccessful candidatures, gaining 36 votes to Fresnel's 20,[3] and in the same year Fresnel had the rare distinction of being elected unanimously.[4] They were followed in 1824 by Cauchy.[5] But the most influential figure to emerge was Fourier,

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1. c.f. F. J. Arago, 'Histoire de ma jeunesse', in Oeuvres Complètes (2nd edn.), ii. 89-92.

2. Proc. Verb., vi. 19 (5 Feb. 1816) and 24 (12 Feb. 1816).

3. Ibid., vii. 420 (27 Jan. 1823).

4. Ibid., viii. 10 (26 Jan. 1824).

5. Ibid., vii. 500 (12 May 1823).

ware treatment since his return from Egypt was hardly worthy of a former instructor at the *École Polytechnique* and a *secrétaire perpétuel* of the Institute of Egypt.[1] Almost immediately, in 1802, he had been appointed Prefect of the Department of Isère and it was at Grenoble that he produced his finest work despite heavy administrative commitments. But even his prize-winning memoir of 1811 was treated unworthily[2] and Fourier languished in the provinces until the second Bourbon restoration. Although Louis XVIII's ministers refused to approve Fourier's nomination as *académicien libre* in 1816,[3] they raised no objection in the following year when he was elected in the normal way to a long overdue place in the physics section. Further honours quickly came his way. In 1822 he defeated Biot and Arago in the election for the post of *secrétaire perpétuel* of the *Académie des Sciences*[4] and in 1827 he joined Laplace and Cuvier as one of only three scientific members of the *Académie Française*. Even his funeral was on the grand scale, possibly grander in fact than Laplace's two years earlier.[5] The anti-Laplacian trend was continued by the election of Arago to succeed Fourier as *Secrétaire perpétuel* for the mathematical sciences and by Dulong's election in 1832 to

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1. Arago, 'Éloge de Fourier', pp.xcix-cxxxii.

2. See p.270, n.1.

3. [Libri], *Rev. Deux Mondes*, 31 Mar. 1840, pp.720-729. See also Arago, *op. cit.*, pp.cxxx-cxxxi.

4. Arago, *Oeuvres Complètes* (2nd edn.), ii. 100-101.

5. Compare Arago, 'Éloge de Fourier', p.cxxxvii with J. B. J. Fourier, 'Éloge historique de Laplace', *Mém. Acad. Sci.*, x (1831), p.ci.

the corresponding office for the physical sciences to replace Cuvier. Arago's control over the Académie, which lasted until his death in 1853, appears to have been considerable and not entirely beneficial, if we are to believe Libri's virulent criticism written in 1840.[1]

Changes were apparent in less influential spheres also, for example in the Société Philomathique of Paris. Since its foundation in 1789, the society had included among its members all the leading Parisian scientists of the day and it had published a useful bulletin containing both original contributions and reports on current work in all the sciences. By 1816 the membership included not only Berthollet and Laplace, as 'emeritus members', as well as Biot, Poisson, Thenard and Gay-Lussac, but also several more recent recruits whose future rôles in the criticism of Laplacian science were not yet apparent.[2] Among these we note Arago (elected in 1808), Blainville and Dulong (both 1812). But once again it was after 1816 that the most significant changes occurred. Between February 1813 and May 1819 Fourier, Petit, Fresnel and Navier were elected and in 1813 Blainville became secretary of the society, a post which he held for four years. The orthodox Laplacian tone of the society's bulletin changed only slowly, with Poisson, who had been on the board of editors since at least 1807 and a regular contributor since 1803, and Biot, who joined the board from 1816,

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1. [Libri], Op. cit., 731-741. For a different view see J. L. F. Bertrand, Éloges Académiques (Paris, 1890), p.61.

2. For details of membership see the lists which appeared annually in the Bull. Soc. Phil.

clearly the leading influences, at least in physical and mathematical science, until 1820. In 1821, however, Fourier took Poisson's place on the board and in the following year Biot was replaced by none other than Fresnel. Notice of Fresnel's work appeared in the bulletin for the first time in 1821 and was understandably even more prominent after 1822, by which time Biot's virtual withdrawal from the scientific world and in particular from the Académie[1] had greatly reduced the opposition to the wave theory. No notice of Laplace's work appeared after 1821 and, although Poisson made intermittent contributions until the bulletin ceased publication for some years in 1826, such names as Fresnel, Arago and Navier (soon to clash bitterly with Poisson over the theory of vibrations in elastic solids[2]) became increasingly prominent.

How caloric theory fared amid this general decline in Laplacian influence is clearly our most important problem here and on this the conclusion must be that generally it fared badly. The scarcity of contemporary comment suggests that the work of even the great caloricts like Laplace and Poisson was being virtually ignored in the 1820s[3] and this was certainly the fate of Poisson's Théorie Mathématique de la Chaleur, a treatment of heat transfer in terms of caloric and a complete anachronism by the time it appeared in

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1. [Libri], Op. cit., p.732.

2. See the papers of Navier and Poisson in Ann. Chim. Phys., xxxvii (1828), 337-355; xxxviii (1828), 304-314; and 435-440; xxxix (1828), 145-151 and 204-211; xl (1829), 99-107 and 107-110.

3. See p.197.

1835. Even explicit criticism of Poisson's book came only from abroad. In Switzerland an otherwise sympathetic review deplored Poisson's retention of the caloric concept in such problems as heat conduction in solids,[1] while in Britain J. D. Forbes commented '...the whole work is to be regarded rather as a mathematical exercitation than as a serious step in physics'.[2] When Poisson died five years later he received few honours. Even his Éloge historique, which Arago was to have delivered,[3] was never given and instead extracts from a biographical memoir by Arago were read to the Académie ten years after his death.[4] For such lesser figures as Carnot and Clapeyron there was, of course, still less prospect of success and it is hardly surprising that by the 1840s the Réflexions had become a rarity.[5]

To contemporary observers, however, especially those outside France, it would have been hardly obvious that caloric theory was a spent force after 1820. Laplace, after all, was still the most eminent mathematical

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1. Bib. Univ., lix (1835), 144-166, but especially 154.

2. J. D. Forbes, A Review of the Progress of Mathematical and Physical Science (Edinburgh, 1858), p.154.

3. [Libri], 'Lettres à un Américain...III. M. Poisson', Rev. Deux Mondes, 1 Aug. 1840, p.347.

4. Arago, 'Poisson', in Oeuvres Complètes (2nd edn.), ii. 593-689. The extracts were read at a public meeting on 16 Dec. 1850, although Arago himself was not present (Comptes Rendus, xxxi (1850), 840). A brief grave-side tribute by Arago appears in Arago, Op. cit., ii. 693-698.

5. Carl Holtzmann, William Thomson and Rudolf Clausius were all unable to obtain copies in the 1840s. See C. H. A. Holtzmann, Taylor's Scientific Memoirs, iv (1846), 190; W. Thomson (Lord Kelvin), Fortnightly Review, [new series] li (1892), 315n; R. Clausius, Pogg. Ann., lxxix (1850), 368n.

physicist in Europe and he did not die until 1827. To a man of such distinction the publication of his views presented no difficulty, so that anyone who was unaware of what was really happening in France would probably not have detected that Laplace's authority in these last years of his life was in any way diminished. Yet, by the time he published the definitive version of his caloric theory of gases, there can be little doubt that he was addressing a generation the most influential members of which found such discussions of little significance. Thus it was that caloric remained prominent in the literature, and in particular in text-book literature, although few leading French scientists could now have been convinced that the fluid really existed. And it was among minor figures, such as Carnot, and among those working outside France that caloric theory continued to exert its influence. If we look at the experimental work on specific heats which we have already examined, we find Haycraft, for example, being noticeably influenced by Crawford's views, which he was 'still disposed to credit to a limited degree'.[1] He explained the cold at high altitudes by the increased capacity of air at low density and thought it an important result that he had shown the capacity of exhaled air at body temperature to be less than that of atmospheric air, a fact which was of interest only to a reader who accepted Crawford's theory of animal heat. His explanations of the intense heat of blast furnaces and of that produced by the combustion of gunpowder were similarly valid only in the context of Crawford's theory. De la Rive

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1. Haycraft, Edin. Trans., x (1824), 195.

and Marcet, on the other hand, were Laplacians. In 1827 they referred to the heat released or absorbed in adiabatic volume changes as 'la chaleur latente ou constituente du gaz'[1] and carefully distinguished it from the 'chaleur spécifique', which was the heat required solely to produce changes in temperature, not in volume. It was on these grounds that in 1827 and 1829 they chose to measure specific heat at constant volume rather than at constant pressure, although it is noticeable that by 1832 they no longer held this view.[2] Dulong too would appear to have been a Laplacian. At least he showed interest in the caloric theory and tried, unsuccessfully, to reconcile his results on the variation of specific heat with pressure with Poisson's formula.[3] The agreement with Clapeyron's formula, however, was remarkably good.

The most widely held opinion concerning the nature of heat almost certainly lay somewhere between outright rejection of caloric theory and acceptance of its literal truth. This emerges most clearly in the views of the text-book writers, especially after 1830. The day of the text-book as a vehicle for the dissemination of original ideas was now rapidly disappearing, but such books, although lacking the historical significance of the treatises by Crawford and Dalton, for example, still reflected the opinions of an influential body of working scientists. Both the vibrational and material

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1. De la Rive and Marcet, Ann. Chim. Phys., xxxv (1827), 6.
2. See pp.292-294 and 296-297.
3. Dulong, Ann. Chim. Phys., lxiii (1836), 330-332.

theories were usually described but, although slight preferences for one or the other are occasionally discernible, Thomas Thomson, earlier a convinced caloriet, summarised the situation well in 1830:

> I think, therefore, that it will be safest for us, in the present state of our knowledge to acknowledge our inability to solve this difficult problem, and to confess that we are incompetent to decide whether it be a substance or a quality.[1]

Similar sentiments were expressed by Lamé (despite a sneaking preference for the vibrational theory), Dumas, Neil Arnott and J. F. W. Herschel,[2] all of whom expressed the view that the study of thermal behaviour could proceed quite satisfactorily without reference to the nature of heat. And J. F. Daniell and Robert Dixon[3] went so far as to omit discussion of the matter altogether. Other writers, among them Eugène Péclet, Edward Turner, Michael Donovan, Francis Lunn and J. G. Fischer,[4] while equally convinced that the nature of heat was unknown, found the language of materiality at least useful

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1. T. Thomson, An Outline of the Sciences of Heat and Electricity (London, & Edinburgh, 1830), p.335.

2. Lamé, Cours de Physique, i. 298-299; J. B. Dumas, Traité de Chimie Appliquée aux Arts (Paris & Brussels, 1828), i. p.vi; N. Arnott, Elements of Physics or Natural Philosophy (4th edn., London, 1829), i. 23-24; J. F. W. Herschel, 'Heat', in Encyclopaedia Metropolitana (London, 1830), Mixed Sciences, ii. 326.

3. J. F. Daniell, Introduction to the Study of Chemical Philosophy (London, 1839); R. V. Dixon, A Treatise on Heat (Dublin, 1849), part 1.

4. J. C. E. Péclet, Traité Élémentaire de Physique (3rd edn., Paris, 1838), i. 336; E. Turner, Elements of Chemistry (6th edn., London, 1837), i. introduction. p.6 (although in the 1st edition, published in 1827, he was a caloriet. See p.7 of this edition); M. Donovan, A Treatise on Chemistry (4th edn., London, 1839), 40-41; F. Lunn, 'Heat', in Encyclopaedia Metropolitana (new edn., London, 1845), Mixed Sciences, ii. 225; J. G. Fischer, Physique Mécanique, tr. J. B. Biot (4th edn., Paris & Brussels, 1830), pp.73-74.

in explanation. At the same time both theories did have their more confirmed adherents. Dalton was still a caloric when the second edition of his New System appeared in 1842[1] and Pierre Prévost, in a highly individual version, Pouillet and Leopold Gmelin were hardly less dogmatic supporters.[2] Also, in 1843, the American chemist and physician Samuel Metcalfe published a two-volume work supporting the materiality of heat and the view that electricity and heat were inter-convertible modifications of the same 'essence'; but the normal text-book treatment of caloric in the 1820s, 1830s and 1840s was rudimentary, amounting to no more than the briefest summary of the supposed properties of caloric and with none of the elaborate details which we associate with earlier accounts. Such refinements as the distinction between latent and free caloric gradually disappeared, leaving Avogadro's detailed exposition of 1840[4] a solitary reminder of the intricacies of the theories of Laplace and Poisson.

The usefulness of the materiality of heat as a teaching concept could only prolong the life of caloric, for the vibrational theory was weak in this very respect. It lent itself less readily to the explanation of such phenomena as latent heat and thermal expansion, and perhaps even more obscure

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1. Dalton, New System (2nd edn.), pp.1-2.

2. P. Prévost, Ann. Chim. Phys., xxxviii (1828), 41-49 and xxxix (1829), 194-197; C. S. M. Pouillet, Elements de Physique Expérimentale (Paris & Brussels, 1829), i. 236-237; L. Gmelin, Hand-Book of Chemistry, tr. H. Watts (London, 1848), i. 212 and 289.

3. S. L. Metcalfe, Caloric (London, 1843), i. pp.xi-xii and 1-14.

4. Avogadro, Fisica de' Corpi Ponderabili, iii. pp.739-748 and 773-824.

on the vibrational theory was the cause of pressure in gases. Despite the criticism of such men as Herapath and J. J. Waterston,[1] neither of whom wielded any appreciable influence, the static gas hypothesis had no serious rival until after the discovery of energy conservation. In these circumstances some explanation of the repulsion between gas particles was indispensible and caloric undoubtedly provided the more convincing answer. In short, the time was not yet ripe for the outright rejection of caloric theory. However apparent its inadequacies, it still had a certain usefulness and, what was still more important, there was no feasible alternative. The decline of interest in the problem of the nature of heat which appears to have occurred during the second quarter of the nineteenth century can therefore be seen as a consequence of this confusing situation. It was only when the way forward once again became clear, in the 1850s, that interest revived.

Specific Heats and the Atomic Theory

We now return to consider further the part played by the Dulong and Petit law in the development of the atomic theory, a concept which in the first half of the nineteenth century occasioned, if anything, even keener dispute than discussions on the nature of heat. In 1819 the law appeared primarily as convincing evidence for the physical reality of atoms but it also had a possible practical application as an alternative method of

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1. On this work see S. G. Brush, 'The development of the kinetic theory of gases', Ann. Sci., xiii (1957), 188-198 and 273-282.

determining atomic weights. The existing determinations, such as those of Berzelius, were laborious and the inevitably arbitrary nature of the assumptions concerning the composition of compound molecules meant that there was often a choice between two or three different atomic weights, depending on the assumptions made. Dulong and Petit were confident not only that their law would allow this choice to be made correctly but also, given accurate specific heat measurements, that it would yield values which were trustworthy in their own right without reference to the better established chemical methods.[1] Unfortunately, the exact nature of the law was never sufficiently established for their hopes to be completely fulfilled, but there could be no doubt that atomic weight and specific heat were closely related and the continuing prominence of attempts to discover true atomic weights after 1820 therefore ensured that the study of specific heats remained a live research interest. Moreover, concern with the problem of atomic weight determinations had now been further stimulated by the emergence of another new method. In 1819 Berzelius's pupil Eilhard Mitscherlich had shown[2] that the atoms of certain elements in isomorphous crystalline compounds could be replaced by those of other elements without altering the crystalline form and that the atomic weights of the 'replacement' elements could then be easily deduced by comparing the relative weights of them in the isomorphous compounds so formed. Berzelius was so impressed by his pupil's discovery, as well as

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1. Petit and Dulong, Ann. Chim. Phys., x (1819), 403-406.

2. E. Mitscherlich, Abhandlungen der physikalischen Klasse der Königlich-Preussischen Akademie der Wissenschaften, (1818-9), 427-437.

by the Dulong and Petit law, that he proceeded to revise his own values for atomic weight in the light of the new work. By 1826 he had produced a modified table[1] in which many of his original weights had been halved, thus bringing them closer to those derived from the Dulong and Petit law and, incidentally, to present-day values. But the apparent reconciliation between the atomic weights determined by the various methods was short lived, for it was in 1826 too that Dumas, then a brilliant young chemist working in Thenard's laboratory, announced his celebrated method for the measurement of vapour densities of a wide range of substances not normally in the gaseous state.[2]

As Dumas recalled some years later,[3] his intention in undertaking the vapour density work had been merely to confirm existing atomic weights. He had no hesitation in putting forward that part of Avogadro's hypothesis dealing with the equal spacing of the particles of all gases at any given temperature and pressure, since all physicists, he declared, were in agreement on this.[4] But more justification was required in connection with the divisibility of elementary molecules which, although it necessarily followed if Avogadro's hypothesis was to be extended to compound gases, only Gay-Lussac had accepted in practice,[5] according to Dumas. Unfortunately there

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1. Pogg. Ann., vii (1826), 414.

2. J. B. A. Dumas, 'Mémoire sur quelques points de la théorie atomistique', Ann. Chim. Phys., xxxiii (1826), 337-391.

3. Dumas, Ann. Chim. Phys., 1 (1832), 172.

4. Dumas, Ann. Chim. Phys., xxxiii (1826), 337-338.

5. Ibid., 338.

is no evidence of Gay-Lussac's support except in so far as it is implied by the very favourable report which he made, with Dulong, on Dumas's paper.[1] However, there was little doubt in Dumas's mind that the vapour densities of elements at least were proportional to their atomic weights and he found good agreement with the accepted results for iodine vapour, one of only two elements examined. Mercury vapour, on the other hand, with a density which indicated an atomic weight one quarter of that originally adopted by Berzelius, gave the first hint of the serious discrepancies which were soon to emerge. Dumas's confidence in the atomic theory was such that he declined to comment further without a more detailed examination of mercury and two years later[2] he reaffirmed his faith in the theory, elaborating his distinction between the 'atome physique' and the 'molecules chimiques', a very small number of which were supposed to compose the 'atome'. While the 'atome physique' could never be split by such physical agents as heat, a chemical reaction, he maintained, could take place between individual 'molécules chimiques'. Dumas found in de la Rive and Marcet's recent demonstration that all gases had identical volume specific heats conclusive evidence that the particles which had identical specific heats were the 'atomes physiques',[3] for it was the number of these and not of the 'molécules chimiques' which remained the same in equal volumes of both a compound gas and of its constituent elementary gases. Hence also in solids the atomic

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1. Gay-Lussac and Dulong, Ann. Chim. Phys., xxxiv (1827), 326-331.
2. Dumas, Traité de Chimie, i. pp.iv and xxxiii-li.
3. Ibid., pp.xli-xlii.

weight deduced from specific heat measurements would be the weight of the 'atome physique' and not of the 'molécule chimique', about which, it seemed, we could know little. The atomic weights which Dumas adopted for metals in 1320 were those deduced from the Dulong and Petit law.[1]

It was as a result of a request from Mitscherlich, who visited Paris in 1832, that Dumas was persuaded to resume the vapour density measurements on phosphorus and sulphur which he had begun earlier.[2] Dumas now confessed that the results he had already obtained for these two elements had appeared so anomalous that he had not dared to publish them before, but there could now be no doubt and the difficulties had to be faced. The vapour density of sulphur, whose vapour is now thought to contain S_8 and S_2 molecules in equilibrium and which has a vapour density corresponding to a molecular formula of about S_7, yielded an atomic weight three times that deduced from specific heat measurements and chemical considerations. The value deduced from the vapour density of phosphorus, which has a molecular formula in the vapour state of P_4, was similarly 'too large' by a factor of two. We can see now that the numerical scale adopted for atomic weights was such that agreement between the weights derived from vapour densities and from chemical analysis taken in conjunction with specific heats could occur only for gases or vapours which, like oxygen (to which all other weights were referred), had diatomic elementary molecules. Dumas came very close to realizing this in the solution to the anomalies which he adopted. It was a solution which

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1. Ibid., pp.1-li.

2. Dumas, Ann. Chim. Phys., xlix (1832), 210-214 and 1 (1832), 170-178.

conflicted with existing views of the atomic theory, but at least it avoided further modification of the table of atomic weights. He suggested that atoms of sulphur in the liquid state might at a certain temperature form groups of three in order to resist vaporization. If, therefore, vapour density could be measured at a temperature just above melting point, before the grouping had occurred, it might be that no anomaly would occur. Certainly the well known changes in the viscosity of liquid sulphur with temperature were not inconsistent with the possible occurrence of such a molecular rearrangement. So the size of the atom in the solid state, the specific heat of which had been measured by Dulong and Petit, would be just one third of that existing in the vapour state. Although the possibility of such unpredictable behaviour put a drastic restriction on the usefulness of Dumas's method, he was satisfied, not to say pleased, with the explanation he had given.

But the satisfaction was short-lived and by 1836 his attitude had changed and given way to a deep distrust of the whole concept of atoms. It was in that year that he delivered the course of lectures at the Collège de France on the history and present state of chemistry which have become celebrated as the Leçons sur la Philosophie Chimique.[1] His attitude to the existing atomic theory had now become one of acute scepticism. Certainly there was little more evidence to hand than there had been in 1832, except for Mitscherlich's discovery of yet another anomaly, for arsenic vapour,[2]

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1. J. B. A. Dumas, Leçons sur la Philosophie Chimique (Paris, 1837).

2. Mitscherlich, Ann. Chim. Phys., lv (1833), 5-41.

yet Dumas could no longer view the molecular re-arrangement hypothesis as a wholly satisfactory way out of his difficulties. The particles of sulphur vapour might well contain three times as many 'atomes chimiques' as the particles of the permanent gases, much as he said in 1832, although he now considered that the particles of even the permanent gases consisted of groups ('groupes moléculaires') of 'atomes chimiques'. Furthermore, the similarity of certain physical properties of gases might lead to the conclusion that these groups, now the 'atomes physiques' of gases, were equally spaced in all gases. But all this, he concluded, in a passage which summarizes well his attitude to scientific enquiry at this date:

> ...ne sera après tout qu'une hypothèse, et sur ce sujet l'on n'en a déjà que trop fait...au lieu de creuser plus à fond ces hypothèses il vaudrait bien mieux chercher des bases certaines pour appuyer des théories plus solides...[1]

Dumas, as we see, was no positivist.[2] Even now, in 1836, he could declare:

> La philosophie chimique...a pour objet de remonter aux principes généraux de la science...de donner l'explication la plus générale des phénomènes chimiques, d'établir la liaison qui existe entre les faits observés et la cause même de ces faits.[3]

However, such explanations of phenomena, if and when they were obtained, would still be in terms of atoms:

> Prise en point de vue de la chimie actuelle, [la philosophie chimique] se compose de l'étude générale des particules matérielles que les

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1. Dumas, Leçons, p.270.

2. For further evidence of this see Dumas's enthusiastic references to the science of thermodynamics in his 'Éloge de Regnault', Mém. Acad. Sci., xlii (1863), p.lviii.

3. Dumas, Leçons, p.2.

> chimistes appellent atomes, et de celle des forces auxquelles sont soumises ces particules. Ainsi, elle comprend la recherche de toutes les propriétés des atomes...[1]

It was simply in not basing speculation solidly on facts that the atomic theory had gone astray. There was nothing wrong with hypotheses in themselves, but those concerning atomic theory had been made too quickly, when present chemical knowledge did not justify them. It was thus with a show of extreme reluctance that Dumas described what seemed to him the probable structure of gases, in the light of the now notorious anomalies.[2] The agreement between the atomic weights of the common elementary gases deduced from density measurements and from combining weights, and the equality of their volume specific heats provided strong evidence that equal volumes of these gases at least contained equal numbers of 'atomes chimiques'. But what of sulphur vapour, for example? Here the atomic weight deduced from specific heat in the solid state agreed with that determined by chemical methods, but the number of atoms in unit volume of vapour was manifestly not the same as for the elementary permanent gases.[3] One further difficulty, which had in fact been merely ignored for some years, now had to be faced. There were certain elements, tellurium for example, for which Berzelius had been unable to reconcile the evidence of chemical analysis and specific heat

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1. Ibid.

2. Ibid., pp.278-280.

3. The solution recently proposed by Berzelius had been to suppose that Avogadro's hypothesis did not necessarily apply to elements which were not gaseous at room temperature. See Jahres-Bericht, xiii (1834), 59-63.

measurements. Berzelius's atomic weight for tellurium was twice that calculated from the Dulong and Petit law. The solution, for Dumas, was a three-fold distinction. Specific heat, he supposed, was associated with the ultimate particles of matter, the true atoms, of which, say, one thousand might constitute a single 'atome chimique' of sulphur, copper or zinc, i.e. of elements for which the Dulong and Petit law and chemical analysis gave the same atomic weight, while two thousand true atoms would make up one 'atome chimique' of tellurium. It was combinations of whole numbers of these chemical atoms which gave rise to the laws of definite and multiple proportions and it was the weights of these atoms which emerged from any chemical analysis. The transition to the vapour state, as we have mentioned, gave rise to yet another grouping between 'atomes chimiques'. The 'atomes chimiques' of mercury would even split in two in the vapour state. Thus, despite his erroneous views on atomic structure, Dumas came to the correct conclusion that the three methods of determining atomic weights were not in fact measuring the same quantity. While isomorphism offered a promising alternative solution for the examination of 'atomes chimiques', specific heat studies now assumed a unique significance for him as a probe into the ultimate building blocks of matter. The situation in one important respect had been completely reversed since 1826, when de la Rive and Marcet's results, since discredited, had persuaded Dumas that chemical forces were more effective than heat in breaking down matter into its simplest form. He now urged the determination of large numbers of specific heats, especially of compound bodies, and showed particular interest in F. E. Neumann's recent extension

of the Dulong and Petit law to certain compounds.[1] Neumann's experiments had shown that the product (molecular weight x specific heat) was very nearly constant for a number of metal carbonates and that a similar relationship, though with a different constant product, held for sulphates. The law for elements, as Lunas pointed out, thus became a particular case of a more general law in which atoms of similar structure, whether elementary or compound, would have identical capacities. It was naturally important to extend measurements to new types of compound and to discover the exact nature of the dependence on structure. In a subsequent lecture Lunas put the case for the study of specific heats, and also of Faraday's laws of electrolysis, even more strongly:

> ...la chimie ne tardera point à prendre un nouvel essor, quand, s'appuyant sur de bonnes observations elle pourra discuter et comparer les chaleurs spécifiques d'un grand nombre de corps, et vérifier la loi de Dulong et Petit sur tous les composés; quand elle pourra, d'après des expériences précises et nombreuses, comparer les électricités spécifiques d'un grand nombre de substances simples, ou composées rien ne peut nous permettre de prévoir les résultats auxquels on parviendrait, par une étude approfondie du rôle de la chaleur et de celui de l'électricité, dans la constitution des molécules du corps.[2]

At, for all the promise of the investigation of forces so closely linked to the individual particles of matter, Lunas was adamant that such theorizing in atomic theory was premature. The unjustified assumptions which had to be made now proved too much for Lunas and in a well known passage, which expresses rather strongly his despair with the present state of the theory, he declared:

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1. F. X. Neumann, Pogg. Ann., xxiii (1831), 1-39.

2. Lunas, Lecons, pp.422-423.

> Si j'en étais le maître, j'effacerais le mot atome de la science, persuadé qu'il va plus loin que l'expérience; et jamais en chimie nous ne devons aller plus loin que l'expérience.[1]

Dumas was by this time not alone in his sceptical attitude to atoms, for the atomic theory had long had influential opponents quite apart from Berthollet's disciples. Wollaston, for example, who did so much to spread knowledge of the atomic theory, had always stressed that he was determining equivalents and not atomic weights. And Davy, even when presenting the Royal Medal to John Dalton on behalf of the Royal Society in 1826,[2] had been careful to distinguish Wollaston's work, 'the practical part of the doctrine', from 'the atomic or hypothetical part'. The positivists too were natural critics, although Comte at least was surprisingly moderate.[3] So even before the 1830s we already detect a certain scepticism which the anomalies discovered by Dumas could only serve to intensify. Here, after all, was experimental evidence which actually contradicted the atomic theory as it was then understood and the effect appears to have been considerable. If we are to believe a comment made by Robert Kane at the meeting of the British Association for the Advancement of Science in 1837,[4] the use of the word 'atom' as if atoms had real physical existence '...could not, with truth, be charged upon any well-informed chemist'. The accompanying discussion is

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1. Ibid., p.290.

2. H. Davy, Six Discourses delivered before the Royal Society (London, 1827), pp.128-129.

3. See p.301.

4. The Athenaeum, 7 Oct. 1837, p.747.

interesting not only for Whewell's objection to the assumption of the physical reality of atoms but also for Sir William Rowan Hamilton's championing of a Boscovichian view of the atom. Faraday, who had already expressed grave doubts concerning the theory,[1] was present and 'emphatically stated, that he was not an atomic theorist'. Liebig too would seem to have attended, for he was introduced to the audience after the above discussion. Whether the comments influenced him is not clear, but by October 1838 he and some other prominent German chemists had expressed their opposition to the atom as a physical reality, as we learn from a hitherto unpublished letter[2] from Liebig to his friend and closest contact in France, Théophile Jules Pelouze. Wöhler, Gustav Magnus, Heinrich Rose, Gmelin and Liebig, it appears, had taken a three weeks holiday in Alsace during which they had discussed the atomic theory. In a passage which seems to reflect the influence of Dumas's observations, Liebig wrote (in far from perfect French):

> Le resultat le plus immediat de nos discussions et de nos entretiens sera je crois de quelque influence. Nous cinq nous sommes convenu d'abandonner tout à fait les nombres d'atomes qu'exprimeut le rapport de volume, nous sommes décidés à adopter dorenavent comme poids d'atome le poids des equivalens et pour nombre d'atomes les nombres equivalens. Ce ne serait que ceux qui ne sont soumis à aucun changement dans l'avenir pendent que tous ceux qui exprimeront les idées reçuntes du jour devraient etre changé a chaque moment. Suivons nous la loi de Mr. Dulong sur les chaleurs spécifiques nous aurons d'autres nombres qu'en admettant pour guide la théorie des volumes ou l'isomorphisme toute ces doctrines sont basés sur des hypotheses; mais pour un emploi aussi simple, il ne nous faut pas des hypotheses, pourquoi treiner nos idées sur l'état moléculaire des corps dans notre mode

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1. M. Faraday, 'Experimental researches in electricity - seventh series', Phil. Trans., (1834), 121.

2. Liebig to Pelouze, 12 Oct. 1838, in dossier 'Pelouze', Académie des Sciences, Paris.

> d'exprimer la composition des corps, d'écrire nos formules. On ne voit pas une seule raison qui puisse justifier un tel emploi. Et particulièrement pour l'enseignement les nombres équivalens ont une utilité réél. faut à...[word unclear]...et à comprendre ce qu'ils signifient il ne troubleront jamais l'esprit de ceux qui suivent les cours de chimie.

He went on to ask whether some French chemists might be persuaded to adopt his view of atoms, but it was Berzelius whom he wanted to see at the head of the movement. The outcome of this request is unclear, but the scepticism towards the atomic theory, although widely felt, probably did not take the form of anything resembling an organised movement.

As a possible way out of the difficulties, Dumas advocated the intensive study of specific heats, as we have seen, and in this, as in his attitude to atoms, he was not alone. In 1836 Baudrimont wrote to the Académie des Sciences[1] claiming to have found a way of removing the discrepancies between the different methods of determining atomic weight by establishing that the specific heats of elementary or compound substances were proportional to the number of 'molecules' they contained. Unfortunately no further details were given and the memoir was never read.[2] There is evidence too of official interest in the problem of specific heats in the announcement of two major prize competitions in 1839. The subject of the first, proposed by the Accademia Reale delle Scienze of Turin on 21 April 1839[3], was as follows:

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1. A. Baudrimont, 'Sur la détermination des poids atomiques et en particulier sur une loi relative aux chaleurs spécifiques', Comptes Rendus, ii (1836), 530.

2. The letter quoted on p.297 suggests that Baudrimont would have used the concept of the polyatomic elementary molecule in his work.

3. Mem. Accad. Sci. Torino, [2] i (1839), scienze fisiche e matematiche, pp.lxi-lxvi and Comptes Rendus, ix (1839), 331.

> determinare sperimentalmente il calore specifico del maggior numero possibile di gaz permanenti, sia semplici, sia composti.
>
> Si desidera che almeno per alcune delle sostanze gazose venga determinato separatamente il calore specifico sotto pressione costante e sotto volume costante, per verificare la relazione stabilita da Dulong tra queste due sorta di calori specifici dei gaz, e per la quale dato uno di essi per un gaz qualunque si potrebbe conchiudere l'altro.[1]

A principal aim of the competition was a further investigation of the atomic theory based on the Dulong and Petit law, a purpose for which gases showed themselves particularly suitable. According to the President of the Accademia, who announced the competition, the absence of attractive forces between gas particles suggested that the law, now generally considered to be no more than approximate, might be observed precisely in the gas state. Certain features of terminology and the assumption that the 'molecoli integranti' in both elementary and compound gases were similarly spaced almost certainly indicate Avogadro's influence in the choice of subject. His problem of relating volume or molecular, specific heat to the composition of compound molecules[2] had been given new prominence by Dumas's recent work, which had indicated that the volume specific heats of even elementary gases might be determined by their molecular structure. Avogadro's problem was mentioned specifically in the announcement with the comment that a solution would be found only by determining a large number of volume specific heats at identical temperature and pressure. In a review

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1. Mem. Accad. Sci. Torino, [2] i (1839), scienze fisiche et matematiche, p.lxi.

2. See pp.254-256.

of earlier work the announcement criticized Delaroche and Bérard's experiments for yielding c_p only and Dulong's for their indirectness, but fully appreciated the difficulty of a direct measurement of c_v. It would be sufficient if, after a direct determination of c_p for various gases, the rises in temperature produced in them by a given compression were measured and examined to see whether they were inversely proportional to the volume specific heats at constant volume, as deduced from the experimental values of $c_p(v)$ taken in conjunction with Dulong's values for γ. Once Dulong's conclusion was thus confirmed, measurements of the temperature changes in adiabatic compression might in themselves yield reliable values not only for c_v but also, since γ would emerge from such experiments, for c_p also.

It is a measure of the extreme difficulty of such work that by the closing date in December 1841[1] no entries had been submitted and that even when the time limit was extended to December 1843, at Avogadro's instigation,[2] there was similarly no response and the question was withdrawn.[3]

The second of the two competitions was probably set in the hope that studies of specific heat might be enlisted in the examination and classification of the rapidly increasing number of organic compounds. In November

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1. Mem. Accad. Sci. Torino, [2] iv (1842), scienze fisiche e matematiche, p.lvii-lx.

2. Ibid., v (1843), p.lix.

3. Accademia delle Scienze di Torino. Registro dei verbali della Classe di Scienze fisiche, matematiche e naturali, ix. 137. Information kindly communicated by Dr. Gianni Mondolino of the Accademia.

1839)[1] Biot suggested an investigation to discover whether specific heat was identical for all the members of a group of isomers and a few weeks later the Académie des Sciences announced that a prize would be awarded for the determination of the specific heats both of elements and of a large number of mineral and organic compounds.[2] Particular emphasis was laid on the possibility of comparing the specific heats of various groups of isomorphous compounds and of isomers. The style of the announcement is interesting in that it emphasizes the observational aspects of the investigation, as Dulong had done in his later work, and it thus forms a notable contrast with the Turin Academy's announcement in which the language of atomic theory was used so confidently. But the French competition was no more successful. In June 1842 Regnault announced, on behalf of a committee consisting of Gay-Lussac, Arago, Becquerel and himself, that no entry had been received and recommended that the subject should be replaced by one on the heat of chemical reaction.[3] Strangely enough, it was Regnault himself who had already made the competition unnecessary, for his own experiments on specific heat announced in 1840 and 1841 had set standards of care and precision which were unlikely to be matched by any contemporary.[4]

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1. Comptes Rendus, ix (1839), 655-656 (21 Nov. 1839).

2. Ibid., 947-948 (30 Dec. 1839).

3. Ibid., xv (1842), 1147 (19 Dec. 1842) and xiv (1842), 1051 (27 June 1842).

4. See pp. 335-336.

It was fortunate indeed that in the young Regnault Laure had so quickly found a man equal to the problems which he had posed in the Legons. As it happened, Regnault was to do far more than Laure could ever have hoped of it in the way of experimentation, as well as the authority, of his experimental work on heat which makes him such a fitting subject for a conclusion to this study. Such was the excellence of Regnault's work that it is easy to see him simply as the originator of a new era in the study of thermal properties. In one sense this would be a true assessment, but it should be borne in mind that equally he belongs firmly to a research tradition dating back to the discovery of Dulong and Petit's law in 1819. It for this tradition and the problems which it raised in the late 1830s we may be sure that Regnault's talent would have been applied in other directions and that he would therefore never have attained the position of distinction which he now occupies in the history of physics.

CHAPTER 7

Conclusion: The Physics of Victor Regnault

A brief concluding chapter can hardly do justice to Victor Regnault's monumental achievements in the study of the thermal properties of matter in all three states. The results of his researches, contained in three forbidding volumes of the Mémoires of the Académie des Sciences[1] and numerous papers, stand as the culmination of the research interests whose history we have been tracing. When Regnault ceased working on the subject about 1870 he had provided authoritative answers to nearly all the most important problems relating to the study of heat which had been tackled, with such limited success, since the middle of the eighteenth century. That Regnault's answers have undergone only minor modifications to this day bears witness to the excellence of his work.

However, it is not our intention here to examine Regnault's experiments in detail. His general philosophy of science, never stated explicitly but implied in the vast compilations of data which he drew up, is of far greater interest, not least for the light which it throws on the state of the physical sciences in France about the middle of the nineteenth century. Naturally any conclusions of this more general nature, based as they are on the work of one man, must be viewed with extreme caution but Regnault, both

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1. Mém. Acad. Sci., xxi (1847), xxvi (1862) and xxxvii (1868-70). These were reprinted with identical pagination in three volumes (Paris, 1847-1870) as H. V. Regnault, Relation des Expériences... and are therefore cited hereafter as Regnault, Expériences, i, ii and iii.

by the influences which he experienced as a young man in the 1830s and by the central position which he occupied in the French scientific community of his day, is of more than ordinary significance for our purpose. Unlike Carnot he was by no means a peripheral figure. His education was conventional,[1] with a brilliant career at the École Polytechnique being followed by studies first at the École des Mines and then under Liebig at Giessen and Boussingault at Lyons. In 1836 he was back in Paris, as assistant to Gay-Lussac and in 1840, when he was still not quite thirty, his distinction as an organic chemist earned him a place in the Académie des Sciences and, shortly afterwards, Gay-Lussac's chair of chemistry at the École Polytechnique. But even then his days as a chemist were numbered. By November 1839[2] he had already performed experiments on the specific heats of isomers which, although unpublished, had attracted the attention of such influential figures as Arago, Thenard, Élie de Beaumont, Gay-Lussac and Dumas. Of these names the most significant is that of Dumas, for it seems that it was largely through him that this early interest in specific heats grew into the task which was to occupy the rest of Regnault's working life. Recalling over forty years later how he helped to effect the transition, Dumas wrote, with obvious pride:

> Peut-être s'est-il permis de rappeler les efforts persistants que j'ai dû faire pour déterminer Regnault à entrer en lutte avec le problème des chaleurs spécifiques. Longtemps il hésita; s'engageant résolument, enfin, dans une carrière qui devait honorer sa vie, il montra...les qualités d'un savant de premier ordre.[3]

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1. For biographical details see J. B. Dumas, 'Éloge historique de Henri-Victor Regnault', Mém. Acad. Sci., xlii (1883), pp.xxxvii-lxxv.

2. Comptes Rendus, ix (1839), 656.

3. Dumas, Op. cit., p.xlix.

Regnault's initial problems were naturally enough Dumas's. In papers read to the Académie in April 1840 and January 1841[1] he demonstrated first the approximate nature of Dulong and Petit's law when applied to solid elements and then the validity, within these limitations, of Neumann's attempt to extend the law to compounds. By the date of the second paper he was probably already convinced that only in the case of gases could the law be observed exactly[2] and he had already performed experiments to determine their specific heats.[3] Whether direct or indirect means were used, it was presumably intended that these determinations should be at constant volume since, in Regnault's opinion,[4] the heat added to a substance in order to effect expansion was a principal cause of the deviations from constancy of the various atomic and molecular heats. Regnault's hopes of finding a case in which Dulong and Petit's law was obeyed exactly were never fulfilled and in 1853, when he eventually described his work, he was in no doubt that the atomic heats of the common permanent gases hydrogen, oxygen and azote were by no means equal and were, in any case, quite different from those of chlorine and bromine.[5] His attempt to classify the volume

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1. H. V. Regnault, 'Recherches sur la chaleur spécifique des corps simples et composés', Ann. Chim. Phys., lxxiii (1840), 5-72 and [3] i (1841), 129-207.

2. For a later statement of this belief see Regnault, Ann. Chim. Phys., [3] ix (1843), 341.

3. Regnault, Ibid., [3] i (1841), 132.

4. Regnault, Ibid., lxxiii (1840), 66 and [3] i (1841), 200.

5. Regnault, Expériences, ii. 302-327.

specific heats of compound gases in terms of the volume changes which occurred during their formation[1] was partially successful, but here again the relationships were at best approximate and certainly gave no support to Avogadro's belief that the specific heat of a compound gas might be predicted exactly in terms of those of its constituent elements.

With Dumas's problems answered it might have been expected that Regnault would return to organic chemistry, but he had now become committed to the study of heat in other ways. As early as 1840[2] he had shown interest in heat-engine operation and soon afterwards he took the fatal step of accepting financial support for his experiments from the Minister of Public Works.[3] Encouraged by the generous official backing he embarked immediately on the systematic re-determination of all the experimental data which could conceivably be required in the theory and practice of steam and other heat engines. The result, as it emerged over the next twenty-five years, was the most precise and yet the most unimaginative of compilations, a warning perhaps of the dangers of dependence on government sponsorship in the practice of science. By the time Regnault finally recognized the enormity of his task[4] it was too late and in the 1850s and 1860s resignation rather than excitement seems to characterize his research.

There was no place in Regnault's papers for the discussion of theory.

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1. Ibid., 310-327.
2. Ibid., p.iii.
3. Ibid., i. 4-5.
4. Ibid., ii. 3. See also Ibid., i. 12.

they contained only experimental results interspersed with digressions on the validity of various empirical laws. Inevitably in an investigation of such unprecedented thoroughness the inadequacy of the simple gas laws was ruthlessly exposed. Between December 1841 and May 1842, for example, Regnault showed[1] not only that the expansion coefficient for gases determined by Gay-Lussac was too high but also that the coefficient varied with both the nature of the gas and with its initial pressure.[2] During the next decade the laws of Clément and Desormes[3] and of Boyle[4] were similarly shown to be no more than approximations and the belief, which had led so many caloriste astray, that the specific heat of a gas decreased as it was compressed was finally and authoritatively dispelled.[5] How differently the caloric theory of gases would have developed had these results been available and accepted half a century earlier is an interesting matter for speculation. There would then have been no reason to believe that matter in the gaseous state was in any sense unique and gases would presumably have attracted correspondingly less attention. Also the work of Laplace, Poisson and Carnot, who had built so much on the ideal gas laws

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1. H. V. Regnault, 'Recherches sur la dilatation des gaz', Ann. Chim. Phys., [3] iv (1842), 5-63 and v (1842), 52-83. Also Comptes Rendus, xiii (1841), 1077-1079.

2. Cf. Davy, Phil. Trans., (1823), 204-205.

3. Regnault, Expériences, i. 635-728.

4. Ibid., 329-428 and Comptes Rendus, xxii (1846), 787-798.

5. Regnault, Expériences, ii. 205-228.

and on Delaroche and Bérard's results, would have taken a very different form and the Irvinist theory would have become quite untenable. By the 1840s, however, caloric theory in the refined sense in which it had been understood during the first quarter of the century was a thing of the past and such theoretical issues as Regnault's work did raise were not of current interest. Indeed, by this time many of the experimental results which he obtained were original only in their extraordinary degree of accuracy and obvious reliability. Thus experiments were already known which cast doubt on the truth of Boyle's law,[1] Gay-Lussac's expansion coefficient[2] and Clément and Desormes's law,[3] while the rigorous truth of Dulong and Petit's law had never been adequately demonstrated.

Doubts, however, were one thing; Regnault's thorough and systematic investigation quite another. And the fact was duly recognized, by the stream of students,[4] among them the young William Thomson,[5] who came from all over Europe to learn the new techniques, by the Royal Society's award of the Rumford and Copley medals, in 1845 and 1869 respectively,[6] and by

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1. C. Despretz, Ann. Chim. Phys., xxxiv (1827), 335 and 443.

2. P. Rudberg, Pogg. Ann., xli (1837), 271-293 and xliv (1838), 119-223. For the work of Gustav Magnus, which was contemporary with but independent of Regnault's, see Magnus, Pogg. Ann., lv (1842), 1-27 and lvii (1842), 177-199.

3. The relevant experiments were by Despretz and Dulong. See C. Despretz, Traité Élémentaire de Physique (4th edn., Paris, 1836), p.212 (and note) and Jamin, Cours, i. 487.

4. Regnault, Expériences, ii. p.lx.

5. S. P. Thompson, Life of William Thomson (London, 1910), i. 121-132.

6. The Record of the Royal Society (4th edn., London, 1940), pp.347 and 348.

Regnault's admission in 1850 as an officer of the Legion of Honour.[1] The official recognition accorded him could hardly have been more generous, but it would seem that the sterility of the work which had occupied the best years of his life did not escape even Regnault himself. The complaints which he made about the unexpected magnitude of the undertaking[2] would surely not have come from a man satisfied with his achievements and we must see in Regnault, as in Dulong some twenty years earlier,[3] a man who had fallen victim to a government commission. In this case, however, Regnault's preoccupation with the tedious accumulation of results was especially unfortunate in view of the momentous developments in the theory of heat which were taking place outside France during the 1840s. In this work the rôle of Regnault was simply to provide much of the data, important data admittedly, which such men as Thomson, Clausius and Rankine were to use in establishing the principle of the conservation of energy, and the only suggestion that he may have had some original thoughts on the matter himself is found in a comment which he made in 1853. After praising the work of Joule, Thomson, Rankine, Mayer and Clausius, Regnault went on:

> De mon côté, depuis longtemps, j'ai exposé dans mes cours des idées analogues, auxquelles j'avais été amené par mes recherches expérimentales sur les fluides élastiques. Dans ces recherches, je rencontrais, en effet, à chaque instant des anomalies qui me paraissaient inexplicables dans les théories antérieurement admises.[4]

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1. See the obituary notice of Regnault by 'T. H. M.' in Nature, xvii (1878), 263.

2. See Regnault, Expériences, ii. 3; also Ibid., i. 12.

3. See p.284, n.2.

4. Regnault, Expériences, ii. p.vi.

Unfortunately there is no independent evidence to support Regnault's claim and, even if he had been teaching energy conservation in his lectures, this would not necessarily have implied originality on his part. As one of three referees for a short paper by Joule[1] Regnault must have known of the famous paddle-wheel experiments by August 1847 and he was evidently sufficiently impressed to allow the paper to appear in the Comptes Rendus of the Académie. In the same journal in the following month he would presumably have seen Marc Seguin's extension of the principle of the equivalence of heat and work to account for the cooling of gases and steam on expansion[2] and there was of course much else which he might have read on the subject in both British and German journals. Yet, despite all this, there is evidence that the new discoveries had little immediate effect on him. In 1849, when his experiments on the specific heats of gases chanced to yield a striking instance of the new principle,[3] Regnault could offer no comment and in the following year during some experiments on gas expansion[4] he quite misinterpreted a small cooling effect which appears to have been precisely the same effect as that to which Joule and Thomson were to give their name when they discovered it independently some two years later.[5] It was only

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1. Comptes Rendus, xxv (1847), 309.

2. M. Seguin, 'Note à l'appui de...M. Joule...', Ibid., 420-422.

3. Regnault, Expériences, iii. 579-583 and ii. p.vii.

4. Ibid., iii. 583.

5. J. P. Joule and W. Thomson, 'On the thermal effects experienced by air rushing through small apertures', Phil. Mag., [4] iv (1852).

in 1853, when the struggle to gain acceptance for energy conservation was all but won, that Regnault finally gave it his support.[1] In an all too characteristic manner he had entered the field when the really creative phase in the early history of thermodynamics was over. He now had only his experimental dexterity to offer but, although he duly embarked on a careful determination of the mechanical equivalent of heat,[2] he was never satisfied with his experiments and so failed even in the one respect in which he might still have been pre-eminent.

Regnault's failure to play any significant part in the development of thermodynamics clearly deserves comment. He was, after all, a man of outstanding ability and by the early 1840s he had that familiarity with steam-engine operation which seems to have been so important to most of the pioneers of energy conservation.[3] Moreover, thanks to the French government, he had been provided with assistants, equipment and a laboratory which would have been the envy of his contemporaries in other countries. With all this, how could he have failed? A partial answer may well lie in the stultifying effect of the government commission, but it is doubtful whether this need have been quite as stultifying as it became in Regnault's hands. Far more relevant to the problem is surely the widespread mood of

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1. Regnault, Expériences, ii. pp.iii-viii.

2. Fuchs, 'Éloge de Regnault', p.lviii. Regnault gave one value for the equivalent in Expériences, iii. 574.

3. See T. S. Kuhn, 'Energy conservation as an example of simultaneous discovery' in M. Clagett (ed.), Critical Problems in the History of Science (Madison, 1959), pp.329-336.

scepticism in French science which we noticed in the last chapter and which had shown itself in some cases in the form of positivism, in others in an extreme caution in the use of such hypothetical concepts as atoms or caloric. It was into this latter category that Dumas's philosophy fell and Dumas, we should recall, was close to Regnault in the late 1830s. There is much in Regnault's work to suggest that the association was a crucial one and that Regnault, like Dumas, did not consider the search for causes as worthless or impossible but was merely opposed to premature theorizing. This view is supported by Dumas himself who recalled of Regnault how, on the one hand:

> Les hardiesses relatives à l'unité de la matière ou à l'unité des forces ne le séduisaient pas. La conversion de la lumière en chaleur, du magnétisme en électricité, de ces quatre forces l'une en l'autre, ne l'avaient pas occupé. Il l'acceptait comme une vue ingénieuse et non comme un résultat certain...[1]

while, on the other, he could enthusiastically accept the interconvertibility of heat and work once this was proved beyond reasonable doubt. If this was in fact Regnault's attitude, and it certainly seems consistent with his work as a whole, then the validity of the single term 'positivist' which has recently been used to describe the state of French physics about the middle of the century[2] becomes doubtful. Regnault was working in the tradition not of Fourier and Comte but rather of Dumas, a vigorous advocate of the accumulation of facts, though only as a preliminary to the establish-

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1. Dumas, Op. cit., pp.lvii-lviii.

2. J. M. Merivel, 'Aspects of French theoretical physics in the nineteenth century', British Journal for the History of Science, iii (1966), 121-132.

ment of true causes. Regnault, as it happened, hardly ever progressed beyond the first and surer part of Dumas's programme, since, by the standards which he set himself, the problems involved even at this stage were simply too great. Others, less sensitive perhaps to the mood of the time, could continue with their theorizing, even in France, but the backgrounds of these men were distinctly unconventional and so, in terms of education, contacts and standing in the scientific community, in sharp contrast to that of Regnault. It is surely significant in this respect that of the only Frenchmen to play any part at all in the establishment of the principle of energy conservation, Marc Seguin, Émile Verdet and Adolph Hirn, not one was a full academician and only Verdet, first as examiner and then as professor of physics from 1862 until his death in 1866,[1] had any close contact with the École Polytechnique, where the influences of Dumas and Lamé, for example, were presumably most strongly felt.

It is unnecessary, in conclusion, to emphasize yet again the magnitude of the changes which had come over physical science since the days when descriptions of the structure and properties of the imponderables were a commonplace, when Biot and Arago could perform experiments to determine the 'affinities' of different gases for light particles and when an academic prize competition could be set in order to examine the behaviour of a hypothetical fluid. Despite the fundamental errors on which this type of physics was based, few historians would deny that, as far as France was

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1. For biographical details see A. de la Rive, 'Notice sur Émile Verdet' in Oeuvres de É. Verdet, 1. pp.x-xi.

concerned, the changes coincided with a genuine decline. The absence of any major French contribution to, say, thermodynamics or electromagnetism, both fields in which there were important developments outside France about the middle of the century, is familiar evidence for this conclusion and our examination of the sterile experiments of Victor Regnault must surely confirm this. However, the problem of accounting for the decline, or even of determining its precise nature or charting its course, is unsolved and will remain so until far more case-histories in the period become available. From this single study, concerned essentially with the rise and fall of the caloric theory of gases, it would seem that the symptoms of the decline were growing disenchantment with theory and a consequent emphasis on the accumulation of data, both of which had set in by the mid-1830s. By then the task of filling the vacuum left by the sudden decline of the firmly established and accepted system of science which we have called Laplacian was becoming difficult, far more difficult in fact than the group of brilliant young physicists who came to prominence after the Bourbon restoration could ever have imagined. Indeed, by the 1830s the group as such hardly existed. With the deaths of two of its most gifted members, Petit in 1820 and Fresnel in 1827, it had suffered important and even crucial losses while, of those who remained, Arago, now Secrétaire Perpétuel at the Académie des Sciences, had virtually withdrawn from scientific work and Dulong, beset by illness and with his best years already wasted on a demanding government commission, was experiencing growing frustration in what little science he was still able to pursue. Within less than two decades the impetus of the exciting years

immediately after 1815 had been lost and it may well be in this loss that we should look for the real tragedy of French physical science during the nineteenth century.

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Specific heats of gases determined at constant pressure

The figures given are volume specific heats on the scale where the volume specific heat of air is unity. Where the authority concerned gave a value for the specific heat by weight this value has been added in brackets, but the scale in this case is such that the value for water is unity.

authority	date	air	oxygen	nitrogen	hydrogen	carbon monoxide	nitrous oxide	carbon dioxide	etiglene	water vapour	page ref. in text
Leslie	1804	1			1						111-112
Lavoisier & Laplace	1805	1.00* (0.33931)	2.17* (0.65)								25-26
Delaroche and Bérnard	1812	1.0000 (0.2669)	0.9765 (0.2361)	1.000** (0.2754)	0.9033 (3.2936)	1.0340 (0.2884)	1.3503 (0.2369)	1.2583 (0.2210)	1.5530 (0.4207)	1.96 (0.8470)	150-155
do. (alternative method)	1812	1.000	0.974	1.000**	0.893	0.983	1.315	1.311	1.680		
Haycraft	1823	1	1	1	1			1			292
Dulong (indirect method)	1828	1	1		1	1	1.16	1.175	1.531		287-290
de la Rive & Marcet	1835	1	1	1	1			1.222	1.5309		296-297
Apjohn	1835	1.080	1.0006	0.9097	1.8948	1.0000	1.1652	1.0146			294-295
Suerman	1836	1.0000 (0.3046)	0.9954 (0.2750)	1.0005 (0.3135)	1.5979 (6.1892)	0.9923 (0.3123)	1.1229 (0.2240)	1.0655 (0.2124)			295-296
Apjohn	1837	1.000	0.908	1.048	1.459	0.996	1.193	1.195			294-295
Regnault	1853	1.0000 (0.23741)	1.0125 (0.21751)	0.9970 (0.24380)	0.9933 (3.40900)	0.9978 (0.2450)	1.4514 (0.2262)	1.3923 (0.2169)	1.7287 (0.4040)	1.2583 (0.4805)	335-336

Key: * indicates that the figure given is calculated from the specific heat by weight with the aid of contemporary values for specific gravity
** indicates an estimated figure

Specific heats of gases determined at constant volume

The figures given are volume specific heats on the scale where the volume specific heat of air is unity. Where the authority concerned gives a value for the specific heat by weight this value has been added in brackets, but the scale in this case is such that the value for water is unity.

authority	date	air	oxygen	nitrogen	hydrogen	carbon monoxide	nitrous oxide	carbon dioxide	ethylene	water vapour	page ref. in text
Crawford	1779	1.00* (18.670)	5.14* (37.000)		1.16* (291)			0.82* (0.270)			23
Crawford	1788	1.00* (1.7900)	2.92* (4.7490)	0.43* (0.7936)	0.92* (21.400)			0.88* (1.0454)		0.53* (1.5500)	26-30
Dalton (theoretical calculation)	1808	1.000* (1.759)	0.834* (1.333)	1.029* (1.866)	0.427* (9.382)	0.840* (0.777)	0.499* (0.549)	0.424* (0.491)	1.477* (1.555)	0.410* (1.166)	119-120
Clément & Desormes	1812	1.000	1.000	1.000	0.6640			1.5000			155-162
de la Rive & Marcet	1827	1	1	1	1	1	1	1	1		292-294
de la Rive & Marcet	1829	1			1		1	1	1		294
Dulong (indirect method)	1828	1.000	1.000		1.000	1.000	1.227	1.249	1.754		287-290

Key: * indicates that the figure given is calculated from the specific heat by weight with the aid of contemporary values for specific gravity

The expansion of air by heat

Authority	Date	Volume (pressure) @ F. Pt. of ice	Vol.(pressure) @ room temp.	Vol.(pressure) @ B. Pt. of water	Vol.(pressure) @ other temperatures	Expansion (pressure increment) per deg C, expressed as a fraction of volume (pressure) @ F. Pt. of ice	Page ref. in text
Amontons	1699 & 1702		1000	app.1333		(1/250)	59-60
	1703	1000		1417		(1/240)	61
Huguet	1705		1000	app.16000		(1/6.7)	61
La Hire	1708		1000	1295		(1/283)	61
Hauksbee	1709	1000			1099 @ 130° on Hauksbee's scale (= app. 102°F)	(1/394)	ref.(1 below
Cruquius	1724-5	1000		1411		(1/243)	61
Poleni	1731-2	1000		1334		(1/299)	61
Musschenbroek	1762	1000		1500		(1/200)	ref.(2
De Luc	1772					(1/250)	62
Mayer	1786					1/266	72
Shuckburgh	1777					1/228	63
Lux	1774	1000		1377.5		(1/265)	66
Roy	1777	1000		1404		(1/207)	63
Lambert	1779	1000		1370		(1/270)	ref.(3
Saussure	1783					1/295	63
Tremblay	1786					(1/229)	63
Vandermonde, Berthollet & Monge	1786					1/231	64
Volta	1793	1000		1370		1/270	66
Guyton de Morveau & Davernois	1789	1000		1937		(1/107)	64-65
Dalton	1801		1000	1325		(1/256)	69-70
Gay-Lussac	1802	1000		1375		(1/267)	70-71
Rudberg	1837	1000		1364(.5)		(1/275)	338
Regnault (i) pressure coeff.	1842	1000		1366.5		(1/273)	337
(ii) volume coeff.	1842	1000		1367.0		(1/273)	337

References: (1) Hauksbee, Physico-Mechanical Experiments (London, 1709), p.173 and Phil. Trans., xxvi (1708-1709), 93-96.
(2) Musschenbroek, Introductio ad Philosophiam Naturalem (Leiden , 1762), ii. 883-884.
(3) Lambert, Pyrometrie (Berlin, 1779), p.47.

Except in the case of Regnault no attempt has been made in this table to distinguish between experiments designed to measure pressure increments and those in which expansion at constant pressure was measured

The figures in the column headed 'expansion (pressure increment) per deg C' which appear in brackets have been calculated from the data given by the authority concerned and do not appear in the original work. They are given only as a guide for comparisons and should not be taken to imply that volume or pressure were supposed to increase uniformly with temperature.

Table 3(b)

The expansion by heat of gases other than air

	Volumes (pressures) at the boiling point of water on a scale such that the volume (pressure) at the melting point of ice is 1000				
	Vandermonde, Berthollet & Monge (1786)	Clayton de Morveau & Duvernois (1799)	Gay-Lussac (1802)	Regnault (1862)	
				(1) constant volume	(2) constant pressure
hydrogen	1043*	1352	1373	1366.7	1366.1
oxygen		1476	1375		
nitrogen		1351	1375	1366.6	1369.0
nitrous oxide				1367.6	1371.9
nitric oxide		2454	1375		
carbon monoxide				1366.7	1366.9
carbon dioxide		1809	1375	1368.8	1371.0
sulphur dioxide			1.29	1366.1	1370.3
ammonia		1601	1.37		
Avge pct. in test	64	64-68	70-71	100	100

* In the original paper it is stated simply that hydrogen expands by 1/101.66 of its initial volume for every deg C rise in temperature. It is assumed that the original volume referred to is that at the melting point of ice

A table of affinities for caloric etc. for use with Chapter 5

	Volume specific heats, as determined experimentally by Delarche & Bérard (Ann. Chim., lxxxv (1813), 157)	Vol. specific heats calc. by Avogadro (for method see text p.238 (Avogadro, Biblioteca Italiana, iv (1816), 489-491 and v (1817), 78 and 83)	Attractive power for caloric	Affinity for caloric	Refractive power, as determined experimentally by Biot & Arago (Mém. Inst. Fr., vii (1806), 320)	Refractive power calc. by Avogadro (for method see text p.243) (Mem. Soc. Ital., xviii (1820), mem. di fisica, 161-162. Read 14 Oct.1817)	Affinity for caloric calc. by Avogadro (for method see text p.248) Mem.Soc. Ital. xix (1823), mem. di fisica, 128. Dated 17 Jan.1822. Also Mem.Accad.Sci. Torino,xviii (1824), 62)	Volume specific heats calculated from the affinities in previous column (Mem.Soc.Ital., xix (1823), mem.di fisica, 129 and Mem.Accad.Sci. Torino, xviii (1824), 39n).
oxygen	0.9765*	0.9765*	0.95355	0.8640	0.0616	0.902	0.8500	0.9706
hydrogen	0.9033*	0.9033*	0.0160	11.1460	6.6144**	6.614**	10.2573	0.8401
nitrogen	1.0058*	1.0058*	1.0116	1.0438	1.0341	1.031	1.0454	1.0075
carbon vapour		1.0085	1.1828	1.4216			1.4296	
carbon monoxide	1.0340*	1.0340*	1.0692	1.1047			1.0984	1.0321
carbon dioxide	1.2583	1.2434	1.5460	1.0174	1.0048	1.012	1.0081	1.2396
nitrous oxide	1.3503	1.2200	1.4884	0.9786			0.9744	1.2191
nitric oxide			0.9326	0.9481				
nitrogen trioxide				0.9304				
nitrogen peroxide			2.91875	0.9189				
nitrogen pentoxide				0.91075				
ethylene	1.5530	1.6777	2.0148	2.8769			2.6931	1.6123
ammonia			1.7298	2.9103	2.1685	2.2114	2.6602	
water vapour			1.2928	2.0685			1.8866	
ammonium carbonate				1.8499				
ammonium bicarbonate				1.5510				
column number	1	2	3	4	5	6	7	8

In all columns figures are given on a scale such that the value for air is unity in each case

The asterisks * and ** indicate that the experimental figures are taken as the basis for the calculation of the theoretical values

Abstract

It is natural, perhaps, that historians should find 'success stories' more attractive subjects for research than failures and it is presumably for this reason that the kinetic theory of gases, which we now accept as being correct, has attracted so much more attention than the 'static' theory which it superseded shortly after the middle of the nineteenth century. Thus existing accounts of the early study of gases understandably lay special emphasis on the work of kineticists like Daniel Bernoulli, in the eighteenth century, John Herapath and J. J. Waterston in the early nineteenth century, but they do little to suggest why these dissenters from common opinion were so few in number and why the great majority of their contemporaries found a quite erroneous view of gas structure so convincing. Moreover, they give no indication why the first quarter of the nineteenth century should have been a 'golden age' for both experimental and theoretical work relating to gases, especially to their thermal properties. Anyone reading the accounts must wonder why such well known authorities as Dalton, Gay-Lussac, Avogadro, Laplace, Poisson and Sadi Carnot considered this a subject so worthy of their attention. What could they achieve, or even hope to achieve, when their opinions on gas structure were so seriously in error? These are questions which historians appear to have ignored and which have provided the basic initial problems for this thesis.

It would be impossible to separate the study of gases in our period from that of heat, for between the 1780s and the 1850s the repulsive forces between the particles of a gas, the existence of which was a necessary postulate of the 'static' theory, were almost universally attributed to the presence of caloric, the imponderable, highly elastic fluid of heat, either round or between the particles. Indeed, as is explained in the Introduction, it is this belief, as much as the general acceptance of the 'static'

theory of gases, which gives the subject of the thesis its unity. Interest in gases, as we shall see, was often closely related to an interest in the nature and properties of caloric and it comes as no surprise, therefore, that the study of gases should so often have taken the form of a study of their thermal properties - of their specific heats, for example, of the extent to which they were expanded by heat or of the temperature changes which were known to accompany their rapid (i.e. quasi-adiabatic) expansion and compression. In following the experimental investigations into these three aspects of the thermal behaviour of gases as our central theme we shall thus be brought repeatedly into contact with the contemporary problems of caloric theory and it is probably as a contribution to our understanding of these problems and of the varying fortunes of the theory in the late eighteenth and early nineteenth centuries that the thesis will prove to have its greatest value. We shall find that Count Rumford's celebrated cannon-boring experiments by no means 'annihilated' the caloric theory, as John Tyndall and so many writers of physics text-books have maintained they did. In fact, at the time they were reported to the Royal Society, in 1798, the caloric theory was only beginning to attain some degree of sophistication and it was not until the mid-1820s, after another quarter of a century of work, that it finally reached its most highly developed form in the hands of Laplace. In this process of development the study of the thermal properties of gases played a prominent and significant rôle and it is this rôle which is examined in Chapters 1 to 4.

It is argued that the association between the study of gases and that of heat became a particularly close one in the early years of the nineteenth century for two reasons. One was the discovery, made almost simultaneously but independently by Dalton in England (in 1801) and by Gay-Lussac in France (in 1802), that for any given increment in temperature all gases expanded to the same extent.

Taken together with the already familiar Boyle's law, this discovery was strong evidence for the essential simplicity of matter in the gaseous state and it gave rise to a widespread and influential conviction that the laws of nature might emerge in their simplest form when observed for the case of gases. The other factor which drew attention to the special relevance of gases for the study of heat was Laplace's demonstration, announced in 1802, that the notorious discrepancy between the experimental figure for the velocity of sound and the value predicted by Newton's theoretical treatment could be removed if it was supposed that heating and cooling occurred respectively in the regions of compression and rarefaction constituting the sound wave. This work did more than provide a correct solution to a long standing problem. It placed adiabatic phenomena, which previously had been little more than a curiosity, at the very centre of the study of heat and, what was even more important perhaps, it brought the phenomena to the attention of the French, among whom they had been virtually unknown. Henceforth our story becomes predominantly one of science in France.

The result was a renewed interest in the study of gases and heat which reached its climax with the French Institute's prize competition of 1812. The competition, as is shown in Chapter 3, appears to have been set above all in an attempt to determine the form which caloric theory was to take. Since the 1780s two main versions of the theory had been available and each had its following. In Britain the version associated principally with the Scottish chemist William Irvine and the English physician Adair Crawford tended to be favoured, while in France support was generally for its rival, associated with the names of Laplace and Lavoisier. The points at issue between the supporters of the two versions, which are examined in Chapters 1 and 3, are somewhat involved and it is sufficient to note here that victory in the 1812 competition went to two young physicists, François Delaroche and Jacques-Étienne Bérard, who

claimed to have discredited the views of Irvine and Crawford. Of course, such a result in a competition set and judged by men who were under strong Laplacian influence should hardly surprise us. Thereafter the Irvinist cause was all but lost and the subsequent development of the caloric theory proceeded in accordance with the principles established by Delaroche and Bérard, culminating in 1823 when Laplace published his definitive caloric theory of gases.

It might have been expected that this sophisticated theory, backed as it was by the authority of Laplace, would have gained wide acceptance, but it is one of the most interesting and significant conclusions of the thesis that this was not the case. By the 1820s Laplace was working in a dying intellectual tradition, one which had been dominant and successful in the Napoleonic period, when Laplace and his great friend the chemist Claude Louis Berthollet exerted their greatest influence, but which had now been rejected by a younger generation of talented physical scientists who first rose to prominence in France after the Bourbon restoration of 1815. The work of Amedeo Avogadro on caloric theory which, as we see in Chapter 5, owed a great deal to Berthollet, appears to contradict this conclusion, but it should be emphasised that Avogadro worked not in the lively scientific community of Paris but in isolation in Italy, where it would not have been easy to sense the changing mood of the time. In France the influence of the 'Laplacian' style of science, in which the imponderable fluids such as caloric occupied an important place, declined rapidly after 1815. In Chapter 6 this decline is traced in the context of the attacks which were levelled at caloric theory by men such as Berzelius, Dulong and Petit, who in the late 1810s gave their support to the view that heats of chemical reaction might be electrical in origin. That these attacks were not isolated but part of a more general reaction against 'Laplacian' principles only becomes clear when

developments in other branches of science are examined. We should note that the years 1815-1820 also saw Fresnel's first attempts to establish the wave theory of light against the corpuscular or fluid theory advocated by Laplace and they saw immediate and vigorous support for the theory coming from Arago and Petit. It was in this period also that the atomic theory, with Dulong as its chief spokesman, began to win support in France, despite Berthollet and Laplace, who never accepted it.

The young Frenchmen who supported these new theories, notably Messrs. Dulong, Petit and Arago, succeeded in exposing much that was wrong and misleading in the science of Laplace and his disciples and it seems to have been widely recognised that they were retrieving the physical sciences from error. Their anti-Laplacian movement was therefore generally successful and this fact must surely be taken into account in any future attempt to explain why the quality of science in France declined during the second quarter of the nineteenth century after some three decades of apparent greatness. No solution to this vast and complex problem is offered here, but the account of the sterile experiments of Victor Regnault and of the research tradition in which he was working is given as a case-history in the process of decline. Clearly any complete solution to this problem will have to take account of social, economic and intellectual factors which we could not consider here but, if this thesis has thrown at least some light on the way in which science was being done in the early nineteenth century, with special reference to France, it will have made a useful contribution.