## ROBERT FOX\*

## What was 'crucial' about Rumford's experiments on the nature of heat?

Historians of an earlier age once placed far greater emphasis on supposedly 'crucial' experiments than we tend to do today. At least, they viewed such experiments differently. When Lavoisier performed his seemingly decisive experiment of passing water vapour through a tube containing heated iron filings in 1785, for example, most of us would now see an ingenious experiment, intended to clinch the case for the new chemistry but whose interpretation, even after the experiment, remained contentious in contemporary eyes. Where Lavoisier and his supporters saw the oxygen from the water vapour combining with the iron to form an oxide – leaving the residual hydrogen to emerge from the other end of the tube – phlogiston-based paradigm.<sup>1</sup>

My initial contention, then, is that 'crucial' experiments have lost something of the central place that they once held in interpretations of scientific change. One reason for this is that, as historians, we now recognize the transition from one theory to another, from one paradigm to another, as a multi-faceted, complex process in which rhetoric and personal alliances lie at centre-stage and experiments and their interpretation rarely have the universally persuasive character that a true 'crucial' might be expected to possess. A second, related reason is that many of the experiments that we might be tempted to view, in retrospect, as 'crucial' were not crucial at all, at least in the sense that matters, or should matter, to us, as historians. By that, I mean that they were not crucial, and had no reason to be crucial, in the eyes of contemporaries. Here, then, we are not talking about mistaken perceptions or prejudice that blinded contemporaries to the obvious, but rather about

<sup>\*</sup> Faculty of History, Broad Street, Oxford OX1 3BD, England.

<sup>&</sup>lt;sup>1</sup> For an elaboration of this point in the context of contemporary perceptions of Lavoisier's experiments, see Golinski, 1992, chapter 5.

perfectly competent observers who saw the world differently. In the terms made famous by Thomas Kuhn, those observers had a paradigm different both from ours and from those whose experiments were intended to lead them to a new way of seeing the world. To stay with Kuhnian terminology, they had not undergone the abrupt Gestalt switch that would have led them to abandon their old beliefs.

Which brings me to the 'crucial' experiment, or group of experiments, that form the core of my paper. They are those of Benjamin Thompson, Count Rumford. The most famous of the experiments was Rumford's demonstration that the friction that occurred in the boring of a brass cannon produced seemingly unlimited quantities of heat: the metal of the cannon and the boring implement went on yielding heat so long as the process continued. Rumford announced his observations and the conclusion he drew from them in a paper to the Royal Society in London in January 1798.<sup>2</sup> The conclusion was simple and unequivocal. Heat could not possibly be a 'material substance'; it was MOTION, a word whose importance Rumford stressed by his use of capital letters.<sup>3</sup> In the paper, Rumford said nothing about the nature of the motion to which he referred, an ambiguity to which I shall return. His aim, as in his paper of the following year, in which he demonstrated that heat, whatever its nature, was weightless,<sup>4</sup> was simply to overthrow the material, or caloric, theory.

As we know, the attack on caloric fell flat; it did not succeed. Experiments that Douglas McKie and Niels H. de V. Heathcote described in 1935 as 'a classic example of what scientific investigation is at its best'5 left opinions on the nature of heat broadly unchanged. This was not for want of a widespread familiarity with Rumford's work. The 1798 paper - the cannon-boring paper - was translated into both French and German, in addition to appearing in the Royal Society's Philosophical Transactions, and the 1799 paper on 'the weight ascribed to heat' (to use Rumford's words) appeared in the Philosophical Transactions and then immediately in French.<sup>6</sup> Rumford's early attacks on caloric, therefore, were widely accessible, as were the later papers, of 1804-1805, in which he returned to the subject, notably in his communications to the First Class, the scientific class, of the Institut de France.<sup>7</sup> The comments by contemporaries confirm this point about accessibility. But what they also confirm is that Rumford's views, though known and read, were not seen as persuasive. Why was this so? Why were experiments that much later assumed the character of telling, even decisive, evidence against the caloric theory regarded at the time as anything but decisive?

- <sup>4</sup> Rumford, 1799.
- <sup>5</sup> McKie, Heathcote, 1935, 148.

<sup>6</sup> For references and a useful bibliography of Rumford's writings on the nature of heat, see Rumford, 1968, 497-503.

<sup>7</sup> Rumford's papers of this period are conveniently collected, in English, in Rumford, 1968, 285-496. For the bibliographical details of the original publications and the translations, see ibid., 5013.

<sup>&</sup>lt;sup>2</sup> Rumford, 1798.

<sup>&</sup>lt;sup>3</sup> Ibid., 99.

The core reason is that there was no such thing as *the* caloric theory. There was a multiplicity of material-based theories of heat, each founded on different premises, each good at explaining certain thermal phenomena, less good at explaining others. The common ground between the theories was slight, and it certainly did not include common ground that could be swept away by any single experimental observation. What we tend to refer to as 'the caloric theory', therefore, was a slippery customer, a multi-headed hydra that the lance of experiment alone could never hope to slay.

Let me elaborate on what I mean. What we might refer to as the 'classic' caloric theory was the one advocated by Lavoisier. It rested on the notion of 'calorique' (a term that seems to have been in use in Lavoisier's circle by 1784) as a substance, an element even, whose mere accumulation was the cause of hotness.8 As Lavoisier described the substance in an unpublished manuscript of 1772 and in papers to the Académie des Sciences in 1777, what at the time he called the matière du feu or fluide igné was capable of combining with a 'base' of ordinary ponderable matter in the manner of a normal chemical union. It was just such a union that would effect the evaporation of a liquid. It was just such a union also that led to the heat of combustion. In this case, the ponderable base of oxygen (or air vital, as Lavoisier called it in these early papers) had a greater affinity for the inflammable substance than it had for the matter of fire, so that it combined with that substance, allowing the fire to escape and become 'free'. Fundamental to this explanation, incidentally, was a distinction (to which I shall return) that Lavoisier always drew between fire (or caloric) in its normal state of combination with ordinary, ponderable matter and fire (or caloric) in its free state. It was fire in its free state alone that affected the thermometer and produced the sensation of heat; combined fire, which acted in opposition to the natural attractive forces between the particles of ordinary matter, had no such effect.

That, then, was one material theory of heat, evidently the main one, that Rumford had in his sights as his interest in the nature of heat grew, by his own recollection, from the late 1770s and on through the 1780s and 1790s. But it was by no means the only one. A still very strong tradition of speculation about heat was one that descended directly from Boerhaave and, as Hélène Metzger argued long ago, more distantly from Descartes.<sup>9</sup> In this tradition, motion (not the accumulation of a matter of heat) was responsible for the phenomena of heat. In the classic expositions by Boerhaave and 'Gravesande, the first of them dating from the 1720s, the motion had a two-fold character.<sup>10</sup> There was motion (conceived as a vibratory

<sup>&</sup>lt;sup>8</sup> In this account of Lavoisier's theory of heat, I draw on Fox, 1971, chapter 2, where full references to the primary sources are given.

<sup>&</sup>lt;sup>9</sup> Metzger, 1930, 221.

<sup>&</sup>lt;sup>10</sup> In my comments on Boerhaave, 'sGravesande, and van Musschenbroek, I draw again on the discussion in Fox, 1971, especially pp. 12-14. But Metzger, 1930, remains the study on which all subsequent work rests.

motion) both in the particles of ordinary matter and in the all-pervading Cartesianstyle subtle fluid. Exactly how the two motions contributed to thermal phenomena was never clearly articulated. Boerhaave, though, seems to have believed that the motion of the particles of ordinary matter was responsible for the hotness of a body, while the motion of the subtle fluid (or 'fire', as he called it) had the function of sustaining the motion of the particles of ordinary matter and transmitting it from hotter to colder bodies. Much about the theory was imprecise. It had no quantitative dimension, and while Boerhaave described the subtle fluid of fire as composed of particles, 'sGravesande for example offered no such elaboration; unlike Boerhaave, he saw the motion (*agitatio*) of the fire as contributing to the hotness of a body, but said nothing about its structure.

What I shall loosely refer to as Boerhaave's theory of heat ('loosely' because there were numerous variants) was a strong survivor into the 1760s and 1770s, and, as I shall want to argue, beyond. Successive editions of the works of Boerhaave himself, 'sGravesande, and Pieter van Musschenbroek ensured that the theory was never lost from view, and in 1775 it was, significantly, to Boerhaave's *Elements of Chemistry* that Joseph Black referred his students at Edinburgh for information on the theory of heat.<sup>11</sup> There is much other evidence too of the vigour of the theory. Euler adopted it in the late 1730s and appears to have continued to believe in the theory until his death in 1783.<sup>12</sup> The French chemist P.J. Macquer used it in his *Elémens de chimie-théorique* in 1749 and was still using it in 1766, in the first edition of his *Dictionnaire de chymie*.<sup>13</sup> And between 1755 and his death in 1777 the Alsatian Johann Heinrich Lambert attempted a mathematical account of the theory, in which he explained temperature as a function of the *vis caloris*.<sup>14</sup> Lambert's 'force' was determined by the number of fire particles in a given volume and by the force contributed by each individual particle.

In the last quarter of the eighteenth century, therefore, three main explanations for the phenomena of heat coexisted. One was Boerhaave's theory, according to which the motion of the particles of an all-pervading ether, often referred to as fire, had an essential role. Either that motion in itself caused the sensation of hotness (as Musschenbroek, for example, believed) or (as Boerhaave believed) it kept the particles of ordinary matter in motion, with this latter motion, rather than that of the ether, constituting hotness. The second was the caloric theory, Lavoisier's theory, according to which hotness resulted from the accumulation of a fluid, caloric: the more caloric was present, the higher the temperature. The third was what I shall call the vibrational theory, the vibration in question being that of the

 $<sup>^{11}</sup>$  The evidence is in a set of lecture-notes taken by an unidentified student, now in the Edinburgh University Library (MS Dc.3.11).

<sup>&</sup>lt;sup>12</sup> Euler, 1739, 11. For a comment on Euler's views on heat, see Fox, 1979, 326n.

<sup>&</sup>lt;sup>13</sup> Fox, 1971, 22-3n.

<sup>&</sup>lt;sup>14</sup> Fox, 1979.

particles of ordinary ponderable matter. There was, in short, no single paradigm, and contemporaries moved between one or another of the main theories. Macquer, for example, seems to have abandoned a version of Boerhaave's theory in favour of the vibrational theory at some time between 1766 and 1778.15 Fourcroy supported the vibrational theory in 1784 but had been won over to the caloric theory two years later in what may well have been a more general move towards caloric in the later 1780s and 1790s as Lavoisier's 'new chemistry' gained ground.<sup>16</sup> My point, however, is that the theories I describe co-existed, and that most contemporaries were either happy with, or at least reconciled to, this state of affairs. Science, whether physics or chemistry, could go on without the issue being resolved: there was certainly no sense of 'crisis', in the Kuhnian sense of a widely shared feeling that work was being impeded or led astray by the failings of the existing paradigm. In the words of Joseph Black in 1775, the cause of the phenomena of heat was 'a subject which promises but little advantage and is very much involved in obscurity'.17 Perhaps, as Lavoisier and Laplace put it in their 'Mémoire sur la chaleur' of 1783, both the some form of material theory and the vibrational theory were both true, and true simultaneously.18

Whether many contemporaries shared the opinion of Lavoisier and Laplace is unclear. But what is beyond question is that preferences were determined, or at least coloured, by the scientific phenomena requiring explanation. The heat produced in the percussion of a solid, for example, lent itself equally well to the vibrational theory (since the motion of the hammer could be imagined as being transferred to the vibrations of the particles of the solid) or (if you imagined heat being squeezed out of the compressed solid) the caloric theory. The heat evolved in combustion or any exothermic chemical reaction, on the other hand, definitely favoured the caloric theory. Indeed, if the caloric theory did gain some ground at the very end of the eighteenth century, it was largely because of the success of the 'new chemistry', with its attendant notion of caloric as an element and hence as a substance with a characteristic affinity for each other element.

So Rumford's papers of 1798 and 1799 were read by a community, whether of physicists or of chemists, that held a diversity of often very flexible views on the nature of heat. It was a community whose engagement with thermal phenomena was proceeding well enough without any rigid commitment to one theory or another. This made it difficult for Rumford to stir up a vigorous reaction either for or against what he was proposing. It was already well known that none of theories of heat offered an entirely convincing explanation of friction. The phenomenon was usually assimilated to that of percussion; hence it was assumed either that the

<sup>&</sup>lt;sup>15</sup> Fox, 1971, 223n.

<sup>&</sup>lt;sup>16</sup> Ibid., 22-3.

<sup>&</sup>lt;sup>17</sup> The phrase is in the lecture-notes cited in note 11, above.

<sup>&</sup>lt;sup>18</sup> Lavoisier, Laplace, 1780, 358.

motion inherent in friction stimulated a more vigorous or rapid vibration of the particles of the body being rubbed or that heat was being squeezed from the body, rather like water being squeezed from a sponge. Neither explanation was backed by any independent evidence, but both explanations allowed the effect to be visualized satisfactorily enough.

It was precisely such independent evidence that one of Rumford's most ingenious experiments sought to provide. In this experiment, which he described in his paper of 1798, Rumford measured the specific heat of the shavings of metal that were produced in the boring of the cannon. He found that the specific heat of the shavings was the same as the metal of the cannon: the process of boring and the release heat that accompanied it had effected no change.<sup>19</sup> Rumford presented his observation as a demonstration that the heat could not have come from the shavings. He did so without explanation, asserting simply that according to the caloric theory the specific heat of the shavings should have been diminished if they were the source of the heat. In fact, not all supporters of the caloric theory would have shared this assumption; indeed, the belief that the quantity of heat in a body was proportional to its specific heat represented a deviant view, probably originating as early as the 1760s, in the work of a pupil of Black's at Glasgow, William Irvine.<sup>20</sup> Although there is no firm evidence that Irvine was committed to a material theory of heat, he recognized the heuristic value of such a theory, and it was (and still is) difficult to describe his doctrines of specific heat without thinking in terms of materiality.

Irvine had begun his association with Black by assisting him with the experiments on the latent heat of steam that led Black to his refinement of the concept. Irvine's explanation of the absorption of heat during vaporization – an explanation for which Black gave him full credit – was that at the boiling-point a sudden change took place in the capacity of the water to contain heat. Steam, according to Irvine, needed more heat than did boiling water in order to maintain its temperature; hence heat – latent heat – had to be added. A similar change occurred at the freezing point. In this case, the capacity of ice to contain heat was less than that of water at the same temperature, so that, in freezing, heat had to be abstracted from the water in order to effect the change of state. Irvine left behind little published work, and most of what we know of his ideas has to be inferred from later writings by Adair Crawford and John Dalton. It was Dalton in 1808, in fact, who conveyed Irvine's conception of the effect of a change of state on specific heat most lucidly through his striking diagram of cylinders as containers of heat with cross-sections proportional to the specific heats of ice, water, and steam (see Fig. 1).<sup>21</sup>

To return to Rumford's paper of 1798, it becomes evident from this discussion of Irvine's theory why the case against caloric was presented as resting so heavily on

<sup>&</sup>lt;sup>19</sup> Rumford, 1798, 81-8.

<sup>&</sup>lt;sup>20</sup> On Irvine's theory, see Fox, 1971, 25-8.

<sup>&</sup>lt;sup>21</sup> Dalton gives a full account of his theory in Dalton, 1808, 3-7. See also Fox, 1968.

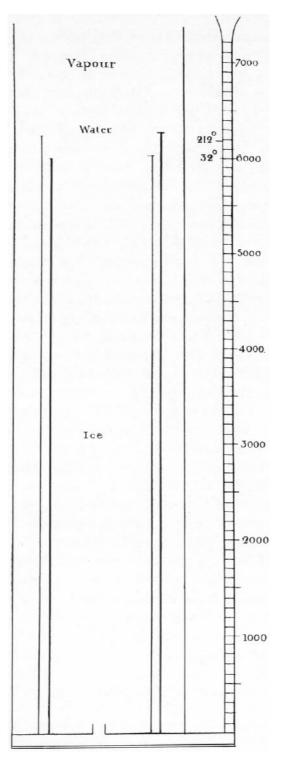


Fig. 1. Cylinders of caloric, used by John Dalton to illustrate his explanation of the latent heats of fusion and vaporization in accordance with William Irvine's doctrines on heat capacity. From John Dalton, *A New System of Chemical Philosophy*, part 1 (Manchester, 1808), facing p. 217.

the identity of the specific heat of the shavings of brass and that of the metal of the main barrel. Rumford was assuming, in the *manner* of Irvine (although Irvine, as a chemist and physician, almost certainly did not consider the phenomenon of friction), that a release of heat would necessarily be accompanied by a decrease in specific heat. When he failed to observe such a decrease, there could, for him, be only one conclusion: the shavings were not the source of the heat. It was a far from convincing conclusion. For readers to take it seriously, they had to adopt the premises of Irvine's version of the material theory of heat. And even if they did adopt those premises, the argument remained open to other objections. As Claude Louis Berthollet observed in his *Essai de statique chimique* (1803), any decrease in specific heat that occurred when the shavings (or the main barrel, for that matter) were compressed would only be temporary; immediately after the boring, the compressed metal would expand and regain its initial specific heat.<sup>22</sup>

My contention, then, is that Rumford's attack on the material theory of heat was read by his contemporaries but, quite properly, found wanting. The theory was too imprecise and it had too many variants for it to be vulnerable to the kind of attack that Rumford launched at it. Most of Rumford's points and evidence were unoriginal and they had long been assimilated into the amorphous congeries of beliefs that constituted the material theory. Friction could easily be interpreted as a form of percussion, and even Rumford's observation that the heat produced in boring his cannon was seemingly inexhaustible could hardly have surprised anyone familiar with the everyday occurrence of the ignition of the wheel of a cart through friction between it and its axle. Then there was the contentious assumption that underlay his point about the specific heats of the shavings. In this, as I have observed, Rumford was attacking a belief that the supporters of the materiality of heat by no means all shared, just as in the following year his demonstration that heat had no weight was only relevant to those few chemists and physicists who had ever believed that it did.

If, as I maintain, Rumford's case against the material theory of heat was not conclusive, it is not surprising that the theory's abandonment had to wait another half century. In that time, belief in caloric steadily – and I stress the word 'steadily' – waned. One reason, I believe, is that the range of phenomena for which caloric was especially effective, namely heats of chemical reaction, came to attract less attention than it had done in the days when Lavoisier's doctrines were being most keenly discussed: it is a mark of this that heat came to adopt a far less prominent place in chemistry textbooks. By contrast, new phenomena in the domain of physics had the effect of making the vibrational theory more plausible, though without ever providing hard experimental evidence. I think, in particular, of the growth of interest in radiant heat, conceived as a wave phenomenon analogous to

<sup>&</sup>lt;sup>22</sup> Berthollet, 1803, vol. 1, 247-50.

light in the treatment of Fresnel. Another reason for caloric's decline, especially powerful in France, was the collapse of the authority of the school of Laplace, who remained a calorist until his death in 1827, long after a younger generation of physicists – Fresnel, Arago, Fourier – had abandoned the Laplacian model of a physics of attractive short-range forces and imponderable fluids, of which caloric was one.<sup>23</sup>

When the material theory of heat was finally abandoned, as it was about the middle of the century, its demise was not the result of a single crucial experiment. The theory had begun to lose its power to convince at least three decades earlier. One sign of this was the rudimentary character of most textbook discussions of caloric through the 1820s, 1830s, and 1840s. Such refinements as the distinction between combined and free caloric and descriptions of its structure (made up of mutually repulsive particles) were things of the past. In fact, the nature of heat was just no longer a leading subject for debate. Caloric retained a certain pedagogical value as a way of thinking about quantities of heat, and it helped the old 'static' view of the structure of gases (according to which the particles of a gas were arranged in a lattice and could be seen as being kept apart by the elastic force of caloric) to survive until the adoption of the principle of the conservation of energy in the 1850s (see Fig. 2). But, as a substantive belief, it had receded to the sideline of debate.

So when the end came for caloric, it did so after a long period of agnosticism in which Sadi Carnot, for example, had constructed his elaborate theory of the heat engine on the basis of a crucial (though erroneous) belief in the conservation of heat but without any attempt to decide between, or even seriously to discuss, the material and vibrational theories.<sup>24</sup> When caloric eventually succumbed, the *coup de grace* was delivered not by any one experiment but by the new energy physics, which made the idea of heat as motion of material particles and a form of energy appear self-evident. Experiments such as those of Joule certainly illustrated and confirmed the interconvertibility of heat and work. But they only carried conviction as one element in a much broader conceptual context. If anything was 'crucial' in effecting the demise of caloric, therefore, it was the change in the way in which the experimental evidence was viewed rather than the evidence itself. To return finally to Rumford, it was through this same change that the canon-boring experiments of the 1790s came to assume, in retrospect, a status as 'crucial' that a contextual historical perspective cannot justify.

<sup>23</sup> Fox, 1974, 109-32, and Gillispie et al., 1997, 243-9.

<sup>&</sup>lt;sup>24</sup> Carnot, 1824.

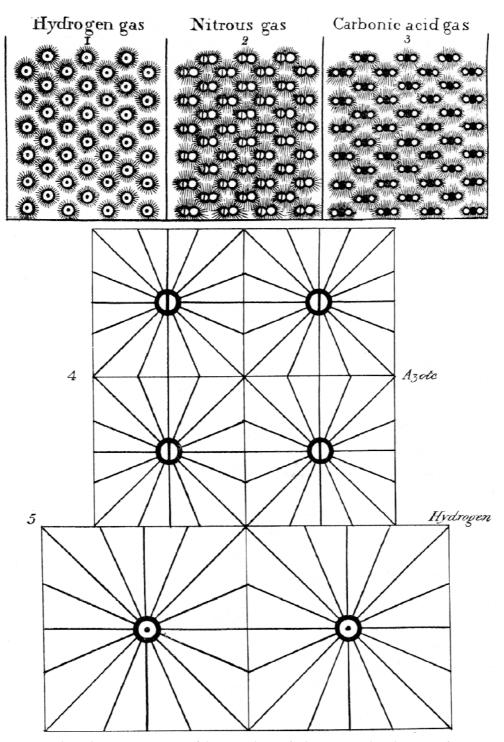


Fig. 2. John Dalton's representation of the atmospheres of caloric surrounding the atoms of gases. Repulsion between the atmospheres accounted for the elastic properties of the gases and was an essential element in the static (Newtonian) theory that was generally accepted until its replacement by the kinetic theory in the mid-nineteenth century. From John Dalton, *A New System of Chemical Philosophy*, part 2 (Manchester, 1810), facing p. 548.

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