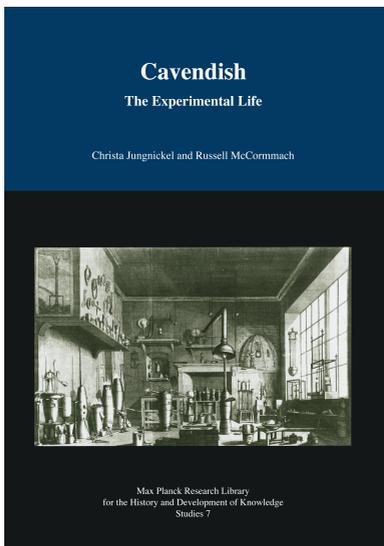


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Studies 7

Christa Jungnickel and Russell McCormach:

Air and Water



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Chapter 14

Air and Water

“Chemistry is the rage in London at present,” John Playfair noted in his journal on a visit in 1782.¹ This observation sets the stage for Henry Cavendish’s next course of experiments and series of publications. In Cavendish’s time, a major achievement of chemistry was the distinction between various kinds of air, the first step in the chemistry of the gaseous state of matter. We have discussed Cavendish’s paper on factitious air, published in 1766. When in 1771 the industrial chemist James Keir brought out an English translation of Macquer’s five-year-old *Dictionary of Chemistry*, he made corrections and added material from Black, Macbride, and Cavendish, since by then a chemical dictionary had to include pneumatic chemistry to cover the “present state of chemical knowledge.”² Two years later the president of the Royal Society John Pringle gave a “discourse” on the history of the subject.³ In 1781 Tiberius Cavallo, an Italian physicist who lived in England, surveyed the field in a book, *Treatise on [...] Air*, in which he observed that over the last ten years, pneumatic chemistry had advanced more than had any other field at any time in so few years. When we see solids transformed into invisible airs and when we see airs lose their elasticity and turn into solids, we have a subject of “the profoundest contemplation, for a philosophical mind.”⁴ Pneumatic chemistry was an indispensable, expanding, and challenging branch of chemistry when Cavendish returned to it after his electrical researches.

Good Air

When Cavendish studied factitious air in 1766, phlogiston provided the framework. In the seventeen years between his first paper on air and his next, Priestley, Scheele, and others relying on the same framework had identified a number of new gaseous substances. The chemistry of phlogiston did not anticipate their discoveries but it proved capable of accommodating them. Yet in the end, it would be the chemistry of gases that most clearly revealed the limitations of phlogiston. In the 1780s, when Cavendish’s last publications on chemistry appeared, phlogiston was on the defensive.

In this chapter we are concerned with the main components of common air, of which there are two, oxygen and nitrogen, which chemists at the time distinguished by the presence and absence of phlogiston, as their names indicated, “dephlogisticated air” and “phlogisticated air.” We are also concerned with two other substances: inflammable air, one of the factitious airs Cavendish investigated in his first paper, which is our hydrogen, and “nitrous air,” which is our nitric oxide, a new air then.

¹Playfair (1822, 1:xxxv).

²Pierre Joseph Macquer (1771, 1:iii–iv).

³John Pringle (1774), Supplement at the end of the volume.

⁴Tiberius Cavallo (1781, 797, 801).

Joseph Priestley was now Cavendish's most important colleague. The son of a cloth-finisher in Yorkshire, Priestley studied for the ministry; in 1767 he acquired a ministry in Leeds, where he began his serious investigation of airs. He first studied known airs, repeating experiments done by others, learning techniques that he soon put to original use. Cavendish, as we have seen, stored water-soluble airs over mercury, a technique which Priestley made a tool of discovery. He invented apparatus, devised clever experiments, and carried them out with skill; he examined airs for solubility, combustibility, respirability, density, and reactions with other airs; and he published regularly and often. In their ways of experimenting, Priestley and Cavendish complemented one another. Priestley experimented on many airs, which were often new, and he made measurements sparingly, whereas Cavendish experimented on a few known airs, and he made copious measurements.⁵ Priestley expanded the field of pneumatic chemistry, Cavendish made it rigorous. Priestley was congenial and outgoing, Cavendish was guarded; Priestley initiated a correspondence on chemistry with Cavendish, but Cavendish did not keep up correspondences and he soon let this one drop. For Cavendish science came before other interests, and in the balance only science mattered, whereas Priestley had many interests outside of science: "let it be remembered, that the taste for science, pleasing, and even honourable as it is, is not one of the highest passions of our nature, and the pleasures it furnishes are even but one degree, above those of sense; and therefore that temperance is requisite in all scientific pursuits." Piety, friendship, and other avocations came before science. In support, Priestley quoted the psychologist David Hartley's advice to scientific investigators to take frequent breaks from their studies to attend to God and men and to resist the temptations of vainglory, self-conceit, arrogance, emulation, and envy.⁶ Temperance in the pursuit of science, as advocated by Priestley, was contrary to Cavendish's practice, and perhaps it was an implicit rebuke. This difference may have colored their relationship on a personal level, though they valued and learned from one another's work (Figs. 14.7–14.8).

As Cavendish had noted in his 1766 paper on factitious air, in a major paper in the *Philosophical Transactions* in 1772 Priestley surveyed the field of pneumatic chemistry, adding to it a new substance, nitrous air (nitric oxide). To this, his first discovery, he had been partly guided by a conversation with Cavendish, which came about in the following way. Priestley was interested in an experiment by Stephen Hales in which common air was mixed with a colorless, insoluble air (nitrous oxide) generated from a certain pyrite and spirit of nitre, generating red fumes, which absorbed part of the common air. He mentioned the experiment to Cavendish, who said that other pyrites and metals would probably do just as well and that the red fumes might depend only on the acid, spirit of nitre. Priestley acted on this suggestion. Having no pyrites, he substituted metals which he placed in spirit of nitre, obtaining, he said, "what I wanted, and a good deal more."⁷

"I hardly know any experiment that is more adapted to amaze and surprise than this is," Priestley wrote in his paper in 1772, "which exhibits a quantity of air, which, as it were, devours a quantity of another kind of air half as large as itself, and yet is so far from gaining any addition to its bulk, that it is diminished by it."⁸ This was the experiment with nitrous air and common air: when the two were mixed, the nitrous air combined with part of the

⁵Aaron J. Ihde (1964, 40–50).

⁶Joseph Priestley (1767, xxii).

⁷Joseph Priestley (1772b, 210).

⁸Ibid., 212.

common air, producing brown fumes, which dissolved in water. He found that the reduction of common air was proportional to the fitness, or “goodness,” of common air for breathing. This new way of “phlogisticating” air suggested to him a test for the goodness of air: he mixed known quantities of nitrous air and the air to be tested over water and then admitted the residual air into a graduated tube, for which he used the word “eudiometer.” The nitrous test was soon taken up by chemists, who regarded it at once as a tool of science and a potential aid to public health.⁹ The name eudiometer was retained after the method was extended to the analysis of gases in general.¹⁰

Upon combining different kinds of air, chemists observed a large change in volume, the basic understanding of which came about only at the very end of Cavendish’s life. To look ahead, in 1809 Joseph Louis Gay-Lussac published the law of combining volumes, according to which gases combine in simple proportions, and their contraction upon combining bears a simple proportion to their original volume; two years later his law received a molecular interpretation by Amedeo Avagadro.

Priestley’s work on airs in turn stimulated Cavendish to return to the subject, at first in connection with Priestley’s nitrous air, the working agent of a new instrument. At the time of his first paper on air, fifteen years earlier, he estimated the combustible, or breathable, portion of common air by the loudness of the explosion when it was detonated with inflammable air, inventing, in effect, a crude sort of acoustic eudiometer.¹¹ The sense of hearing is discriminating, but when the stimulus is explosions, accuracy in making comparisons is limited. This is clear from the table that Cavallo made of Cavendish’s observations of the comparative loudness of explosions upon mixing inflammable and common air in different proportions, on a scale of 1 to 10.¹²

Infl. Air	Common Air	Effects
1	9	Fired with difficulty, little noise
2	8	Fired easily, moderately loud
3	7	Loud
4	6	Louder
5	5	Same
6	4	Less loud
7	3	Gentle
8	2	Burned without notice

With a desire to improve on the method of loudness, Cavendish invented a mechanical apparatus to measure the strength of detonation of inflammable air with other airs, the pressure lifting a pivoted board to different heights.¹³ Given his interest in the composition of the atmosphere, he welcomed the new instrument, the chemical eudiometer, for determining the breathable portion of air. In 1783, he published a paper on a “new eudiometer,” which he

⁹Cavallo (1781, 453–457).

¹⁰Idé (1964, 47).

¹¹Wilson said this technique might be called an “Acoustic Eudiometer” (1851, 41).

¹²Cavallo (1781, 665).

¹³Cavendish, Mss II, 5:130.

began: “Dr. Priestley’s discovery of a method of determining the degree of phlogistication of air by means of nitrous air, has occasioned many instruments to be contrived...”¹⁴

Among Cavendish’s scientific papers is a large bundle of small, carefully indexed sheets, over 400 in number, labeled “Experiments on Air.”¹⁵ Here and there they bear dates, telling us that Cavendish began his new experiments on air in 1778 and effectively ended them in 1786, though the last group of sheets carries the watermark 1800. The account of the first experiment is accompanied by a drawing of a eudiometer, essentially two bottles inverted in water, one containing either dephlogisticated air or common air, the other nitrous air, the two connected by a siphon. (Figs. 14.1–14.3). With air collected from several gardens, William Watson’s, William Heberden’s, and his own, he subjected samples to repeated tests, varying the procedure and the apparatus.

An example shows how carefully Cavendish investigated the working of a eudiometer. He wanted to know if any fixed air was produced by mixing common and nitrous airs. Before mixing them, he washed both airs with lime water to remove any fixed air that might already be present as an impurity. He then combined the two airs in a bottle inverted in a vessel of lime water, which he had filtered through paper to make certain it was clean, and set it by for a day. He observed no clouds or sediments “in the smallest degree,” which if present would have indicated fixed air. To make certain that the lime water was effective and not saturated by dissolved fixed air, he breathed through it, observing clouds formed from the fixed air in his breath. “Lest it might be supposed” that the clouds in the lime water were owing to a volatile alkali in his breath, he breathed the same way through distilled water” to which he had added a reagent, finding that no clouds were formed.¹⁶ This test of a test of a test shows Cavendish’s circumspect awareness of experimental deception.

The main problem with eudiometers was that they gave irregular results. (No one at that time understood the varying reactions of nitric oxide and oxygen.) The eudiometer Cavendish preferred, as did several other chemists such as Cavallo and Jan Ingen-Housz, was invented by the Florentine Felice Fontana in 1775. Fontana succeeded where others had not in devising a eudiometer capable of giving consistent results when used in a prescribed manner. Cavendish called it “by much the most accurate” of any that had been published, the reason he preferred it. He altered Fontana’s instrument and the method of using it to make the results “still more certain and regular.” Fontana’s method was to measure the reduction in the volume of the gases upon the removal of the soluble part, which Cavendish found subject to “very considerable errors.” His own method was to determine the quantities of the airs not by volume but by weighing the vessels containing them underwater. He weighed the two airs separately and then he weighed the mixed airs, the difference giving the diminution upon mixing. He also found that his method of mixing the two airs was “rather more accurate” than Fontana’s, and to be certain of this point he tried combining Fontana’s method of mixing with his own method of weighing.¹⁷ Most of his paper is about precautions to be taken to minimize the errors the method was liable to. They could arise from the order of mixing, the

¹⁴Henry Cavendish (1783a, 127).

¹⁵Most of the sheets are small folded pairs, with an occasional sheet folded four ways. Cavendish (1784a, Cavendish Mss II, 5).

¹⁶*Ibid.*, 27–28.

¹⁷Cavendish (1783a, 129, 137). The eudiometer Cavendish described in 1783 was not what later became known as the “Cavendish Eudiometer,” which the Cavendish Society adopted as its emblem in the early nineteenth century. The emblem is a pear-shaped, later version of the instrument, which Cavendish would not have recognized, an electrically detonated eudiometer invented by Alessandra Volta. Cavendish used an electrically detonated globe in

impurity of the water, the impurity of the nitrous air, the time taken to transfer the nitrous air to the respirable air, and the briskness with which the bottle containing the airs was shaken.¹⁸ Cavendish investigated all of these variables, showing the kind of attention to detail that characterizes all of his chemical work.

Because the eudiometer was a measuring instrument, Cavendish defined a set of quantitative terms to use with it. He called a bottle of a size that held 282 grains of water one “measure”; in mixing airs, he used three bottles, holding three, six, and twelve measures. He defined the “test” of an air as the diminution that it and the nitrous air suffer upon mixing. He introduced a “scale” together with a “standard”: the upper fixed point of the “scale” was the “standard” 1, which stood for the goodness of common air (a mixture of nitrogen and oxygen); the lower fixed point was the standard 0 of perfectly phlogisticated air (nitrogen). By this scale, the standard of pure dephlogisticated air was nearly 5. “If common air, as Mr. Scheele and La Voisier suppose, consists of a mixture of dephlogisticated and phlogisticated air,” the standard of any sample of the air was proportional to the quantity of dephlogisticated air (oxygen) in it. In general, if the standard of a sample is S , it has S times as much dephlogisticated air as common air has. Cavendish’s use of the word “standard” was clarified by Blagden in his instruction to Cavendish’s translator. “Standard [...] means properly that fixed measure to which others [of the samed kind] are compared, but in a more general sense is used by us to express the proportion which any thing [of whatever kind] bears to a fixed measure: thus if a mixture was made of 3 parts of gold & one of base metal, we might say the *standard* of the mixture was 3/4.” As he had the fixed points of the thermometer scale, Cavendish wanted an agreement on the eudiometer scale. It was important for investigators of the purity of factitious airs to “reduce their observations to one common scale, as the different instruments employed for that purpose differ so much, that at present it is almost impossible to compare the observations of one person with those of another.”¹⁹

Once he was assured that his eudiometer gave consistant readings, Cavendish applied it to a question of interest at the time, the constancy or variability of the atmosphere. In the year Cavendish began his researches on the eudiometer, 1781, Cavallo brought out his comprehensive *Treatise on [...] Air*, which we draw on it for the state of the question when Cavendish addressed it. The Swiss physicist H.-B. de Saussure toured the Alps, finding the air purer at the middle altitudes than at the top or on the plain. Marsillio Landriani, an Italian physicist who coined the word “eudiometer,” toured his country comparing the air at various places and altitudes; upon scaling a mountain he found the air to be purer the higher he went, though on Mt. Vesuvius he found the opposite. Wherever the air was reputed to be bad, Landriani found it to be bad, confirming his theory, leading Cavallo to conclude that he was biased and that his instrument was inexact. Jan Ingen-Housz, a Dutch physiologist and chemist, found the air at or near the sea purer than the air on land, and generally he found the air to vary in purity from place to place and from time to time. Cavallo thought that Ingen-Housz’s portable barometer was inexact too. Fontana, who carried out

his experiments involving the production of water, discussed later in this chapter, but he never referred to it as a eudiometer. Wilson (1851, 42–43). Kathleen R. Farrar (1963).

¹⁸A.J. Berry (1960, 58–59). Jan Golinski (1992, 125).

¹⁹The standard for an air containing less oxygen than common air is found by making an artificial mixture of common air and nitrogen, and adjusting the mixture until one measure of common air and a variable measure of nitrogen experience the same contraction, that is, have the same test. Cavendish gives a formula for calculating the standard in this case. If x is the quantity of nitrogen added to 1 part of common air, the standard of the air in question is $1/(1+x)$. Cavendish (1783a, 130–131, 141–142). Wilson (1851, 228).

his experiments before Ingen-Housz, said that accounts by several authors of the purity of air were “not to be depended upon,” because their methods were “far from being exact.” The great differences they found in the air from different countries and at different times were the “fallacious effects of uncertain methods.” His own measurements showed that air differed very little from place to place, but varied considerably from time to time and season to season. He also thought that people were wrong to believe that the purity of the air affected their health; what was unhealthy were vapors carried by the air, which could be noxious like “so many particles of arsenic swimming in the atmosphere.”

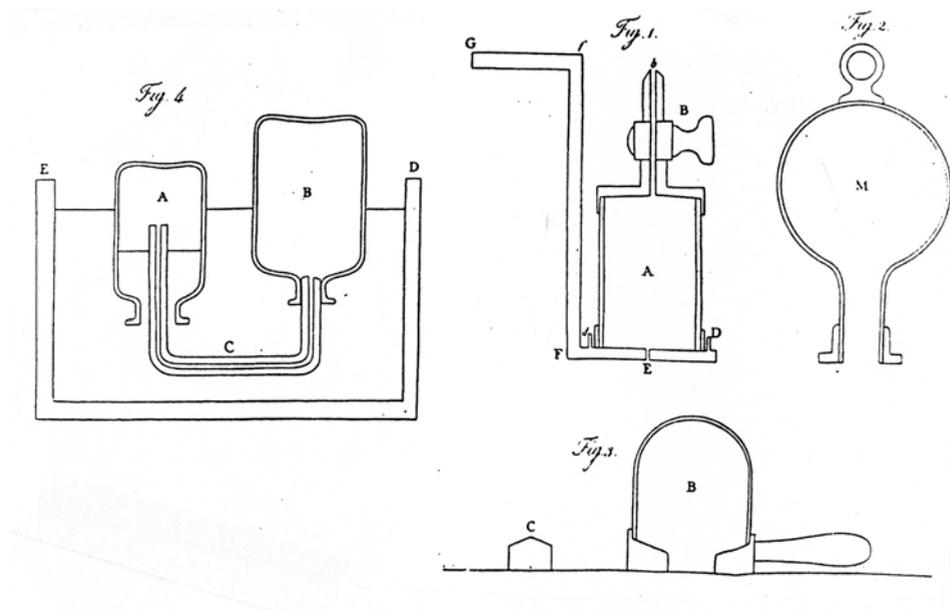


Figure 14.1: Eudiometer. Figure 1 shows the main apparatus, a glass cylinder A with brass cap and a cock at the top and an open brass cap at the bottom fitted into a socket of a bent brass holder as “a bayonet is on a musket.” The whole is submerged in a tub of water. Figure 2 is an inverted bottle for holding air, and Figure 3 is a standard measure of air. Cavendish’s method was to put a certain measure of nitrous air (nitric oxide) into the inverted bottle and a certain measure of common or dephlogisticated air into the glass cylinder. The cylinder was then set on the socket and the bottle over the cock, and the two kinds of air were mixed in the bottle. Figure 4 shows a different eudiometer. Bottle A contained common air, B nitrous air, which was slowly introduced through tube C into the common air without coming into contact with the water in the tub. Cavendish (1783a, 134).

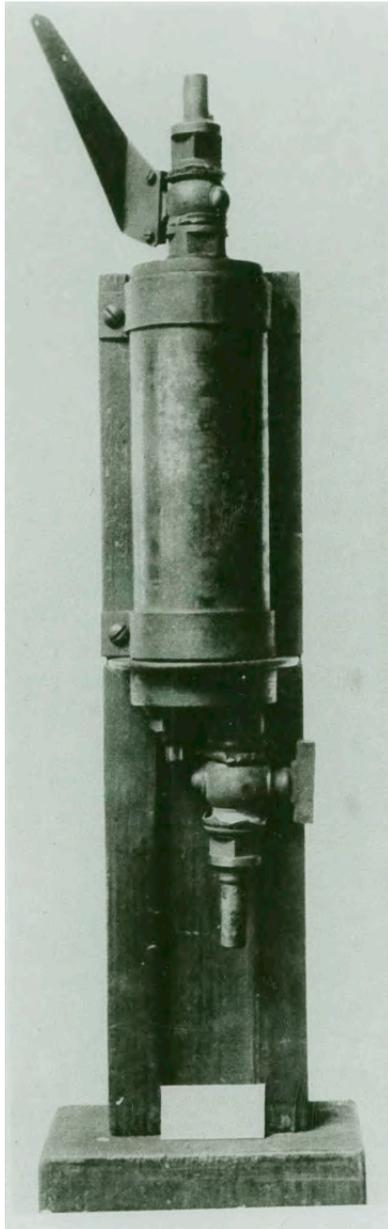


Figure 14.2: Eudiometer. The metal eudiometer belonging to Cavendish was presented by Humphry Davy to the Royal Institution, where the authors took this photograph. The instrument is about 6 inches long and 2 inches across. The stop-cock on the top served to fill and exhaust the cylinder, the one on the bottom to remove the water resulting from explosions of airs in the cylinder. Reproduced by permission of the Royal Institution of Great Britain.

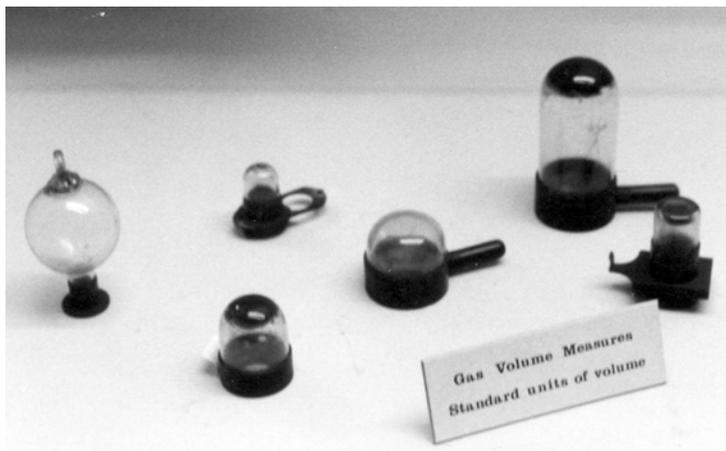


Figure 14.3: Standard Volume Measures for Air. These measuring glass vessels with brass caps on the bottom are described and drawn in Cavendish’s paper on the eudiometer. Henry Cavendish (1783a, 106–135, Plate III). The standard volume measures are kept in the Royal Institution of Great Britain. Photograph by the authors. Reproduced by permission of the Royal Institution of Great Britain.

Cavallo accepted Fontana’s conclusions about the purity of air in different places and at different times, and also about its irrelevance to problems of health, “but the essential part seems to be still in the dark; it is therefore requisite that philosophical people, in various parts of the world, would make as many and as various experiments, concerning the purity of the air at different times [...] in order to investigate the laws of those changes; which study is perhaps the most interesting part of the study of elastic fluids.”²⁰ Cavendish made the experiments that Cavallo wanted, though his finding was not what Cavallo expected.

With his new eudiometer, Cavendish measured air taken in London and in Kensington under variable conditions, on clear, soggy, and wet days, and early in the day and late. Over a course of sixty days, during which he made no fewer than 500 trials, he concluded that within the error of measurement, there was no difference in the degree of phlogistication of the air from place to place and from time to time.²¹ Twenty-four years later an author in the *Philosophical Transactions* wrote that Cavendish’s “masterly analysis” of the air in London and Kensington had an “accuracy” that had been “more distinctly perceived the more the science of chemistry has advanced.”²² Subsequently chemists translated his results into terms and quantities corresponding to our understanding of the atmosphere: according to Cavendish, the concentration of oxygen in the atmosphere is 20.83%, which is remarkably near the currently accepted value of 20.95%. In making this comparison, it should be noted that Cavendish is credited with a somewhat greater precision than he would have claimed.²³

²⁰Cavallo (1781, 458–467, 477). Felice Fontana (1779). Rembert Watermann (1968, 302–303).

²¹Cavendish (1783a, 140). Wilson (1851, 226–227).

²²William H. Pepys (1807, 249).

²³Separated off from his “Experiments on Air” is a 14-page paper containing eudiometer tests made in London, at his home at Great Marlborough Street, and in Kensington. “Miscellaneous Data on Eudiometer Experiments, 1780–81” (not Cavendish’s label), Cavendish Mss II, 8. He continued his tests after moving to Hampstead in 1782,

To judge by the results he obtained with it, Cavendish's improved eudiometer was very good. Several years after his paper, Blagden advised Benjamin Thompson on instruments to acquire from England: "Of Eudiometers Mr. Cavendish's [...] is undoubtedly preferable to any other."²⁴ Although investigators would come to regard eudiometers as unreliable,²⁵ the interest in continuing to improve them remained strong for a good while to come, with claims made for their "precision and accuracy" and "present perfection."²⁶ In a discussion with Blagden on a paper about eudiometer tests made by Alexander von Humboldt, Cavendish referred to "my paper on Eudiometers," then fifteen years old. Humboldt tried the quantity of nitrous air remaining after the mixing, which had the "appearance" of an improvement, but it made the experiment "liable to the error of 2 operations instead of one." "However that may be, the great difference which he [Humboldt] finds in the purity of common air convinces me that there must be some fault in his method; for though I tried the air of 60 different days, I could not find any difference; & though a faulty method of trying will make the purity of the air appear different at different times when in reality it is not, I do not see how it can make it appear always the same when in reality it is different."²⁷ Cavendish was knowledgeable about sources of error, confident of his experiments, skeptical of methods resulting in conclusions that differed from his, and unexceptionable in his reasoning.

At the end of his paper on the eudiometer, Cavendish compared its action with the sense of smell. The eudiometer is not like the telescope, an instrument for extending the human senses, but on the contrary, the sense of smell can detect "infinitely smaller" quantities of impure air than can be measured by the eudiometer. Cavendish gave an example, no doubt drawing on his own experience: a person can detect ten ounces of nitrous air released into a twelve-by-twelve-by-twelve-foot room, a measure which would not alter the eudiometer test by more than 1/47,000th part, an immeasurably small quantity. What the nitrous test does show is the degree of phlogistication "and that only," a limitation which does not detract from the usefulness of the test; for our smell is no "test" of phlogistication. There are ways of phlogisticating air that do not impart a smell to it, just as there are ways of imparting a smell that do not phlogisticate.²⁸ Cavendish's conclusion is a realistic affirmation of this instrument of measurement of limited sensitivity in science.

Around the time that Cavendish measured the composition of the atmosphere, it became a medium of human transport. The balloon was invented, and with it a new kind of adventurer came onto the scene, the "aeronaut." Balloons offer their passengers "scenes of majestic grandeur," inciting in them "enthusiastic rapture and pleasure," a balloon traveler wrote.²⁹ Much about this earliest human flight was derring-do and wonder, but there was a limited role for science in it too, both in the principles of flight and in the use of flight for carrying out meteorological measurements. A new field of applied pneumatic chemistry was born.

Cavendish was regarded as a founding father of balloon flight. From his description of inflammable air (hydrogen) in his first publication on air, it was self-evident to Joseph Black

where he recorded "Register of Test Air," Cavendish Mss, Misc. There is another untitled manuscript comparing his, Fontana's, and Ingen-Housz's methods. Peter Brimblecombe (1977). Bent Søren Jørgensen (1967).

²⁴Charles Blagden to Benjamin Thompson, 27 May 1787, draft, Blagden Letters, Royal Society 7:55.

²⁵Golinski (1992, 93).

²⁶Pepys (1807, 259). W. Allen and W.H. Pepys (1808, 249).

²⁷Henry Cavendish to Charles Blagden, 18 Dec. [1798]; in Jungnickel and McCormach (1999, 713).

²⁸Cavendish (1783a, 144).

²⁹Thomas Baldwin (1785, 2).

that balloons filled with this lighter-than-common air were a practical possibility. Black spoke about it with friends and in his lectures, but he did not do the experiment.³⁰ “Theoretical flying,” Blagden said, “has been a topic of conversation among our philosophers as long as I can remember, at least ever since Mr. Cavendish discovered the great lightness of inflammable air.”³¹

“Practical” flying was a French specialty. The relevant chronology of events is as follows. In 1782 the French brothers Joseph and Étienne de Montgolfier filled a small silk bag with heated air as an experiment. In June 1783 they gave a public demonstration: a large balloon was suspended over burning straw and wood, and upon release it rose several thousand feet and sailed about a mile and a half.³² The brothers did not attribute the flight to the rarefaction of air with heat but to a light air given off by the burning material. When news of the experiment reached Paris, people came up with the idea of using inflammable air instead of hot air, and in August a large inflammable-air balloon was flown with considerable success. Animals soon were sent up with balloons and then people, the first successful manned flight taking place in November 1783. The same month saw the first balloon fly over England. The first man to fly there, on 15 September 1784, was Vincenzo Lunardi, secretary to the Neapolitan ambassador in London; his balloon was filled with inflammable air obtained by dissolving zinc in dilute vitriolic acid, the same way Cavendish obtained it in 1766. The second successful manned flight was made on 16 October 1784 by the professor of anatomy in the Royal Academy John Sheldon and the French inventor Jean-Pierre Blanchard, who had come to England to raise money. On 30 November 1784 Blanchard made a second flight with the American physician John Jeffries.³³

Interested in the science of flight,³⁴ Cavendish was naturally interested in balloons from the start. When balloons appeared in the skies above England, Cavendish and his colleagues came out in force to observe them. From the top of Aubert’s house at Austin Friar’s, Cavendish and Blagden made observations of Lunardi’s balloon every one or two minutes for above an hour. From a house on Putney Heath the next month, Cavendish and Dalrymple observed the balloon carrying Blanchard and Sheldon. Using a different method than the others, taking altitudes only, Cavendish calculated the height of the balloon as 3000 feet.³⁵

Cavendish was not attracted to the adventure of balloon flight, and he did not go up in one, but he was interested in what he could learn from them. Through Blagden, he enlisted

³⁰In a letter from Joseph Black to James Lind, in William Ramsay (1918, 77–78).

³¹Charles Blagden to Le comte de Cat[–]lan., 2 Apr. 1784, draft, Blagden Letterbook, Yale.

³²W.A. Smeaton (1974). Charles C. Gillispie (1983, 15–31).

³³Charles Hutton (1795–1796, 1:35–39).

³⁴For his sketch of Cavendish in 1845, Henry Brougham borrowed two manuscripts which are now lost: “Theory of Kites” and “On Flying.” Their existence and loan to Brougham are noted in Cavendish’s manuscripts at Chatsworth.

³⁵Alexander Aubert to William Herschel, 13 Sep. 1784, Royal Astronomical Society, Herschel Mss M1/13. Charles Blagden to Joseph Banks, 16 Sep. 1784, Banks Correspondence, Royal Botanic Gardens, Kew, 1.173. Charles Blagden to Joseph Banks, 17 and 21 Oct. 1784, BM(NH), DTC 4:75–76, 77–78. Henry Cavendish, “Air Taken by Dr. Jeffries: Tried Dec. 3, 1784.” The standard was taken of this air for several samples and compared with “Air Taken at Hampstead at the Time of the Trial.” Two years earlier, samples of air from a balloon were compared with air “taken out at Mr. Cavendish’s S. window at Hampstead at the same time. Nov. 28, 1782.” Henry Cavendish, “Path of Balloon,” for Blanchard and Sheldon’s ascent on 16 Oct. 1784. Cavendish Mss VIII, 9, 24. Henry Cavendish, “Result of Observations of Balloons,” Blagden Collection, Royal Society, Misc. Notes, No. 86. Cavendish’s papers contain a testimonial signed by Benjamin Franklin, among others, of a Montgolfier experiment on 21 July 1783, and also an extract, in Blagden’s hand, about Montgolfier from the *Journal Encyclopédique*. Archibald and Nan L. Clow (1952, 156).

Jeffries to sample the air during his flight with Blanchard: Jeffries took with him jars filled with distilled water, which he emptied at various heights, bottling the air. On the ground with his eudiometer, Cavendish tested the samples and compared them with air taken on the ground at Hampstead, establishing that there is little systematic variation with height in the concentration of dephlogisticated air (oxygen) in the lower atmosphere.³⁶ For Cavendish balloons were a means of elevating his scientific observatory thousands of feet above the Earth, their principal value.

The inflammable-air balloon was fully understood on the basis of weight, but the hot-air balloon raised a question. To decide if hot air alone caused the balloon to rise or if the balloon also depended on a substance lighter than common air given off by the burning material, as the Montgolfier brothers thought, Cavendish and Blagden collected air from burning straw and leather. Determining it to be a mixture of gases heavier, not lighter, than common air,³⁷ they concluded that hot-air balloons ascend solely because of the rarefaction of air.³⁸ In practical terms, hot-air balloons were impractical and perilous, and Blagden expected nothing from them, but he thought that inflammable-air balloons could bring about an “important revolution in human affairs.”³⁹

Balloons fulfilled an age-old dream of flight, creating a sensation in France and mixed feelings in Britain. Not without a touch of envy, the British spoke of “Balloon madness” or else of missed opportunity. Banks said that it was to be hoped that the English would “not rise to the absurd height we have seen in France.”⁴⁰ Blagden regarded Sheldon and Blanchard’s flight a failure, their having made no observations and using a worthless barometer,⁴¹ chalking it up to vanity and foolishness.⁴² After 1785 the enthusiasm for balloon flight abated for a number of reasons: sated curiosity, danger, expense, and uselessness as transportation (ballons could not be steered but drifted with the wind). Very few “philosophical observations” were made from balloons besides those that Cavendish planned.⁴³

Water

In 1784 Cavendish published a paper “Experiments on Air,” which is remembered today for its “first clear and incontestable proof of the compound nature of water and of the nature and relative proportion of its constituents.” The proof is clear, but Cavendish’s explanation of his experiments is not. His primary interest was not the composition of water but the diminution in volume of common air in various chemical reactions, to which his paper on the eudiometer

³⁶He did not publish this finding, the credit for it going to Gay-Lussac for his research twenty years later. Henry Cavendish, “Eudiometer Results of Air Taken by Dr. Jeffries,” and “Test of Air from Blanchard Balloon,” Cavendish Mss II, 9. Thorpe (1921, 22). Jeffries’s air samples were numbered, but because Cavendish’s manuscripts do not contain the explanation of the numbers, the test was believed lost. However, recently it was located in Jeffries’ account of his flight, from which the earliest atmospheric profile, the “Cavendish-Jeffries profile,” has been reconstructed. It shows that at the various sampling elevations, between one and three kilometers, the amount of oxygen in the air over London was virtually constant. Brimblecombe (1977, 365).

³⁷Notations in both Blagden’s and Cavendish’s hand, beginning “Smoke of Straw,” Cavendish Mss Misc.

³⁸Charles Blagden to Claude Louis Berthollet, 5 Dec. 1783, draft, Blagden Letterbook, Yale.

³⁹Charles Blagden to Claude Louis Berthollet, 19 Dec. 1783, draft, *ibid.*

⁴⁰Joseph Banks to Charles Blagden, 22 Sep. and 12 Oct. 1783, Blagden Letters, Royal Society, B.29–30.

⁴¹Charles Blagden to Joseph Banks, 24 Oct. 1784, *ibid.*, 83–84.

⁴²Charles Blagden to Joseph Banks, 26 Oct. 1784, Blagden Letters, Royal Society, B.32.

⁴³Hutton (1795–1796, 1:139).

can be seen as a preliminary. The wider setting was investigations by Priestley, Lavoisier, and Scheele into the air lost during phlogistication.⁴⁴

Observed to occur in many chemical processes, the loss of air was an important question, and chemists had different opinions on its cause. In his paper of 1772, Priestley discussed the prodigious loss common air experiences when it is combined with his newly discovered nitrous air or when a candle is burned in it, consuming a gallon of air in a minute. He was curious about the diminution of common air accompanying other processes too: breathing of animals, putrefaction of animal and vegetable substances, calcination of metals, and exposure of steel filings and pounded brimstone to air. Cavendish was helpful to Priestley again, giving him an account of experiments he had made on the diminution of common air when it was passed it through a red-hot iron tube filled with charcoal dust. Priestley concluded from the many experiments he had made that the “cause” of the diminution of air is the “same in all the cases,” the phlogistication of the air: as he put it, when common air is diminished, it has more than its “usual quantity of phlogiston.” The decisive experiment was the calcination of metals, a process in which metals give up their phlogiston to the diminished air.⁴⁵ Cavendish took this to be a description rather than an explanation, falling short of the understanding he was looking for. He posed a related but different question, which incorporated Priestley’s finding: “to find out the cause of the diminution which common air is well known to suffer by all the various ways in which it is phlogisticated.”⁴⁶

The immediate occasion of his new research was experiments carried out by Priestley and his colleague John Warltire. When Priestley, in what he called a “random experiment,” electrically fired a mixture of inflammable air and ordinary air or dephlogisticated air, Warltire observed that moisture was deposited in the vessel. Priestley did not consider the moisture significant, and Warltire was interested in the experiment for another reason. As reported by Priestley, when Warltire electrically fired a mixture of inflammable and common air in a closed vessel, he observed a generation of heat and light and a loss of weight, which he attributed to the escape of a ponderable matter of heat. This was in the spring of 1781.⁴⁷

In his 1784 paper, after mentioning his unsuccessful attempts “to find out what becomes of the air lost by phlogistication,” Cavendish proceeded “to some experiments, which serve really to explain the matter.” His first experiment had been carried out in the summer of 1781, which appears in his laboratory notes as “Explosion of Inflamm. Air by El. In Glass Globe to Determine Mr Warltires Experiment.”⁴⁸ Cavendish took Warltire’s conclusion about the ponderability of heat seriously enough to carry out experiments using different proportions of the airs, finding that no more than one fifth of a grain was lost and commonly none at all. The absence of a weight loss could not have surprised him, since he believed that heat is not a ponderable matter.⁴⁹ It was the dew that interested him. He found by experiment that all of the inflammable air and about one fifth part of the common air lost their “elasticity” and “condensed” into the dew lining the vessel, and that the weight of the

⁴⁴Cavallo (1781, 401–420). It is indicative of the activity in pneumatic chemistry that in his 1784 paper Cavendish referred to eight current investigators: Bergman, Kirwan, Lavoisier, Priestley, Scheele, Senebrier, Warltire, and Watt.

⁴⁵Priestley (1772b, 162–163, 210–212, 225, 228, 232).

⁴⁶Henry Cavendish (1784b, 161). Thorpe (1921, 23).

⁴⁷Joseph Priestley (1781, 395–398).

⁴⁸Cavendish (1784b, 165). His laboratory accounts: “Experiments on Air,” Cavendish Mss II, 5:115.

⁴⁹This discussion draws on Russell McCormach (1969, 305).

airs that disappeared equaled the weight of the dew that replaced them. To examine the dew qualitatively, he changed the apparatus. By conducting the two airs into an eight-foot long, narrow glass cylinder and firing them, he obtained a relatively large amount of dew, which he tested, finding that it had no color, taste, or smell and left no sediment upon evaporation; that “in short, it seemed pure water.”⁵⁰ The lost fifth part of the common air was the new air that Priestley had announced in 1774, which was discovered independently by Scheele, “dephlogisticated air” (Figs. 14.9–14.10). Today we would say that Cavendish synthesized water by combining hydrogen and oxygen.

We might expect that just as he and Joseph Black had replaced the ancient element air with distinct gases, he would announce that the ancient element water is a combination of airs, but it is uncertain if that is what he thought his experiments showed. He concluded that dephlogisticated air is “in reality nothing but dephlogisticated water, or water deprived of its phlogiston,” and that inflammable air is either “pure phlogiston,” as Priestley and Kirwan thought, or in all probability “phlogisticated water” or “water united to phlogiston.”⁵¹ This statement has been read in more than one way. Wilson in his biography of Cavendish was concerned to establish two points: that Cavendish was the first consciously to observe the synthesis of water from the two airs, in 1781; and that he was the first to recognize that water is a compound substance, by January 1783.⁵² The first point is generally accepted; the second point is Wilson’s interpretation. As evidence, Wilson quoted Cavendish: “These two substances [inflammable air and dephlogisticated air] united together form pure water.” By this wording, Wilson said, Cavendish is on record as saying that water is a chemical compound of two simple material substances, inflammable air, our hydrogen, which he identified with phlogiston, and dephlogisticated air, our oxygen. As further evidence, Wilson cited a paper in which Kirwan stated that Cavendish believed that water is formed by the union of phlogiston with the dephlogisticated part of common air. Cavendish criticized Kirwan’s paper but he let pass his statement.⁵³ A contrary reading is that Cavendish rejected the simple nature of dephlogisticated air and of inflammable air or phlogiston, attributing the simple nature to water instead. Cavendish’s language would seem to support this interpretation too.

Thorpe coming to the subject seventy years after Wilson said that it was “impossible to gather from [Cavendish’s] statement as it stands, whether Cavendish was convinced that water was actually a compound substance.” Thorpe thought that the difficulty lay partly in the uncertainty surrounding Cavendish’s understanding of phlogiston, whether it was a material substance or a quality that is transferred from body to body determining their natures. A contemporary historian of chemistry William Brock writes that for Cavendish, the production of water from hydrogen and oxygen “was not a synthesis of water at all; instead, as a phlogistonist, he preferred to see inflammable air as water saturated with phlogiston and oxygen as water deprived of this substance,” and when the two were united, nothing remained but water, a “simple substance.”⁵⁴ This is a paraphrase of what Cavendish wrote in

⁵⁰Cavendish (1784b, 167).

⁵¹*Ibid.*, 171–173.

⁵²Wilson (1851, 435).

⁵³*Ibid.*, 329.

⁵⁴Thorpe (1921, 35). The chemist Berry, Cavendish’s biographer, writes that there is ambiguity in Cavendish’s statement, “I know no way by which phlogiston can be transferred from one body to another, without leaving it uncertain whether water is not at the same time transferred.” Brock writes, “The difficulty is centred around the question as to what Cavendish understood by phlogiston. . . . He seems to have regarded hydrogen as a hydrate of phlogiston.” Brock (1992, 110). Berry (1960, 86–87).

his paper of 1784 and a plausible alternative to Wilson's interpretation. Chemists at the time differed on Cavendish's meaning. Kirwan agreed with Wilson, and apparently so did Watt and Deluc, but the Swedish chemist Berzelius held the opposite interpretation. Cavendish who valued clarity of expression failed to meet his standard in this instance, as the history of his paper of 1784 proves.

Exactly what importance Cavendish attributed to the nature of water we probably can never know with certainty. The object of his experiments was to find the cause of the diminution of air by all the ways it can be phlogisticated, and the production of water gave him his answer. It was the kind of answer scientists like, a single cause for an effect brought about by different agencies, and the cause in this instance did not depend on deciding the nature of water. In arriving at his answer, Cavendish relaxed another standard of his, caution. Normally he did not draw conclusions beyond what his experiments allowed, but in the case of his experiments on the phlogistication of air, he did. As a phlogistonist, he supposed that inflammable air explains every case of phlogistication, and consequently that the phlogistication of air always diminishes the bulk of the air because it always produces water. As generalizations, these statements are incorrect. We know that not every body that can be oxidized contains hydrogen and yields water when oxidized.⁵⁵ He generalized before he made the required experiments.

What Cavendish thought he did in his experiments on air was important to Wilson because of the rival claims in the water controversy. The interpretation that mattered to chemistry was Lavoisier's, which was not long in coming. Wilson observed that if the "discovery of the composition of water" had remained within phlogiston chemistry, it would have made very little difference to chemistry. It would have meant only that instead of transferring phlogiston from one body to another, water would be transferred and be decomposed and composed, as required. The discovery needed Lavoisier to see its significance.⁵⁶

Following his conclusion that dephlogisticated air is water deprived of phlogiston and that inflammable air is phlogisticated water, Cavendish commented on Watt's statement that water is "dephlogisticated air and phlogiston deprived of part of their latent heat." In his paper the year before on the freezing of mercury, Cavendish had stated his difference with Black on "latent heat." Latent heat having come up again with Watt, Cavendish again rejected it, explaining that he thought that heat is not a fluid, and that the admission of latent heat would encumber the "language" of chemistry. For example, diluted mineral acids would be said to consist of "concentrated mineral acids united to water and deprived of part of their latent heat," and a similar way of speaking would be needed for other chemical combinations, for almost all of them are attended with an increase or decrease of heat. The term "latent" would lead to "false ideas" in chemistry and "cause more trouble and perplexity than it is worth."⁵⁷

In his paper of 1784 Cavendish said that he found no role for fixed air in the various instances of phlogistication of common air, contradicting Kirwan, who published a criticism. In a second paper that year Cavendish answered Kirwan, correctly refuting his claim. A possible value of this digression is that Kirwan's reference to the effect of passing an electric

⁵⁵Wilson (1851, 326–328).

⁵⁶Ibid., 248.

⁵⁷Cavendish (1784b, 173–174).

spark through air may have caught Cavendish's attention. In any case, the electric spark was the agency of his second discovery, our next subject.⁵⁸

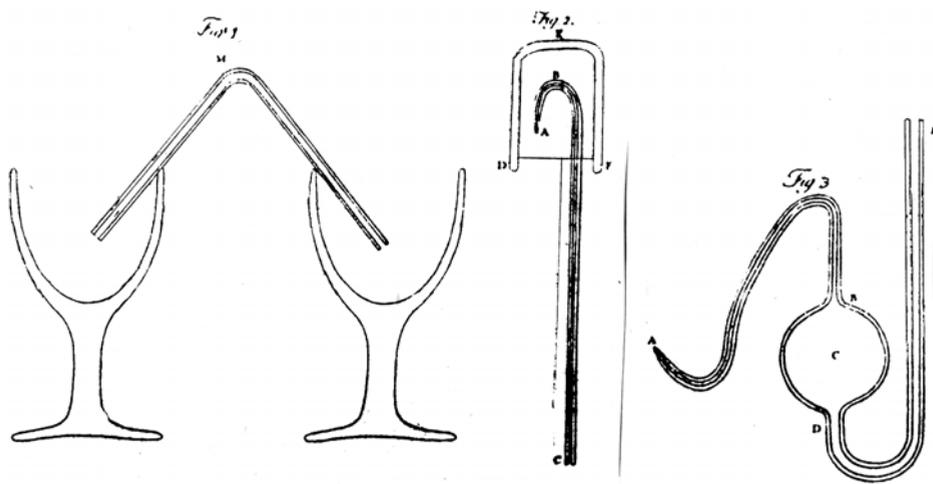


Figure 14.4: Apparatus for Experiments on Air. For converting phlogisticated air (nitrogen) into nitrous (nitric) acid, a spark is passed through air trapped in the bent tube shown in Figure 1. Filled with mercury, the tube is inverted into two glasses containing mercury. Figures 2 and 3 show small-bore tubes used to insert the nitrous air into the bent tube. "Experiments on Air," PT 75 (1785): 348.

Nitrous Acid

Much of Cavendish's paper of 1784 is taken up with a related question, the source of acidity of some of the dew. To further examine it, he repeated his experiments using a large glass globe; he found that when he substituted dephlogisticated air for atmospheric air in the experiments, the dew occasionally was acidic to the taste, and when the dew was combined with fixed alkali it yielded nitre, showing that it contained a small amount of nitrous acid. He also found that on these occasions, the dephlogisticated air was a little in excess of the inflammable air. He prepared dephlogisticated air from several sources, red precipitate, red lead, plants, and turbith mineral, finding that the condensed liquor was acidic in every case. He concluded that regardless of the source of dephlogisticated air, if it is in excess when it is exploded with inflammable air, the dew contains some nitrous acid. He explained the appearance of the acid drawing on his understanding that phlogisticated air is nitrous acid united to phlogiston: he supposed that dephlogisticated air (oxygen) contains a trace of phlogisticated air as an impurity, which it deprives of its phlogiston, turning it into nitrous (nitric) acid. By enhancing the effect, he produced the "decisive argument": when he deliberately added a quantity of phlogisticated air (nitrogen) to the mixture of inflammable and dephlogisticated air and sparked the mixture, he found that the resulting dew was more

⁵⁸Henry Cavendish (1785). Thorpe (1921, 47).

strongly acidic. Because he clearly regarded water and nitrous acid as equally important products of phlogistication, until he understood both he was not finished with his investigation, accounting for the long delay in publishing his experiments on the production of water.⁵⁹

The next year, 1785, Cavendish published a second paper under the same title, "Experiments on Air." In the first paper he said that an electric spark probably ignited some inflammable matter in the apparatus causing the airs to explode, but he had made no experiments. His new paper was about experiments he had recently made using the electric spark to detonate the airs. His apparatus was simple: a narrow glass tube bent at an angle was filled with mercury, and the two open ends were immersed in two vessels containing mercury. (The apparatus is similar to the one his father invented for Watson's experiment on electrical conduction across a vacuum.) He forced air (by an ingenious method) into the tube, collecting it at the bend, where he sparked it electrically. (Fig. 14.4). He found that dephlogisticated air by itself suffered very little diminution in volume and phlogisticated air by itself none at all, but that a mixture of the two airs always did. When the mixture was five parts of dephlogisticated air and three parts of common air, nearly the entire air disappeared, leaving behind nitrous acid. Cavendish concluded from the experiments with the electric spark that dephlogisticated air and phlogisticated air "form a chemical combination," wording which shows that he viewed the two airs as distinct substances. He knew that the electric spark itself did not enter into chemical combination, and nothing in the experiments suggested that it contributed phlogiston, a subject of speculation at the time. His explanation was that dephlogisticated air aided by the heat caused by the spark deprived phlogisticated air of its phlogiston, reducing it to nitrous acid, agreeable with his explanation in his paper the year before. His new experiments on the production of nitrous acid paralleled those on the detonation of dephlogisticated air and inflammable air producing water, completing his investigation of the causes of the diminution of common air by phlogistication. To the interpretation of dephlogisticated and inflammable airs discussed above, another was added: the other part of common air, phlogisticated air, our nitrogen, is "nothing else" than nitrous acid united to phlogiston; Cavendish had said this in his paper the previous year, but now he had experimental proof.⁶⁰

Word of Cavendish's new experiments traveled quickly. Two weeks after his paper was read to the Royal Society, Blagden heard from Berthollet that one part of Cavendish's experiments had been repeated in Paris, but given another interpretation: "we think that Mr. Cavendish has combined dephlogisticated air with phlogisticated air, instead of having decomposed the latter."⁶¹ The different interpretations had to do with Cavendish's disagreement with Lavoisier on the formation of acids, described below.

In the course of his experiments, Cavendish had discovered nitrites and nitrates, which drew considerable interest and puzzlement. Lavoisier and his colleagues in Paris were unable to repeat the experiments; Cavendish could not imagine why but for "want of patience." In Holland Martin van Marum also failed, even with the help of his new electrical machine,

⁵⁹Cavendish (1784b, 169–171). Thorpe (1921, 33). Wilson (1851, 442). Berry says that "nowhere in his chemical work does the genius of Cavendish appear more clearly" than in his explanation of the appearance of nitric acid upon exploding the gases with an excess of oxygen. (1960, 73).

⁶⁰Cavendish (1785, 191, 194).

⁶¹Berthollet told Blagden that his letter created great interest in Paris in Cavendish's "beautiful experiments." Claude Louis Berthollet to Charles Blagden, 17 June 1785, Blagden Letters, Royal Society, B.126.

the largest in existence; Cavendish again did not know why, though he thought that the apparatus might be faulty.⁶² Instead of guessing what went wrong in experiments by others, Cavendish demonstrated what was right in his own. At his request, the clerk of the Royal Society George Gilpin repeated the experiments using the same apparatus during several days in late 1787 and early 1788, witnessed by ten or more fellows of the Royal Society, most of whom came to each part of the experiment.⁶³ Gilpin worked Nairne's electrical machine a half hour at a stretch, obtaining 2 or 300 sparks a minute, whereas Cavendish had only worked his machine for ten minutes at a time, but details of procedure aside, Gilpin's experiments fully confirmed Cavendish's. These repeated experiments were the substance of Cavendish's last publication in chemistry, in 1788.

Cavendish's contributions to pneumatic chemistry were widely separated, the first in 1766, the second in 1781–85. The first contribution was basic to the development of chemistry as a science; following Hales's early experiments on fixed air, it together with Black's study of *magnesia alba* opened a necessary field of investigation. His later contributions—the constancy of the composition of the atmosphere, and the conversion of airs into water and nitrous acid—were important too, though they were among other important contributions by a number of able investigators in a field that was well established. What was most important about Cavendish's last papers on chemistry may have been the example: to have studied them was to have taken a master class in the art of experiment. Jean Senebier, a Swiss pastor who examined the oxygen given off by plants, and who published insightful essays on the experimental method, wrote to Cavendish after reading his recent papers on airs to express his admiration for Cavendish's "exactitude," characterizing him as "a master and a great master in the difficult art of making experiments."⁶⁴

Atmosphere

Daniel Rutherford, Black's and Cullen's student, wrote his medical dissertation in 1772 at the University of Edinburgh on Black's fixed air or, as Rutherford called it, "mephitic air." In the course of his experiments, Rutherford isolated another, similar air, phlogisticated air, our nitrogen, which he distinguished from fixed air, though he considered it as common air saturated with phlogiston rather than as a distinct air. Because Rutherford's dissertation was published, he is given credit for discovering nitrogen, but many years earlier Cavendish had studied this air. In a paper written for a correspondent, who had shown him a letter from Priestley discussing "mephitic air," by which Cavendish understood Priestley to mean air that "suffocates animals," Cavendish said that "in all probability there are many kinds of air which possess this property," and he knew of at least two, Black's fixed air and common air in which something had burned, or "burnt air" (nitrogen). Cavendish gave his correspondent the results of an earlier experiment of his, in which he reduced the volume of common air by passing it through a red-hot tube containing charcoal dust (the experiment mentioned earlier,

⁶²Martin van Marum to Henry Cavendish, 6 Jan. 1786; Henry Cavendish to Martin van Marum, undated, draft; in Jungnickel and McCormmach (1999, 622–625). Cavendish published this letter in his paper, "On the Conversion of a Mixture of Dephlogisticated and Phlogisticated Air into Nitrous Acid by the Electric Spark," (1788b, 232).

⁶³The witnesses were Banks, Blagden, Heberden, Watson, John Hunter, George Fordyce, J.L. Macie, and Johann Caspar Dollfuss; William Higgins and Richard Brock came on the day after an "accident" happened, and Cavendish did not list them in his paper. T.S. Wheeler and J.R. Partington (1960, 33, 66).

⁶⁴Jean Senebier to Henry Cavendish, 1 Nov. 1785; in Jungnickel and McCormmach (1999, 611–618)

given to Priestley). He removed the fixed air produced by the charcoal and measured the specific gravity of the remaining burnt air. What he referred to as “common air which has suffered a change in its nature from the fire” was nitrogen, which he gave the “first clear description” of. This paper by Cavendish is undated, but Priestley gave a version of it in his paper of 1772.⁶⁵

In his paper of 1785, Cavendish said that little was known about the “phlogisticated part of our atmosphere,” not even if there are “in reality many different substances confounded together by us under the name of phlogisticated air.” To see if the phlogisticated air of the atmosphere contained anything other than “nitrous acid united to phlogiston,” he repeatedly sparked a mixture of common air and dephlogisticated air until he was unable to diminish the volume any further. Using a standard method, he removed any remaining dephlogisticated air from the residue, leaving a small “bubble” of air unabsorbed in his apparatus, no more than 1/120 part of the whole, which he probably regarded as an experimental error or an impurity. A hundred years later, the bubble was recalled by William Ramsay, who had read George Wilson’s biography of Henry Cavendish when he was a student. He drew the passage to the attention of J.W. Strutt, Lord Rayleigh, who like Ramsay was concerned with a third decimal difference in the density of the nitrogen in the atmosphere and the density of the nitrogen produced chemically.⁶⁶ On a larger scale, they repeated Cavendish’s experiment, recognizing that Cavendish’s bubble contained a new gas of the atmosphere, the chemically inert argon, later determined to contain traces of four other gases. In a jointly authored paper on the new inert gas argon in 1895, Ramsay and Rayleigh paid tribute to their predecessor: “Attempts to repeat Cavendish’s experiment in Cavendish’s manner have only increased the admiration with which we regard this wonderful investigation. Working on almost microscopical quantities of material, and by operations extending over days and weeks, he thus established one of the most important facts in chemistry. And what is still more to the purpose, he raises as distinctly as we do, and to a certain extent resolved, the question above suggested,” the possibility that atmospheric nitrogen contains another gas.⁶⁷ In his history of the gases of the atmosphere, Ramsay observed that of all the experimenters, Cavendish was “undoubtedly the greatest.”⁶⁸

If Cavendish’s later work is looked upon as a kind of chemical meteorology, it takes on an additional significance. The title he gave to his two chemical papers in 1784 and 1785, “Experiments on Air,” referred to common air, the air of the atmosphere, a mix of dephlogisticated and phlogisticated airs. Cavendish intended the first paper to “throw great light on the Constitution and Manner of production of dephlogisticated air.”⁶⁹ In his paper of 1785 he had a similar objective, only this time the air was phlogisticated air, the other half of common air. Blagden sent his brother three papers by Cavendish and Watt, which taken together seemed to him “fully to explain the nature of our atmosphere,” noting that the most

⁶⁵Henry Cavendish, “Paper Communicated to Dr Priestley,” Cavendish Mss, Misc. Vernon Harcourt, Presidential Address, British Association Report (1839), 3–68, on 64. Scheele too studied this gas, perhaps as early as 1771, but he did not publish his results until 1777. E.L. Scott (1975). Priestley came upon it independently too. Ihde (1964, 38).

⁶⁶There are two versions of the way Cavendish’s experiment came to the notice of Rayleigh. We have given Ramsay’s. Rayleigh’s was that he was first informed of Cavendish’s experiment by James Dewar. Morris W. Travers (1956, 100–107).

⁶⁷Berry (1960, 178–179).

⁶⁸William Ramsay (1896, 143). Bruno Kisch (1965, 8).

⁶⁹Cavendish (1784a, 161).

important of the three was Cavendish's paper on the origin of nitrous acid (and not the paper on the production of water, if that was one of the three papers), for it showed that the greatest part of the atmosphere "is nothing but that acid in aerial form."⁷⁰ Likewise Priestley wrote to Cavendish that his study of phlogisticated air was "one of the greatest, perhaps the very greatest, and most important, relating to the doctrine of air."⁷¹

We conclude our account of Cavendish's late chemical researches on air by reviewing his long-standing interest in the atmosphere. He improved the eudiometer, tested the composition of the atmosphere, and studied the nature of its components. At the request of the Royal Society he examined its meteorological instruments, and under his direction the Society instituted regular observations with their use. He experimented extensively with his own meteorological instruments as well. He measured the specific heat of air and the expansion of air with heat. He examined the hot-air balloon and observed the flight of balloons. Because of reports of extraordinarily low temperatures of the atmosphere in Russia, he made a study of the freezing point of mercury, the usual expansive agent of weather thermometers. He measured the temperature of spring water and water from deep wells as a means of determining the average climate of different regions. In connection with his geological tours he determined elevations on the Earth by means of a barometer, the measurer of the pressure of the atmosphere. He made optical studies of the refraction of light by the atmosphere. He studied the communication of electricity to the air. With reference to Newton's work, he made mechanical studies of the effect of the resistance of air on the trajectory of projectiles, of the motion of sound, and of the law of force of air particles responsible for Boyle's law.⁷² Given what was knowable about the physical and chemical behavior of air in his time, there was little that Cavendish did not know firsthand.

New Chemistry

Had there been no "chemical revolution," the progressive development of techniques in chemistry in the eighteenth century would have gone on as it had under the old chemistry. But there was a chemical revolution—an assertion which is accepted by most historians of chemistry even as they disagree about what the revolution was, what its boundaries were, and what place the overthrow of phlogiston had in it⁷³—and consequently the historical interest in Cavendish has been largely in relation to that event. Cavendish's contribution to chemistry was not among the conceptual changes that marked the chemical revolution. In contrast to Cavendish, Lavoisier broke with the science he had started out with; from the early 1770s he consciously strove to bring about a "revolution" in physics and chemistry, and twenty years later he had accomplished it or, depending upon one's interpretation, he had completed the first part of the revolution (Fig. 14.6).

A change of this magnitude in chemistry required a number of developments, one of which was pneumatic chemistry, which replaced the idea of elementary air with that of

⁷⁰Charles Blagden to Thomas Blagden, 8 Dec. 1785, Blagden Letterbook, Yale.

⁷¹Joseph Priestley to Henry Cavendish, 30 Dec. 1784. Priestley's letter was in reply to Cavendish's, written in late 1784, which summarized the main points of what would become the published paper of the following year. Henry Cavendish to Joseph Priestley, 20 Dec. 1784, draft; in Jungnickel and McCormmach (1999, 598–599, 602–603).

⁷²Henry Cavendish, "Projectiles," "On the Motion of Sounds," Cavendish Mss VI(b), 14, 35. Cavendish (1771, 43).

⁷³"Introduction," A.L. Donovan (1988, 5–12, on 5–6); Siegfried (1988, 34–50, on 34–35).

chemically active, distinctive airs, or the gaseous state of matter. Cavendish's production of water from gases was important for Lavoisier, who saw that it showed that water is a compound, giving him the answer to the critical question of what happens when metals are dissolved in acids: the inflammable air, or hydrogen, that flies off does not come from the metals, as the phlogiston theory said, but from the dissociated water. According to Thomson, Cavendish's discovery and Lavoisier's subsequent experiments "contributed more than any thing else to establish the antiphlogiston theory."⁷⁴ In order to build as well as destroy, Lavoisier had to work out a new chemical understanding and a new nomenclature to express it, and he had to win disciples. These things, of course, he did. His *Traité élémentaire de chimie* in 1789 would instruct the next generation of chemists in the new chemistry.⁷⁵

Lavoisier was slow to recognize the importance of Cavendish's early chemical work. In his *Essays Physical and Chemical*, published in 1774, he showed a full appreciation of the work of Hales, Black, and Priestley, while his discussion of Cavendish was relatively brief. A historian of chemistry writes, "What is difficult to understand is how Lavoisier failed to grasp the significance of the work of Cavendish," which should have impressed him, especially Cavendish's determination of the densities of inflammable and fixed air, given the value Lavoisier placed on quantitative work in chemistry. Copies of Lavoisier's book were sent to the Royal Society and to Priestley, but not to Cavendish. What impressed Lavoisier at the time was Priestley's paper of 1772: more than any other modern work, it showed "how many new roads philosophy and chemistry still point out to travel over."⁷⁶ As a stimulus to a chemist who saw his vocation as the remaking of his field, Cavendish's careful measurements could not compete with Priestley's discovery of a new air and an up-to-date review of the field.

At the time of his new experiments on air, Cavendish was familiar with Lavoisier's efforts to eliminate phlogiston from chemistry and to introduce oxygen in its place. At the end of his paper of 1784, he conceded that the phenomena of nature could be about equally well explained on Lavoisier's chemistry as on the old. To show this, he described the phenomena of interest using Lavoisier's "theory." He did not adhere strictly to the theory, and he allowed additions and alterations to suit the phenomena, but he came close. By Lavoisier's "hypothesis," he said, water consists of "inflammable air united to dephlogisticated air," and he gave comparable reformulations of the composition of airs, acids, and metallic calces. Cavendish thought that it would be "very difficult to determine by experiment which of these opinions is the truest," but there was "one circumstance, which though it may appear to many not to have much force, I own has some weight with me." This was that on the phlogiston theory, plants give off phlogiston when they are burned, and it seemed obvious to Cavendish that plants are more compounded than their ash; on Lavoisier's theory, the ash, containing oxygen, is the more compounded.⁷⁷ Cavendish's "new modelled" phlogistic theory of 1784 was impossible to refute at the time, and French chemists did not try.⁷⁸

It might seem that Cavendish was slow to see the superiority of Lavoisier's chemistry, but this would be a misreading of the state of chemistry in 1784. It was not until the following year that the first French chemist, Berthollet, agreed with Lavoisier on the need to give up

⁷⁴Thomas Thomson (1830–1831, 2:115).

⁷⁵Changes that underlay the Chemical Revolution are summarized in Brock (1992, 84–85).

⁷⁶Greenaway (1776/1970, xxiii, xxix).

⁷⁷Cavendish (1784b, 179–181). Thorpe (1921, 37).

⁷⁸Thomson (1830–1831, 2:136–137).

phlogiston.⁷⁹ That year Blagden wrote to Berthollet that with Cavendish phlogiston was a “doubtful point.” Whether the “old hypothesis of p” is right or Lavoisier’s hypothesis that dephlogisticated air is a “simple substance,” Blagden said, is a “question which I think cannot remain long undecided.”⁸⁰ He thought that the English had not yet “given up” on phlogiston, and he mentioned its advocacy by Kirwan, explaining “it belongs to the temper & character of the philosophers of this country” to retain a familiar hypothesis “as long as they can explain the phenomena upon it.” Of the recent work in France, Blagden wrote to Priestley, a staunch proponent of phlogiston, “I will not say [it] *overturns* the doctrines of phn but shakes it to its very foundations.”⁸¹ In a letter to William Cullen about the “question now warmly agitated relative to the existence of phlogiston,” Blagden said that “which ever of the two systems, Stahl’s or Lavoisier’s,” was adopted, Cavendish’s experimental work was of equal importance in either.⁸² Two years later, in 1787, Blagden told Berthollet that his memoirs had answered the “principal objections made by the supporters of the old doctrine of phlogiston.” The arguments of the new chemistry were so much clearer than those of phlogistic chemistry that the “combat must soon be at an end.”⁸³ In these letters written at the turning point of the Chemical Revolution, Blagden was expressing his own opinion, which was that of a convert, but we wonder to what degree, if any, it was in opposition to the opinion of the chemist he worked with daily. Following Cavendish’s lead in his paper of 1784, when describing Cavendish’s work to others, Blagden gave both explanations, the old and Lavoisier’s.

If Kirwan is to be believed, by the time of the new chemical nomenclature, Cavendish had already given up the old chemistry. In a postscript to a letter of one of the authors of the *Nomenclature chimique*, Guyton de Morveau, Kirwan wrote that “Mr. Cavendish has renounced phlogiston.” Kirwan did not give his source or elaborate, but what he said is consistent with what Blagden had been saying to and about Cavendish. The date was 2 April 1787, only a few weeks after Marum had told Lavoisier that he rejected phlogiston. Cavendish and Marum would seem to be the first chemists outside of France to abandon the foundation of the old chemistry, phlogiston, but there would soon be many.⁸⁴ In late 1787, Cavendish was busy disseminating the new chemistry in London: having received a bundle of Berthollet’s anti-phlogistic memoirs sent over with the *Nomenclature chimique*, he directed the publications to the “diff’t gentl for whom they were intended,” himself included, “all in the best manner he was able.”⁸⁵ In 1788–89 the major exponents of the anti-phlogistic chemistry in France were elected foreign members of the Royal Society. Cavendish signed all of their certificates, and in the case of the leading chemist among them, Lavoisier, he was the *first* to sign.⁸⁶

At the end of his paper in 1784, where he said that the principle of phlogiston and Lavoisier’s hypothesis seemed to work about equally well, Cavendish raised a difficulty for Lavoisier’s idea of dephlogisticated air, or oxygen, as the “acidifying principle.” For

⁷⁹Ibid. 2:101, 130.

⁸⁰Charles Blagden to Claude Louis Berthollet, 21 and 24 May and 28 June 1785, drafts, Blagden Letterbook, Yale.

⁸¹Charles Blagden to Joseph Priestley, 11 June 1785, draft, *ibid.*

⁸²Charles Blagden to William Cullen, 5 July 1785, draft, *ibid.*

⁸³Charles Blagden to Claude Louis Berthollet, 17 Nov. 1787, draft, Blagden Letters, Royal Society 7:85.

⁸⁴Scottish chemists were receptive. Black early lectured on the new chemistry, though he did not commit himself until 1790. Thomas Charles Hope, who succeeded him at Edinburgh, lectured on the new theory after 1787.

⁸⁵Blagden to Berthollet, 17 Nov. 1787.

⁸⁶3 Apr. 1788, Certificates, Royal Society 5.

some acids it worked, Cavendish said, but not for all, in particular not for marine acid, our hydrochloric acid,⁸⁷ and this was correct. The chemist Thomas Thomson thought that if the chemical world had not paid “total inattention” to Cavendish’s criticism in 1784, the success of the anti-phlogistic school would not have been as rapid as it was.⁸⁸ If Cavendish abandoned the phlogiston theory three years later, as we have reason to think he did, he did not necessarily subscribe to Lavoisier’s viewpoint, certainly not entirely. It is likely that he accepted the version he gave in his paper in 1784, or part of it, and that he qualified Lavoisier’s acidifying principle.

Cavendish had strong feelings about the language of chemistry, as we know from his correspondence with Blagden, who was away from London on the French and English triangulation project in 1787. The French party crossed the Channel carrying anti-phlogistic chemical publications including a copy for Cavendish of the new *Méthode de nomenclature chimique* written by Lavoisier and his colleagues.⁸⁹ Having read the preface, Cavendish wrote to Blagden that the nomenclature was a move to impress the new theory on chemistry. Nothing, Cavendish said, serves “more to rivet a theory in the minds of learners than to form all the names which they are to use upon that theory.” If this precedent were to succeed, every chemist with a new theory would present it along with a new language, with the result that no one could understand what was being said without first learning the new theory. Moreover, every experimental advance in chemical composition would be followed by renaming. A systematic nomenclature did not lead to clarity, as its proposers believed, but to “confusion,” causing “great mischief.” Because traditional names of chemical substances had no connection with their composition, no bias was built into them. Cavendish made an exception for uncommon neutral salts, accepting that naming them by their components made sense because there were so many of them. He apologized to Blagden for his uncharacteristic “long sermon” on the “present rage of name-making.” He thought that the nomenclature would likely pass as a “fashion,” a word Cavendish used three times in his “sermon.”⁹⁰ Blagden’s reaction was much the same. The authors of the chemical nomenclature had been seduced by the Linnean natural history, Blagden said, which was a false analogy. The objects studied by natural history remained the same over long periods, but in chemistry discoveries came so rapidly that names would have to change constantly. Like Cavendish, he saw “little danger that the systematic names will be adopted.”⁹¹ Other proposals of chemical nomenclature and shorthand around the same time were met with skepticism by Blagden and, we suppose, by Cavendish.⁹² Cavendish clearly did not think about chemical nomenclature as its authors did, as a tool like mathematics capable of directing researchers to discoveries.

⁸⁷Cavendish (1784b, 181).

⁸⁸Thomson (1830–1831, 2:348).

⁸⁹From Dover, Blagden wrote to Cavendish in London that he had the book and would hold it if Cavendish planned to join him or forward it to Banks’s address where Cavendish could pick it up. Because of foul weather, Cavendish did not go to Dover, with the result that he and Blagden discussed the nomenclature by letter. Charles Blagden to Henry Cavendish, 16 Sep. 1787; Henry Cavendish to Charles Blagden, n.d. [after 16 Sep. 1787], draft, in Jungnickel and McCormack (1999, 634–635, 638–640). Charles Blagden to Claude Louis Berthollet, 17 Nov. 1787, draft, Blagden Letters, Royal Society 7: 85.

⁹⁰Cavendish to Blagden, [Sept. 1787].

⁹¹Charles Blagden to Henry Cavendish, 23 Sep. 1787, in Jungnickel and McCormack (1999, 641–644).

⁹²“Dr Black has just made a new chl nomenclature: I think he might have been better employed”; J.-H. Hasenfratz’s chemical shorthand was thought to serve no “useful purpose” in England; and James Watt risked his reputation with his chemical algebra. Charles Blagden to M.-A. Pictet, 12 Feb. 1790, draft, and to James Watt, 6 Dec. 1788, draft, Blagden Letters, Royal Society 7:402 and 7:185.

In 1788 an English translation of the new nomenclature came out. Adoption of it was relatively slow, given British reluctance to use French words or their Anglicized versions and, in some cases, to part with phlogiston. In his treatise on chemistry in 1790, William Nicholson said that the phlogistic and anti-phlogistic hypotheses were equally probable; in his dictionary of chemistry in 1795 he regarded the anti-phlogistic hypothesis as the most probable, but he did not use the new nomenclature because he did not want to “anticipate the public choice.” Priestley never adopted the new language or gave up phlogiston. Black soon gave it up, but he accepted the new language only selectively and invented a partially new one of his own. In the 1790s the French nomenclature was commonly used in Edinburgh and in London.⁹³ In a letter in 1794 Blagden wrote of Thomas Beddoes’s apparatus and the “dephlogisticated dog” inside it; he crossed out “dephlogisticated” and wrote instead “oxygenated.”⁹⁴

Late in life, Cavendish used Lavoisier’s names on occasion.⁹⁵ Around 1800, he returned to an experiment he had carried out much earlier, probably in or around 1783, on the distillation of charcoal producing fixed and inflammable airs. Upon carrying out new computations, he concluded that the experiment showed that either the “charcoal contains hydrogen as well as carbon & water or else that the charcoal after distillation contained some oxygen.” In this passage he used terms he had not used at the time he made the experiment, “carbon,” “hydrogen,” and “oxygen.” He also spoke of “phl. Air” not “azote” in the same place. His chemical vocabulary was a mix in this case.

Chemists

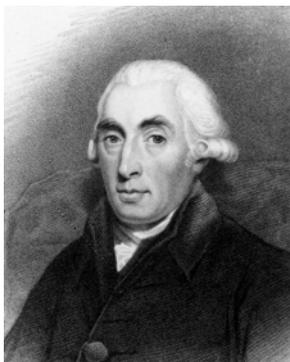


Figure 14.5: Joseph Black. Painted by Henry Raeburn, engraved by T.A. Dean. Courtesy of the Smith Image Collection, Van Pelt Dietrich Library, University of Pennsylvania.

⁹³Nicholson (1790, viii; 1795, 1:vii). Maurice Crosland (1962, 193–206).

⁹⁴Charles Blagden to Georgiana, duchess of Devonshire, 4 Jan. 1794, Devon. Coll.

⁹⁵In computations around 1800, Cavendish used “hydrogen” and “oxygen”: Henry Cavendish, “Experiments on Air,” Mss II, 5: 390. In a letter to Blagden about a paper by Humboldt on the eudiometer, Cavendish used Lavoisier’s name for phlogisticated air (our nitrogen) “azote.” This was in 1798, some ten years after his “sermon” on Lavoisier’s new chemical nomenclature. Henry Cavendish to Charles Blagden, 18 Dec. [1798], Blagden Papers, Royal Society.



Figure 14.6: Antoine Laurent Lavoisier. Drawing by J. Boilly, engraving by Nargeat. Courtesy of Smith Image Collection, Van Pelt Dietrich Library, University of Pennsylvania.



Figure 14.7: Joseph Priestley. Leeds portrait of Priestley around 1765. Courtesy of Smith Image Collection, Van Pelt Dietrich Library, University of Pennsylvania.

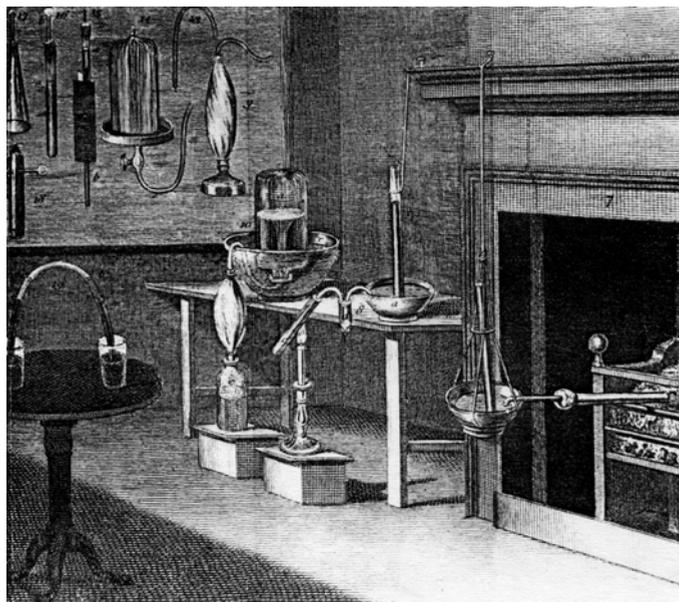


Figure 14.8: Priestley's Chemical Apparatus. From the first volume of Priestley's *Experiments and Observations on Air*, 1774.



Figure 14.9: Carl Wilhelm Scheele. Engraving. Courtesy of Smith Image Collection, Van Pelt Dietrich Library, University of Pennsylvania.

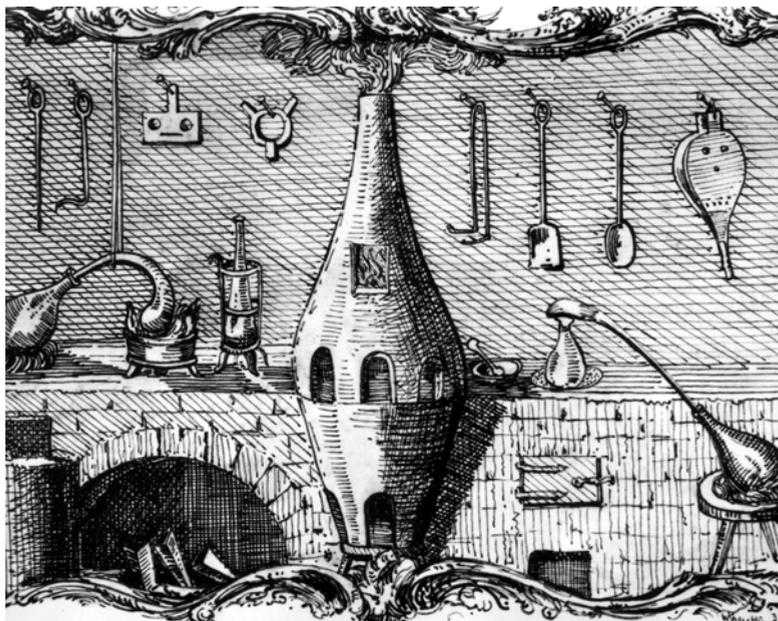


Figure 14.10: Scheele's Laboratory. Woodcut by W. Kreuter. Courtesy of Smith Image Collection, Van Pelt Dietrich Library, University of Pennsylvania.

Earlier in this book where we take up Cavendish's chemical work in the 1760s, we discuss phlogiston. Having considered Cavendish's explanation of his experiments in the 1780s, we return to the discussion here. The Stahlian principle provided a theory that covered a wide range of chemical behaviors, not only combustion but also acidity, alkalinity, chemical reactivity, and chemical composition. As with most any general theory, it met with difficulties. One difficulty was accounting for the gain in weight of combustibles when burned and of metals when calcined, since according to the theory they have lost something, phlogiston, and so there ought to be a loss of weight rather than a gain. Not all chemists accepted that metals gained weight, and chemists did not consider it a serious problem until they studied gases from the 1760s, when they began to attribute odd properties to phlogiston to explain what they observed. In 1785, the year after Cavendish's paper on experiments on air, Lavoisier published an essay on the principle of phlogiston. Like Cavendish, he recognized that chemical phenomena could be explained with or without phlogiston, but he drew a different conclusion, casting doubt on the existence of phlogiston, which he saw as a vague principle, always changing to meet the explanations demanded of it. He gave examples: sometimes phlogiston has weight, sometimes not; sometimes it is free fire, sometimes it is fire combined with an earth; sometimes it passes through the pores of vessels, sometimes it finds them impenetrable. It explains at once causticity and non-causticity, transparency and opacity, colour and the absence of colour, a "veritable Proteus" that changes its form every instant.⁹⁶

⁹⁶Brock (1992, 83–84, 111–112).

Like other phlogistic chemists, Cavendish observed the gain of weight of the product, the *caput mortuum*, of burned and calcined substances without seeing it as an important problem. In his first surviving chemical research, he explained the weight of the *caput mortuum* of arsenic by its retention of some of the aqua fortis used in making it, even performing an experiment to support his conclusion.⁹⁷ Not drawn to speculations about phlogiston like those mentioned by Lavoisier, Cavendish regarded phlogiston as a respectable chemical substance, which happened to be wrong.

Wilson, Cavendish's biographer, was educated in the chemistry that Lavoisier's revolution set in motion. Much closer to the era of phlogiston chemistry than we are, his opinions were correspondingly stronger. He considered Stahl's theory to be nearly empty of content, scarcely deserving "to be called a scientific hypothesis," amounting to no more than "the assertion, that a body was combustible because it contained something combustible." He likened it to "vulgar belief," "poetical" thought, and a child's idea of power as inhabiting objects "resembling a living or vital agent." Instead of recognizing it for what it was, a chimera, chemists used it as "a perfect theory." Phenomena that conflicted with it, such as the increase in weight of combustibles when burned, they overlooked or downplayed. This was the "crude and clumsy hypothesis" that passed for a fundamental principle of chemistry at the time Cavendish began his experiments.⁹⁸

With hindsight, what Lavoisier and Wilson said about phlogiston is reasonable, for what came after was ever so much better. Yet something can be said in defense of phlogiston, which Cavendish's later biographer Berry recognized: "Cavendish was able to use the phlogistic hypothesis successfully for his own purposes, and that for him was sufficient. The progress of science has shown that its pathways are littered with discarded theories, which, nevertheless, rendered good service in bygone times."⁹⁹ Phlogiston provided chemistry with a theory, and without a theory Cavendish would not have done any work in chemistry. With the theory available to him he was able to make major contributions to the science. If there had been a better theory when he started out, he would have used it, and the results he obtained would have reflected it. We can say that his experiments on air were a late success of phlogiston chemistry, while acknowledging that the significance of his late experiments became evident with Lavoisier's anti-phlogistic chemistry.

Lavoisier and his colleagues brought together British pneumatic chemistry with Continental analytical chemistry in a "new synthesis of chemical theory." Cavendish helped prepare the groundwork for the new theory of chemistry, but he had no part in formulating it. After his experiments on air in the early 1780s, he published no more new experiments in chemistry, and he said nothing more in print about the changes that chemistry was undergoing. It has been said that chemistry after Lavoisier emerged as "a self-contained discipline, with its own theoretical problems, its own methods of thought and inner logic."¹⁰⁰ If that description fits, it remains that Lavoisier's synthesis did not resolve all the important questions of chemistry or deny that it raised new ones.¹⁰¹ Cavendish disagreed with at least two

⁹⁷Cavendish, "Arsenic," Cavendish Mss II, 1(b), 14.

⁹⁸Wilson (1851, 36–38).

⁹⁹Berry (1960, 183).

¹⁰⁰Henry Guerlac (1959, 109, 112).

¹⁰¹Following the publication of Lavoisier's *Treatise*, writings of chemists revealed "widespread confusion and uncertainty" over the nature of elementary substances and the naming of compounds, as if they "knew they couldn't go back to the old way of thinking, but were quite unsure of which way was forward." Robert Siegfried and Betty Jo Dobbs (1968, 275–276).

parts of it, the theory of acids and the caloric theory of heat, and he would be proved right about both.

The Jacksonian professor at Cambridge, Isaac Milner, saw the handwriting on the wall; in his final lecture in 1788, he discussed Lavoisier's experiments, commenting that the "ancient hypothesis of Phlogiston seems overturned at one Stroke, and a new and simple theory substituted in its place—a Theory founded on direct and satisfactory Experiments."¹⁰² In 1792, the Scottish physician and chemist George Fordyce wrote in a paper on the gain in weight of metals when they are calcined that "many chemists are at present satisfied of the nonentity of what was formerly supposed to be a body, called phlogiston." He justified going over the subject again on the grounds that phlogiston "has interwoven itself so much into chemistry in general, and has been so universally received."¹⁰³ Fifteen years later, in his Bakerian Lecture in the Royal Society, Davy said that the "discovery of the agencies of the gases destroyed the hypothesis of Stahl."¹⁰⁴ The rejection of phlogiston was not the whole of the Chemical Revolution, but it played a significant part. Cavendish, it seems, went that far but possibly no farther, showing no inclination to join the vanguard of the new chemistry. He was fifty-four years old in 1785, possibly a relevant fact.

Water Controversy

In a paper in early 1784, as we have seen, Cavendish identified the product of the explosion of two airs with water. He, Watt, and Lavoisier, the principals in the "water controversy," had different explanations. If it had been about these differences, it would have been a controversy of a familiar kind in science, but this one was also about character.

Basically a priority dispute, the water controversy arose from the following events, which are partly familiar to us. In the spring of 1781, Priestley and Warltire made experiments on the electrical detonation of inflammable air with common and dephlogisticated airs, noting a deposit of dew. That summer Cavendish repeated the experiments, determining that the dew was pure water.¹⁰⁵ He mentioned the experiments to Priestley, who repeated them and drew up a paper for the Royal Society. Learning of Priestley's experiments, Watt wrote to Priestley with his explanation of them: when inflammable and dephlogisticated airs are detonated, the two airs unite and then disappear, and the weight of the water that takes their place is equal to the weight of the airs. He concluded that "water is composed of dephlogisticated air and phlogiston, deprived of part of their latent or elementary heat."¹⁰⁶ In the summer of 1783, Blagden made a trip to Paris, where he told Lavoisier about Cavendish's experiments and Watt's explanation. Lavoisier and Laplace repeated Cavendish's experiments, and Lavoisier made further experiments dissociating water into its component airs. In a report on his experiments, he concluded that "water is not a simple substance but is composed, weight for weight, of inflammable and vital air."¹⁰⁷ Deluc went to Paris at the end of 1783, returning to England early the next year. In the meantime, Cavendish's paper

¹⁰²L.J.M. Coleby (1954, 256).

¹⁰³George Fordyce (1792, 374).

¹⁰⁴Humphry Davy (1808, 33).

¹⁰⁵Wilson (1851, 282).

¹⁰⁶*Ibid.*, 285, 290–293.

¹⁰⁷*Ibid.*, 337, 344–345.

was read to the Royal Society. Blagden gave an imperfect account of the paper to Deluc, who asked to see it, and Cavendish gave him permission.

The water controversy begins here. After reading Cavendish's paper, Deluc wrote to Watt that Cavendish "expounds and proves your system, word for word, and makes no mention whatever of you." He wrote a second letter a few days later cautioning that "it is yet possible Mr. Cavendish does not think he is pillaging you, however probable it is that he does so." Deluc told Watt that Cavendish must have read the letter he wrote to Priestley, which circulated among fellows of the Royal Society, before drawing up his own paper. Cavendish was a plagiarist.¹⁰⁸ Watt accepted Deluc's suspicions about Cavendish. By not revealing all of what Blagden had told him about Cavendish's and Watt's work, Lavoisier also laid himself open to the charge of plagiarism. Distressed by Lavoisier's representation of Cavendish's work, Blagden took a variety of measures, public and private, to set matters right. Lavoisier readily acknowledged that Blagden had told him about Cavendish's experiments before he carried out his own.¹⁰⁹ He stood corrected; he did not covet a discovery so much as all of chemistry, and the experiments on water had told him how to get it.

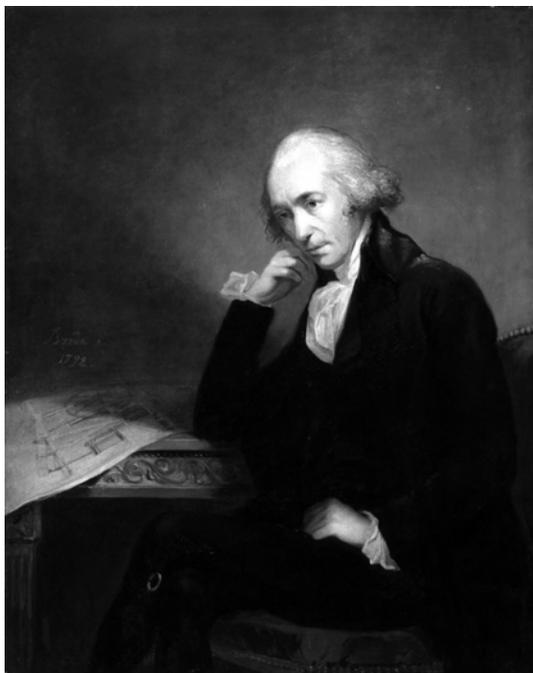


Figure 14.11: James Watt. Painting by Carl Frederik von Breda. Engineer and inventor, best known for his improvement of the Newcomen steam engine. Wikimedia Commons.

The passion behind the water controversy was decidedly Watt's. He told Deluc that he did not depend on the favor of "Mr. C: or his friends; and could despise the united power

¹⁰⁸Jean André Deluc to James Watt, 1 Mar. 1784, Watt (1846, 48–49). Wilson (1851, 407–408).

¹⁰⁹Wilson (1851, 362).

of the *illustrious house of Cavendish*, as Mr. Fox calls them.”¹¹⁰ Cavendish was a rich man with a mean spirit, Watt wrote to another correspondent.¹¹¹ When Watt saw Cavendish’s paper he recognized that it was different than his, and next year, 1785, Watt and Cavendish met in Birmingham, where they discussed steam engines, a subject on which Watt was the authority. That year Cavendish recommended Watt for fellowship in the Royal Society, his name appearing third after Smeaton’s and Priestley’s in the long list of Watt’s supporters.¹¹² The same year, Watt came to London, where he “was received very kindly by Mr. Cavendish and Dr. Blagden.”¹¹³ (Fig. 14.11). Clearly there were no lasting hard feelings.

Much of the controversy revolved around datings of experiments, publications, and meetings. The datings were genuinely tangled, as this brief review will indicate. Soon after Warltire’s experiments on the ponderability of heat were published in 1781, Cavendish began his experiments on the production of water from the explosion of airs. Before 26 March 1783 his experiments were communicated to Priestley; before 26 April 1783 Priestley’s repetition of Cavendish’s experiments was communicated to Watt, who promptly sent Priestley an explanation of them; and before 24 June 1783 Cavendish’s experiments were communicated to Lavoisier by Blagden. Cavendish’s own account of his experiments was only read to the Royal Society on 15 January 1784. A further complication came from the Royal Society’s practice of permitting authors to make changes in their papers between the time they were read and their publication. Cavendish’s paper contained three insertions, made at different times, in one of which he said that his experiments on the explosion of inflammable air with ordinary or dephlogisticated air were made in the summer of 1781. The year 1781 was an important date because the Royal Society did not learn of the experiments until 1784. Watt and Lavoisier did their researches later than Cavendish, but since they made their views known earlier, they appeared, Wilson said, “with a *primâ facie* character of priority to him [Cavendish], as claimants of the disputed discovery.”¹¹⁴

The controversy was started by Deluc. Wilson thought that Deluc was an honorable man “whose motives are beyond suspicion,” but who was guilty of the “grave charge” of accusing Cavendish of stealing Watt’s theory without informing himself thoroughly. The charge was baseless, as Deluc could readily have determined.¹¹⁵ Deluc and Cavendish had a long association. When for financial reasons, Deluc left his native Switzerland to settle in England, Cavendish brought him as his guest to a meeting of the Royal Society a month before his election.¹¹⁶ He and Deluc served together in the Society, performed experiments together, corresponded, and disagreed civilly. Drawing on a common fund of knowledge about human behavior, we can imagine that the reason for Deluc’s intervention was more complex than carelessness alone, but lacking evidence as to its nature, we accept Wilson’s appraisal.

Like Deluc, Blagden had a role in the water controversy not as a claimant to the discovery but as an intermediary between persons who were. As Deluc’s complicity was built into his relationship with Watt, Blagden’s was with Cavendish. Blagden’s association with Cavendish was his scientific passport, while at the same time his zealous regard for the rep-

¹¹⁰James Watt to Jean André Deluc, 6 Mar. 1784, Watt (1846, 48–49)

¹¹¹James Watt to Mr. Frey of Bristol, 15 May 1784, *ibid.*, 61.

¹¹²24 Nov. 1785, Certificates, Royal Society 5.

¹¹³Watt, quoted in Samuel Smiles (1874, 169).

¹¹⁴Wilson (1851, 60–61).

¹¹⁵*Ibid.*, 408.

¹¹⁶13 May 1773, JB, Royal Society 28:132.

utation of Cavendish was a vulnerability, which was compounded by his duty as secretary of the Royal Society of editing papers for publication in the *Philosophical Transactions*. Latter-day champions of Watt made out Blagden to be a villain, but he was guilty not of the unfairness and venality with which he was charged but only of neglecting his own best interest. Nor was Cavendish guilty of exploiting Blagden's dependent position to get him to commit fraud on his behalf.

With the remote exception of Deluc, there was no malice on the part of anyone. When the steps leading to the dispute are examined one by one, as Wilson and others have done, this conclusion seems inescapable: a major reason for the "controversy," as distinguished from a common scientific disagreement, was the casual way scientific information was communicated in the eighteenth century. The discovery of the nature of water was timely, and the stakes were high, so that otherwise tolerable exchanges by letters, conversations, and visits, with their indifferent datings, could, with proper incitement, seem darkly suspicious. As it turned out, precisely because there was also disagreement of the usual kind, different interpretations of the same experiments, there was recognition to go around. Cavendish was the first consciously to produce water by detonating airs; Lavoisier was the first to analyze water into its component airs; and Watt and Lavoisier were first to state unequivocally the compound nature of water.

A second water controversy arose long after the participants in the first were dead, prompted by the secretary of the French Academy D.F.J. Arago, who in his *éloge* of Watt asserted that Priestley was the first person to prove that airs could be converted into water and that Watt was the first person to understand it.¹¹⁷ The consequent furor was initiated by Vernon Harcourt in his presidential address at the British Association for the Advancement of Science meeting in 1839. Because the revived controversy was the occasion for Cavendish's unpublished scientific work to begin to be made public and for a biography of Cavendish to be written while persons who knew him were still alive, it had that value if perhaps no other.

In his biography of Cavendish in 1851, after meticulously examining all the documents relevant to the water controversy Wilson reached the conviction he began with, that Cavendish was the discoverer of the compound nature of water and that his character was blameless. He returned to the subject in 1859, after two new documents had come to light, strengthening his argument. One of them was a publication on meteorology by Deluc, who related a conversation with Priestley in 1782, which Wilson said removed "all trace of charge against the fair-dealing of Cavendish." The other document was by Laplace, who said that Cavendish was the first to point out that water is produced by the combination of hydrogen and oxygen and that the weight of the water is equal in weight of the gases. Wilson published this further vindication of Cavendish in the *Proceedings of the Royal Society of Edinburgh*.¹¹⁸

Keeping up with Chemistry

As a result of the water controversy, Cavendish and the German journal *Chemische Annalen* had started off on the wrong foot. The editor Lorenz Crell published two accounts of the discovery of the production of water in which Lavoisier was named the discoverer and Cavendish the confirmer. For more information about Cavendish's work, Crell wrote

¹¹⁷As Harcourt summarized Arago's claim, in his Presidential Address, British Association Report (1839), 15.

¹¹⁸Berry (1960, 87–88).

to Banks, who passed the letter to Blagden. The latter replied to Crell with a “short history of the discovery,” correcting the claims of Lavoisier, who had “suppressed part of the truth.” Blagden complimented Crell on the quick publication of translated extracts from Cavendish’s paper containing the true discovery and for Crell’s correct dating of the paper, 1784, instead of 1783, as the separately printed cover of the paper had erroneously put it. In a note printed with the extracts, Crell graciously acknowledged that he was under an obligation to Cavendish because he, like others, had made an “error” in ascribing the discovery to Lavoisier, whereas the “*first Discovery*” belonged to Cavendish. This initial letter from Blagden to Crell included the latest scientific news from Britain, meant to entice Crell to join in a regular scientific exchange between the two countries.¹¹⁹

Crell wanted to publish Blagden’s short history of Cavendish’s discovery, and although Blagden had not intended it for the public, he had no objection, since it was “strictly true.” He only hoped that Crell’s German translation would rather “soften than strengthen the expressions,” since however poorly Lavoisier had behaved in this affair, he was “upon the whole a very respectable character & eminent as a philosopher.” In keeping with his invitation to Crell, Blagden enclosed scientific news having to do with “Mr. Cavendish, whose name I shall so often have occasion to mention in this correspondence.” This time it was about Cavendish’s new work on the freezing of mercury rather than the history of his old work.¹²⁰

The German chemist knew that Cavendish was an aristocrat but little about English titles. “The Honourable Henry Cavendish (not My Lord),” Blagden corrected him, “desires to become one of your subscribers.” To this end, Cavendish had given directions to the post office to ensure that he received the journal promptly.¹²¹ Six months later, Blagden wrote to Crell that the postmaster at Amsterdam had told him that some of Crell’s packets were held up because of their large size and were probably irrecoverable, a problem which could have been anticipated, since Banks had gone through it with Crell the year before.¹²² Crell had sent the material not by post but by stagecoach or wagon, Blagden said, conveyances which were not “connected with but in opposition to the Post.” When Cavendish succeeded in receiving a few issues of the *Chemische Annalen* and its supplement, the *Beiträge*, by post, Blagden instructed Crell to send Cavendish the rest by post as well. However, when after three months the remaining issues had not yet arrived in London, Blagden complained to the post office and then to Crell: “Mr. Cavendish pays many times the original value of the work to have it in this manner quick by the post; but the various delays have entirely frustrated that object.”¹²³ The post office proved not to be a better way. Two years later the business of delivery was at last settled and the correspondence on that subject ended: “Mr. Cavendish

¹¹⁹ Among Cavendish’s manuscripts is a translation into English, not in Cavendish’s hand, of Crell’s translation into German of extracts from Cavendish’s paper of 1784, with Crell’s retraction of his earlier error. “Translation from Mr. L. Crell’s Chemical Annals, 1785. part 4, 324.” Charles Blagden to Lorenz Crell, 28 Apr. 1785, draft, Blagden Letterbook, Yale. Blagden’s letter, in English, clarifying the discovery to Crell was translated into German by Crell and translated back into English by Wilson (1851, 362–363). Wilson’s translation is reproduced in Berry (1960, 81–82).

¹²⁰ Charles Blagden to Lorenz Crell, 2 Dec. 1785, draft, Blagden Letters, Royal Society 7:738.

¹²¹ Charles Blagden to Lorenz Crell, 20 Jan. 1786, draft, *ibid.* 7:742.

¹²² Lorenz Crell to Joseph Banks, [1785], 17 Dec. 1785, 1 May 1786, 4 Mar. 1790, BL Add Mss 8096:69–70, 239–240, 284–285, and 8097:296–297.

¹²³ Charles Blagden to Lorenz Crell, 4 July, 12 Aug., and 13 Oct. 1786, drafts; Charles Blagden to Charles Jackson at the post office, 10 Oct. 1786, draft, Blagden Letters, Royal Society 7:26, 44–45. By 4 July Cavendish had received the first and second issues of the *Annalen* and the fourth issue of volume 1 of the *Beiträge*. On 6 August, he was

finds it more convenient to get the *Ch Annalen*,” Blagden wrote to Crell, “in the common way, tho’ a little later, then to be perplexed with the post office; he [...] will not give you any further trouble on the subject.”¹²⁴

There were other complications, for example, the manner of payment for the subscription, of how much and to whom; Blagden told Crell to appoint some person to collect Cavendish’s money. Kirwan and Banks wanted to subscribe, and the journal could not be sent to everyone “through the same channel under one cover.” In addition to the journal, there were other publications by Crell that Cavendish wanted. He had ordered Crell’s *Auswahl aus den neuen Entdeckungen*, but his German bookseller had disappointed him. Crell offered to copy out the material Cavendish wanted, but Cavendish wanted the entire volumes.¹²⁵

To convey scientific publications from Britain to Germany was not simpler. Blagden sent a copy of Cavendish’s latest paper to Crell in a packet, which he gave to William Herschel, who was going to Göttingen to erect one of his telescopes. From Göttingen, Herschel forwarded the packet by the nearest conveyance to Helmstadt, where Crell picked it up. Blagden apologized to Crell: “It is extremely difficult to get an opportunity of sending you any thing from England, otherwise you should be furnished sooner with such publication.”¹²⁶ The business of Cavendish and Crell was not unrelieved frustration. Cavendish thanked Crell for offering “the Old Hock,” and Blagden assured Crell that “we shall endeavour to form such a party of gentleman as would be required.”¹²⁷

Cavendish took evident interest in Crell’s *Chemische Annalen*, a monthly journal that in 1784 replaced the quarterly one he had been editing. It had the support of German chemists and favored, as he still did, the phlogistic approach to chemistry. As Cavendish’s negotiations with Crell bear out, it was no simple matter to obtain foreign journals in England in the eighteenth century. In this episode we see the trouble Cavendish went to to keep abreast of chemical research and to keep his library current. We also see the value to him of having an associate, Blagden.

Theory

In his work in the basic fields of electricity, heat, and chemistry, Cavendish developed general theories for two of them, electricity and heat. His publications and manuscripts do not contain a comparable theory of chemistry. This could mean that he was content with the given theory or that chemistry was a different kind of field and in a different state of development. In this section, we return to several subjects, phlogiston, forces, and affinities, and to several chemists we met earlier, whose connections to chemical theory come up in the following brief account.

Chemists mostly agreed that the object of chemistry was to separate compounds into their parts, to study the parts, and to reunite them to form the original compounds or to produce new compounds. That describes what chemists did in the laboratory, but it fails to mention the help they had from outside, which included theory. In his *Dictionary of*

still waiting for the third through the sixth issues of the *Annalen* and the first through the third issues of volume 1 of the *Beiträge*.

¹²⁴Charles Blagden to Lorenz Crell, 4 Apr. 1788, draft, Blagden Letters, Royal Society 7:137.

¹²⁵Blagden to Crell, 4 July and 12 Aug. 1786.

¹²⁶Blagden to Crell 4 July 1786.

¹²⁷Charles Blagden to Lorenz Crell, [1786], draft, Blagden Letterbook, Yale.

Chemistry, Macquer said that theory and experiments necessarily went hand-in-hand: “If experiments, undirected by theory, are only a blind feeling; theory without experiments is a deceitful and uncertain vision,” since advances in chemistry owed to the “joint assistance of both.”¹²⁸

It was common for textbooks on chemistry to present the “theory” of chemistry followed by the “practice” of chemistry, as is seen by their titles: Stahl’s *Fundamenta Chymiae dogmaticae et experimentalis*, Boerhaave’s *New Method of Chemistry: Theory and Practice of That Art* and Macquer’s *Elements of the Theory and Practice of Chemistry* are examples. The “practice” part of Macquer’s text, which was a separate volume in the original French, gives operations performed on mineral, vegetable, and animal substances, a common classification of the time. The “theory” part is organized by types of substances—for example, saline substances, metallic substances, and acids—followed by types of fermentation and chemical decomposition. Macquer based his discussion of these substances on “affinity” and on four primary “principles”—the ancient elements of air, water, earth, and fire—and “secondary principles,” which are combinations of them.¹²⁹ Because Cavendish did not write a treatise on chemistry, he had no occasion to organize the science as a whole, and so we do not know what he thought about elementary substances or what his general “theory” of chemistry in this sense would look like.

We know a good deal, however, about Cavendish’s thoughts on “specific theories”¹³⁰ of chemistry, which showed how chemical phenomena of certain kinds were related to one another. Examples of specific theories are the “theory of neutral salts,” which Lavoisier considered the “most certain and complete part of chemistry”; Lavoisier’s “theory” of acids, which was that acids are composed mainly of pure air, or oxygen; and Black’s “theory” of fixed air in earths that are reducible to quicklime by calcination. For Cavendish, the most important specific theory was the theory of phlogiston, which originated in a general theory of chemistry.

We briefly recall the original theory. According to the chemist and historian of chemistry Thomas Thomson, the first chemist to establish a general “theory” of chemistry “by which all the known facts were connected together and deduced from one general principle,” was Becher, whose theory contained an interesting fatty earth responsible for combustible properties of bodies. Stahl adopted and modified Becher’s theory in 1718, renaming his fatty earth “phlogiston”; his major improvement in the theory was to show how phlogiston explains both combustion and calcination. So convincing was Stahl’s theory, according to Thomson, that it was “adopted by every chemist without exception.” Of Stahl’s theory, Macquer said that it was “of all theories the most enlightening, and the most conformable with the phenomena of chemistry, “making it the “surest guide that we can take for our conduct in chemical researches,” as proven by experiments made daily. Having Stahl’s theory of phlogiston to direct their work, and knowledgeable in the art of experiment, Macquer said, chemists had the “advantage of seeing the best days of chemistry.”¹³¹ Because nearly all chemical processes were explained by phlogiston or its absence, Stahl’s theory of chemistry came to be regarded as a theory of phlogiston and combustion. Over the next six decades

¹²⁸Macquer (1771, 1:xi–xii).

¹²⁹Macquer (1758, 1:15–18).

¹³⁰Term used by Mi Gyung Kim (2003, 5).

¹³¹Macquer (1771, 1:xi–xii).

chemists worked with, extended, and altered his theory. They raised questions about phlogiston, but generally they thought that its existence was proven by experiments.

In Berlin Stahl created a school of phlogistic chemists, who included Caspar Neumann, professor of chemistry at the Royal College of Physic and Surgery.¹³² Well known to the Royal Society as a foreign member and contributor to the *Philosophical Transactions*, Neumann's lectures were published after his death in an abridged edition in English translation in 1759. Without elaboration, Neumann introduced "phlogiston," the "inflammable principle," which was the same in metals and throughout the mineral, vegetable, and animal kingdoms.¹³³ In this edition of his lectures, his treatment of chemistry was practical, giving straightforward descriptions of operations and reactions, and having little to say about the theory of chemistry. His lectures were considered an excellent introduction to chemistry, which were still of value at the time of Thomson's history of chemistry in 1830.

As mentioned earlier, unless they read foreign works, English chemists learned about phlogiston through Neumann's lectures and a successful textbook on chemistry by Macquer, *Elements of the Theory and Practice of Chemistry*. Macquer's version of phlogiston differed considerably from Stahl's. One of the traditional four elements or principles—fire, air, water, and earth—Macquer's fire existed in two states, one fluid and one fixed, a combination of elementary fire with another substance constituting a "secondary principle," or "phlogiston."¹³⁴ Macquer's text appeared in English translation in 1758, one year before Neumann's, and six years before the earliest dated chemical researches of Cavendish's, which originated with Macquer.

Cavendish's chemical researches made extensive use of phlogiston; more than that, they were *directed* to phlogiston and its activity, the core of the current theory of chemistry descended from Becher and Stahl. The most important result of his publication on factitious air was his determination of the properties of inflammable air, which he identified with phlogiston. When he returned to experiments on air, it was to determine what happens to air in all the ways it can be phlogisticated. Phlogiston was the cornerstone of his researches in chemistry, both in their planning and in their interpretation. To hold a specific theory of phlogiston, Cavendish did not have to accept other parts of Stahl's theory.

There is the beginning of a specific theory in Cavendish's paper "On the Solution of Metals in Acids," which he intended for his paper on arsenic and then rewrote for his first published paper, on factitious air. Bringing together two of the main chemical concepts, affinities (discussed below) and phlogiston, he described and explained the action of acids on perfect and imperfect metals. It was accepted by chemists that when imperfect metals dissolve in acids they lose their phlogiston, but it had "usually been thought" that acids do not deprive perfect metals (gold and silver) and mercury of their phlogiston. Cavendish disagreed, giving an argument from the relative strengths of affinities to show why: these metals actually have so great an affinity to phlogiston that they reacquire it from the substance that is added to separate them from the acid ("there seems no reason to think that the pure fixed alkali, or even lime, is quite free from phlogiston"). By a more intricate argument, he explained why gold requires two acids, nitrous (nitric) and marine (hydrochloric), to dissolve it. He called his explanation of the solution of perfect metals and mercury in

¹³²Thomson (1830–1831, 2:250–263).

¹³³Casper Neumann (1759, 53, 165).

¹³⁴Macquer (1758, 1:9–10).

acids a “hypothesis,” which had not yet been proven “true.”¹³⁵ When he made a theory, he usually began with a hypothesis and then confirmed it; in the case of metals and acids he lacked the confirmation that would turn his hypothesis into a theory.

We turn to another line of chemical theory, introduced earlier in this book. Newton was a main authority for the physical approach in chemistry. He published only one paper on chemistry, but in his *Opticks* he made a good many statements about it, with consequences for chemistry into Cavendish’s time. The last Query in the late editions of the book begins: “Have not the small Particles of Bodies certain Powers, Virtues, or Forces, by which they act at a distance, not only upon the Rays of Light ... but also upon one another for producing a great Part of the Phaenomena of Nature?”¹³⁶ Newton speculated that such forces, which extend only over extremely short distances between particles, are capable of explaining chemical reactions and many physical processes. His first example was salt of tartar running per deliquium, which he explained by the attraction of the particles of the salt to the particles of water. By similar reasoning, he explained why metals replace one another in acid solutions, naming the order of replacement of six metals in nitric acid. The examples of the last Query are concerned with the heat of chemical activity as much as with the chemical attraction. When aqua fortis (nitric acid) is poured on iron filings, “great Heat and Ebullition” are produced by a “violent Motion of the Parts,” caused by the attraction between particles. The violence of the internal commotions of chemical bodies contrasts with the stately motions of the planets, yet both are compatible with the “Tenor and Course of Nature.” Attractions move the planets and they move the particles of bodies in chemical interaction, for nature “is very consonant and conformable to her self.”¹³⁷

Newton and his followers considered forces that obey different laws than the inverse square. In 1708 John Keill, one of the first to teach the Newtonian philosophy, published a theory of forces, which included a force that falls off faster with distance than gravitation, confining its action to minute distances. Reasoning from principles that belong to the “foundation of all physics,” Keill laid down theorems about attraction and about particles of different figures, demonstrating how chemical and physical actions can be seen to arise from the intimate force.¹³⁸ The next year the professor of chemistry at Oxford John Freind said that chemistry had made progress in experiment but not in theory until Keill showed the true principles of chemistry, which were mechanical, “taken from the very Nature of Things.” Freind applied Newton’s laws of nature, as modified by Keill, to the main operations of chemistry. Like Keill, he did not state a mathematical law for the new force, postulating only that it falls off faster than the force of gravity, and in references to it he relied on common sense to make his points.¹³⁹ Keill’s and Freind’s work can be called “theoretical chemistry,”¹⁴⁰ which relates chemical practice to concepts and laws that order the universe. Their theorems were remote from the activity of the laboratory, but they were not forgotten.

The most important early developer of Newtonian chemistry was Stephen Hales, whose experiments on air were published in his *Vegetable Staticks* in 1727, discussed earlier. Hales

¹³⁵Henry Cavendish (1921e, 2:305–307).

¹³⁶Isaac Newton (1952, 375–376).

¹³⁷*Ibid.*, 376–77, 380–81.

¹³⁸John Keill (1708).

¹³⁹John Freind (1712). Translated from *Praelectiones Chymicae* (London, 1709).

¹⁴⁰Kim’s term, which applies here (2003, 4).

said that his experiments on air proved that there are particles “capable of being thrown off from a dense body by heat or fermentation into a vigorously elastick and permanently repelling state,” and that by actions of the same kind the particles can be reunited in a dense body. Freind had given an “ingenious Rationale” for calcination, distillation, and other chemical processes, Hales said, and he applied the same principles to the study of air, which he regarded as responsible for “the main and principal operations of Nature.”¹⁴¹ Cavendish was well acquainted with Hales’s *Vegetable Staticks*.

In 1727, the same year as Hales’s book, there appeared an English translation of Herman Boerhaave’s *New Method of Chemistry*, which influenced British chemists, especially the Scottish. Boerhaave laid down as “laws, or axioms of the art,” the general truths that chemists had arrived at by experiment, which constituted the “theory” of chemistry. He contrasted his presentation of chemistry with those by other authors, which were “without any certain design or coherence.” Another representative of the physical approach in chemistry, Boerhaave wrote that “every *change* which chemistry produces in bodies, is the effect of *motion*,” and chemists “who deny the changes produced by chemical operations to be *mechanical*” are misled. Instead of “force” and “attraction,” he spoke of “uniting” and “separating,” words which described what chemists actually observed. In their annotations, his translators Peter Shaw and Ephraim Chambers discussed the forces producing the motions, following Newton who had established that “there are such motions in the *minima naturae*, and that they flow from certain powers, or forces not reducible to any of those in the great world.” They referred to Keill and Freind who explained all chemical phenomena by a novel attraction, “but this seems a little too precipitate,” for the laws of the intimate motions of the world were not yet known,¹⁴² a hard fact that successive chemists would rediscover.

The law of universal gravitation together with the definition of quantity of matter—all matter has weight, which is proportional to its quantity and remains constant¹⁴³—entered the thought and practice of chemistry. The instrument that measured the quantity of matter by its weight, the chemical balance, received a theoretical foundation in the new natural philosophy, and the corpuscular philosophy of chemistry was adapted to the new understanding of forces. By analogy, the law of gravitation, which was deduced from motions of the large bodies of the universe, was applied to the smallest parts of the bodies, or corpuscles, an implication of its universality. This comparison appealed to the scientific intuition, an affirmation of the unity and simplicity of nature, and it supported a physical approach to chemistry. A principal advocate of this design for chemistry was the French naturalist Georges-Louis Leclerc, Comte de Buffon. His answer to chemists who like Keill and Friend thought that chemical forces obey different laws was that the action of gravitation is modified by the figure of the particles of chemical substances. Newton strangely had overlooked the full implications of gravitation in the “plan of the world” by failing to recognize the effect of the figure of particles in his speculations on chemical forces in his *Opticks*. Eminent chemists such as Guyton de Morveau, Baumé, and Bergman agreed with Buffon

¹⁴¹ Stephen Hales (1727). Thomson (1830–1831, 2:303).

¹⁴² Herman Boerhaave (1727, 1:170–174). This book was based on student lecture notes, 1724. In 1732 Boerhaave published a treatise, *Elements of Chemistry*, which was translated by Peter Shaw in 1741. J.R. Partington says that in this book Boerhaave maintains that acid dissolves substances by motion, and that although he quotes Newton and uses mechanical analogies, the motion has a cause that is not mechanical. “Chemistry through the Eighteenth Century,” in *Natural Philosophy*, supplement to *Philosophical Magazine*, 1948, 47–66, on 48. The popularity of *Elements of Chemistry* warranted another English edition, 1753.

¹⁴³ Newton, *Principia* 1:1.

about the central role of gravity in chemistry.¹⁴⁴ Macquer in the article “Gravity” in his *Dictionary of Chemistry* wrote that the law of gravitation, which has been found to differ from the inverse square law for very small distances, is at the same time the force of falling bodies and the force between particles, producing chemical “combinations and decompositions,” and that for this reason gravitation is “undoubtedly the most important and decisive object for the general theory of chemistry.” Macquer thought that this speculation is the “true key of the most hidden phenomena of chemistry, and consequently of all natural philosophy.” Chemical attractions are not to be thought of as real, for there is only one true law giving rise to a great variety of effects, the law of universal gravitation, which chemists should keep in mind, though chemical theory and practice could not be built on it at the time.¹⁴⁵ One day someone sufficiently versed in both mathematics and chemistry may “lay the foundation for a new physico-mathematical science” of chemistry, though it is also possible that chemistry is too complicated, “beyond the reach of human understanding.”¹⁴⁶

Cavendish was a chemist such as Macquer described, one of the very few who were skilled in both mathematics and chemistry. Although he did not transform chemistry into a “physico-mathematical science,” he accepted that chemical behavior arises from the forces of particles, as understood by mechanics. His ideas on the forces of particles were first put forward by Newton and later by the Croatian Jesuit Roger Joseph Boscovich in a treatise published in 1758, and in English translation in 1763. In this work, Boscovich developed a theory of natural philosophy based upon a law of force more complicated than the inverse-square law at close distances, which could explain in principle all physical and chemical phenomena. Any explanation had to be qualitative though, since there was no mathematical law describing attractions and repulsions at close distances to particles. Chemists who thought in terms of forces knew that they could not deduce chemical reactions from them in the present state of the science. To get on with their work, they did not need to concern themselves with laws of forces or configurations of particles, and it seems that the most productive chemists did not.¹⁴⁷ Cavendish’s papers contain no attempt to calculate chemical processes from forces.

Newton’s discussions of chemical actions and heat as a combined subject were continued by Cullen and Black and further developed by Cavendish, who believed that all bodies that have an affinity for one another generate heat when they are combined. The connection he saw between chemistry and heat is seen in their juxtaposition in a number of his writings. The manuscript of his researches on air contains experiments on chemical combinations of airs and also on physical experiments on the expansion of airs with heat. The manuscript of his paper on specific and latent heats contains experiments on the heats of changes of state and also on the heats of chemical reactions.¹⁴⁸ A separate paper presenting the law of latent heats as a “hypothesis” states that the main cases of a change from an inelastic to an elastic state were “the evaporation of liquors & the separation of fixed air from alkaline substances.”¹⁴⁹ Likewise his manuscript on the theory of heat contains a section “On the Heat & Cold Produced by Chymical Mixtures & by a Change from a Solid to a Fluid Form.”

¹⁴⁴Buffon explained his ideas about gravitation in his *Histoire naturelle* in 1765. Hélène Metzger (1930, 57–60, 63). A.M. Duncan (1962, 228).

¹⁴⁵Metzger (1930, 61).

¹⁴⁶Macquer (1771, 1:324).

¹⁴⁷A.M. Duncan (1970, 31).

¹⁴⁸Henry Cavendish, (1921c, 347).

¹⁴⁹Henry Cavendish, “Hypothesis All Bodies in Changing from a Solid State . . .,” Cavendish Mss, Misc.

Parallel statements are made about chemical change and physical change of state: “It seems a natural consequence of this theory [of heat as the motion of particles] that the mixture of two substances which have a chemical affinity should commonly be attended by an alteration of sensible heat”; likewise “it seems a necessary consequence of the theory” that the change of state of a body, from a solid to a liquid or from either of those forms to an elastic fluid or air, should be accompanied by a change in the heat.¹⁵⁰ The phenomena of chemical reactions and those of changes of state are different, but from the point of view of particles and their forces there is no difference between chemistry and physics.

In importance, calorimetry, the quantitative study of heat, was a “close rival to the new pneumatic chemistry in the eyes of chemists and other men of science during the last quarter of the eighteenth century.”¹⁵¹ This statement applies to Cavendish’s researches. Through his theory of heat, he acquired a degree of understanding of chemical phenomena such as the release of air fixed in bodies. He faced the familiar difficulty in developing chemical theory starting from mechanics, the forces and arrangement of particles being unknown, but in his theory of heat the exact laws of the forces did not need to be known. His starting point in studying the behavior of particles of bodies was the law of conservation of energy including the energy equivalent of heat, which is compatible with an infinite range of central forces. With the help of the conservation law, and reasoning from particles interacting through unspecified attractions and repulsions, he could explain the chemical behavior of bodies. In addition to the phlogiston theory, which explained chemistry at the level of phenomena, Cavendish had an explanation at the level of invisible particles. Because it was based on the identification of heat with energy and on the law of conservation of energy, it would become a valuable theory for chemistry in the next century. Cavendish and Lavoisier, once past their differences on phlogiston and oxygen, were close in their recognition of the importance of heat in the advance of chemistry. Lavoisier explained different states of matter and chemical processes as the outcome of the attractive forces of particles and the repulsive force of the material of heat, “caloric,” and he looked to calorimetry to determine the strength of the attractions. He and his collaborators sought a “theoretical structure for chemistry” in which chemical constitution would be explained by the “interplay of heat and affinities.” They did not yet know how to realize their plan quantitatively and mathematically.¹⁵² Cavendish made a start.

The word “affinity” has come up several times. In place of “attraction,” some chemists preferred “affinity,” which implied nothing about laws of force. They recognized that substances have specific affinities for one another, forming unions, which are discovered in the laboratory. Historically, affinity was associated with the alchemists’ animistic sympathy or love, which was still a way of thinking in chemistry in the eighteenth century. Stahl thought that chemical combinations came about because of a similarity between the combining substances. In his *Elements*, Macquer agreed with Stahl, but later in his *Dictionary of Chemistry* he stated simply that affinity is a tendency to unite and adhere. In the second half of the eighteenth century, both “affinity” and “attraction” were understood to stand for the empirical fact of chemical combination. Bergman spoke of “attraction,” as did Hales, Cullen, and Black, while Boerhaave, Priestley, Kirwan, and Cavendish spoke of “affinity.”¹⁵³ By the

¹⁵⁰Henry Cavendish, “Heat,” in Russell McCormach (2004, 182–183).

¹⁵¹Robert Fox (1971, 22).

¹⁵²Kim (2003, 15, 387, 392–393).

¹⁵³A.M. Duncan (1962, 184–185; 1970, 33–34). Macquer (1771, 1:22–23).

use of the word “affinity,” they did not necessarily forfeit the analogy of nature, for attraction could be taken as implicit in chemical affinity.

Affinities drew the attention of chemists around the same time as phlogiston, in the middle of the century.¹⁵⁴ After the writings by Stahl and Boerhaave early in the century, there was a lull in theoretical interest, as chemists concentrated on building the factual basis of chemistry, but by the time of Macquer’s *Elements*, chemists were again seeking patterns in their work. Proved by “all the experiments hitherto made,” affinity “whatever be its cause, will enable us to account for, and connect together, all the phenomena that Chymistry produces,” Macquer wrote in his text.¹⁵⁵ After introducing the four elements and phlogiston, he laid down six “fundamental truths” about affinity, from which he set out to “deduce an explanation of all the phenomena of Chymistry.”¹⁵⁶ Twenty-five years later in his book on “elective affinities,” Bergman wrote that they were the “key to unlock the innermost sanctuaries of nature; the “whole of chemistry” rests on the doctrine of affinities, a “solid foundation at least if we wish to have the science in a rational form.”¹⁵⁷ Throughout his chemical work, Cavendish made use of affinities in his reasoning.

When Cavendish took up chemistry, affinities were arranged in empirical tables, many versions of which were proposed through the eighteenth century, the majority of them in the middle decades, the 1750s through the 1770s. They served chemists as a guide to chemical processes, an advance over Newton’s displacement series of metals and Stahl’s “order in which metals dissolved.”¹⁵⁸ The first table was published in 1718 by the French physician and chemist Etienne-François Geoffroy, who used a neutral term “rapport,” which dissociated his table from the two main ways of referring to chemical combination, affinity and attraction. His table consists of sixteen columns and nine rows, each column headed by a substance or a group of substances, written compactly using the old symbols rather than words for chemicals; beneath each head is a list of substances it combines with, ranked in order of strength of affinity, which is the order of displacement, the guiding observation of which was that one substance has more disposition than another to unite with a third. The construction of affinity tables was laborious. Bergman, who made the most important improvement in them, said that his sketch of a completed table in his book on affinities in 1775 would require over 30,000 experiments to perfect, and he hoped for a long life and assistance. He said that to determine the order of attractions in a table took “all the patience and diligence, and accuracy, and knowledge, and experience of the chemist,” who was required to analyze the smell, taste, form, solubility, tendency to effervescence, and other properties of his reacting substances.¹⁵⁹ With a few exceptions such as Cullen, Black, and Lewis, chemists who made or modified affinity tables were European not British.

It took some time for Geoffroy’s table to receive notice in Britain. Peter Shaw referred to it in his lectures from 1733 and in his translation of Boerhaave in 1741. In Scotland, William Cullen included it in his lectures from 1747. The table itself was published by the physician Robert Poole in 1748, by Macquer in 1749, and by William Lewis in 1753.¹⁶⁰ At the end of his publication on *magnesia alba* in 1756, Black published a revised version of

¹⁵⁴Kim (2003, 222). Duncan (1970, 190).

¹⁵⁵Macquer (1758, 1:12).

¹⁵⁶*Ibid.* 1:14. Kim (2003, 207).

¹⁵⁷Torbern Bergman (1785b, 9).

¹⁵⁸Metzger (1930, 50). Duncan (1970, 177).

¹⁵⁹Bergman (1785b, 65–70).

¹⁶⁰Georgette Nicola Lewis Taylor (2006, 61–63).

Geoffroy's table. John Hadley included it in his plan of chemical lectures at Cambridge in 1758. From English and French sources, probably from both, Cavendish became acquainted with affinity tables. On a page of his laboratory experiments on arsenic, he drew two groups of four symbols each, the two groups being identical except for one symbol, the one for arsenic replacing the one for regulus of antimony (pure antimony). (Fig. 14.12). The first group gives us a clue which table of affinities Cavendish used at that time. It was not Geoffroy's, which lacks an entry for arsenic, but probably the expanded, twenty-eight column table published in 1751 by Christlieb Ehregott Gellert in his textbook on metallurgical chemistry,¹⁶¹ (Fig. 14.13) which although it was directed to industry was of interest to chemists generally. It was talked about in the Royal Society, which apparently requested an English translation. Gellert used Stahl's phlogiston, and he drew on the work of chemists Cavendish was interested in, Marggraf among others. Macquer referred to Gellert frequently, and the translator of his *Dictionary* James Keir added both Geoffroy's and Gellert's tables. Gellert's table was referred to by Macquer's collaborator Baumé in his *Manuel de chimie* in 1763 and by other chemical authors.¹⁶²

Tables of affinity were overly simple, occasionally exceptionable, and because of the complexity of salts they were incomplete, among other shortcomings. Most chemical reactions involved more than two substances, and the effect of the circumstances of a chemical reaction, particularly the temperature, qualified the usefulness of the tables, though later ones corrected for some of the deficiencies. Imperfect as they were, tables nevertheless were highly useful. They showed the building blocks of chemical compounds and the known compounds corresponding to a given substance, bringing order to the bewildering variety of chemical operations, analogous to the later periodic table, and like the periodic table they were predictive.¹⁶³ They had the additional virtue of not being linked to a particular theory of chemistry, instead providing common ground for chemists holding different views. Chemists sometimes associated affinities with Newtonian natural philosophy, but this was not fundamental, as is shown by other chemists who used affinities to make chemistry an autonomous science independent of natural philosophy. Chemists were more likely to speak of the "doctrine" of affinity than of the "theory," though the ultimate goal of affinity tables was theory, and the tables received criticism for lacking a theoretical base. A historian of chemistry writes of affinities as a "theory domain," which by the 1770s, around the time Cavendish first published on chemistry, was the "frontier of theoretical chemistry."¹⁶⁴ Affinity tables did not represent nature in the way that theories of natural philosophy did, identifying the causes behind the phenomena, but they ordered and foretold the phenomena that chemists regularly dealt with in their daily work, accomplishing what theories do, qualifying perhaps as a theory of a different kind or a proto-theory.

¹⁶¹Christlieb Ehregott Gellert (1751).

¹⁶²Gellert's book was translated by John Seiferth in 1766 as *Metallurgic Chymistry*, though it was not published until ten years later. Fathi Habashi (1999, 34–35). Duncan (1962, I:187–189; II:220–221). Antoine Baumé (1763, 7).

¹⁶³Ursula Klein and Wolfgang Lefèvre (2007, 152).

¹⁶⁴Duncan (1962, I:181; 1970, 34). Taylor writes that though affinity was not tied to a certain theory, affinity tables were "guided and determined by theoretical assumptions," and that different chemists had different theories of affinity (2006, 8, 16, 21, 28). Kim (2003, 222).

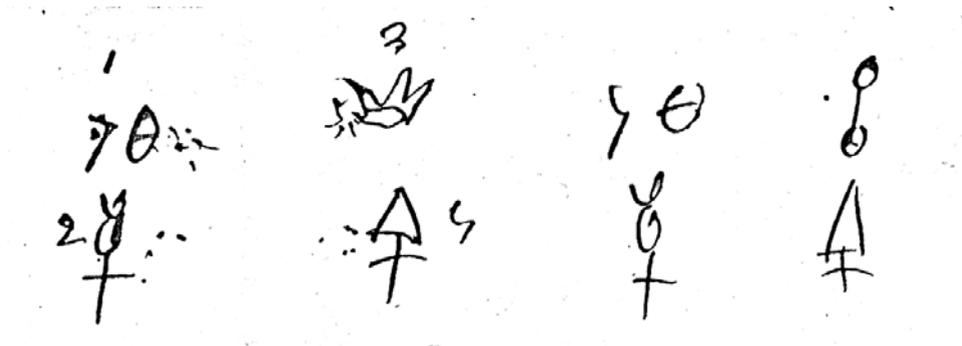


Figure 14.12: Affinities. Normally Cavendish spelled out the names of chemical substances, with the exception of mercury, for which he used the standard symbol. His unusual use of symbols to describe chemical reactions reproduced here is from his experiments on arsenic, Cavendish Mss II, 1(a), 3.

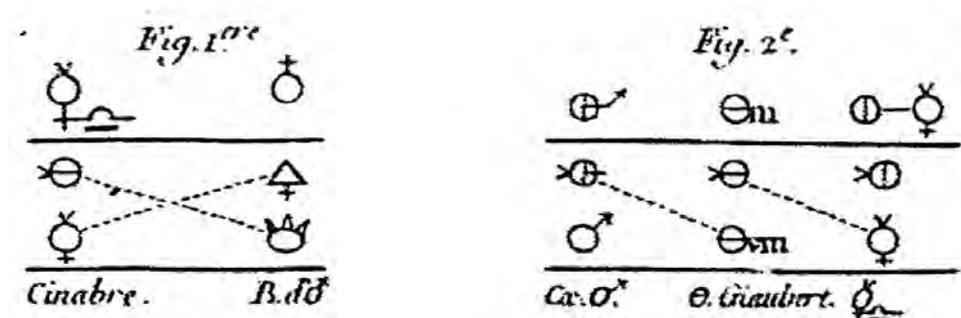


Figure 14.13: Affinities. The two figures showing examples of chemical reactions are a detail in the lower right corner of Gellert's table of affinities in 1750. The similarity with Cavendish's drawing in the previous figure is seen. The table is reproduced in Kim (2003, 223).

Some chemists foresaw a central role for affinities in a perfected science. Macquer's and Bergman's opinions on affinities as the foundation of the entirety of chemistry are quoted above. Antoine Fourcroy, Macquer's successor as lecturer in chemistry at the college of the Jardin du Roi, wrote in 1787 that "all chemistry" reduces to elective attractions, and "when the strength of this force between all natural substances has been determined, chemistry will be as complete as it possibly can be."¹⁶⁵ Lavoisier wrote that when sufficient chemical facts were known, the "geometer will be able to calculate, in his study, the phenomena of any chemical combination whatever, so to speak in the same manner as he calculates the movement of celestial bodies." At the time, he was collaborating with the mathematician and astronomer Laplace, planning experiments to measure chemical attractions.¹⁶⁶ In his treatise

¹⁶⁵Fourcroy quoted in Arnold Thackray (1970, 202).

¹⁶⁶Duncan (1970, 29).

on the new chemistry in 1789, Lavoisier wrote that “the part of chemistry most susceptible, perhaps, of becoming one day an exact science, is that which deals with affinities or elective attractions.” His list of elements resembles an affinity table, supplemented by hydrogen, oxygen, nitrogen, light, and heat. He had some criticisms of the current affinity tables, but his thinking was rooted in the tradition of affinity chemistry. He added a column for oxygen to affinity tables.¹⁶⁷

Newton’s ideas did not have much effect on the practice of chemistry or on the Chemical Revolution, but their legacy extended through the first half of the nineteenth century in the form of affinities defined as attraction at short range. During this time the attention of chemists was redirected to atoms and definite and multiple proportions in chemical combinations. The existence of atoms (or corpuscles or indivisible particles) had long been commonly accepted, and attempts had been made to relate their shapes and positions to the observed properties of substances. John Dalton selected a different property to relate to the observed properties, the weights of the atoms, a change which one historian of chemistry called the “most important step ever taken in the quantification of chemical theory.” Dalton’s first published statement on atomic weights came in 1805, and in 1808, two years before Cavendish’s death, Part One of his *New System of Chemical Philosophy* set out his atomic theory in detail.¹⁶⁸ In the second half of the nineteenth century, chemists returned to the project of quantifying chemical affinities.¹⁶⁹

Chemists in the eighteenth century had different opinions on the nature of chemistry. Some thought that it was a science, others that it was not yet, the former opinion gaining numbers as the century progressed. Some who thought that chemistry was a science thought of it as a separate science while others thought of it as a part of natural philosophy. Stahl regarded chemistry as a body of theoretical and practical knowledge distinct from mechanics, a chemical as opposed to a physical viewpoint. Macquer regarded the “science” of chemistry as a “fundamental and essential part of natural philosophy.”¹⁷⁰ He was criticized by his translator James Keir for conflating affinity with attractions belonging to “natural philosophy” such as cohesion and gravitation, arguing that they may have the same cause but their effects are so different that they should be treated separately.¹⁷¹ William Lewis likewise thought of chemistry as a science distinct from natural philosophy: in some cases “no boundaries can be established between them,” but in other cases there were “essential and important differences.” He said that whereas natural philosophy considers bodies whose parts have the same properties, “subject to mechanical laws, and reducible to mathematical calculation,” chemistry considers different species of matter whose properties give color, taste, and smell, and are “not subject to any known mechanism, and seem to be governed by laws of another order”; “attraction” in natural philosophy is different from “chemical attraction,” or affinity, by which two bodies become one, the properties of which are not “discoverable by any mathematical investigation,” and the failure to distinguish between chemical and mechanical effects has resulted in error in the past.¹⁷² Cavendish said nothing directly about how he thought of chemistry in relation to natural philosophy, but pneumatic

¹⁶⁷Ibid., 5, 41–42. Kim (2003, 342–343).

¹⁶⁸Henry Guerlac (1961, 206–207).

¹⁶⁹Kim (2003, 14, 16, 220).

¹⁷⁰Macquer (1771, 1: Advertisement)

¹⁷¹Ibid. 1:22–23.

¹⁷²William Lewis (1763, iii–iv).

chemistry, his special field, was by its nature a bridge between chemical and physical approaches. Airs, its subject, were freed and combined by chemical means, and they were studied individually by weights and volumes. Cavallo began the second part of his treatise on air with a prescription: the “branches of natural philosophy are so intimately connected with one another” that to advance one branch required knowing the others; in particular, to advance pneumatic chemistry, not only chemistry but mathematics, electricity, and hydrostatics needed to be known.¹⁷³ Cavendish studied phlogiston in its chemical combinations, and he studied it separately as an air in the same way he studied common air, as a ponderable elastic fluid. To analyze chemical activity, he used affinities, a concept equally useful in chemical and physical approaches, allowing him to proceed beyond bare facts without losing himself in unproductive theory. The evidence suggests that Cavendish did not concern himself with the distinction between chemical and physical approaches. He was a natural philosopher who carried out chemical researches, using what means were called for. In the catalog of his library, chemical books did not have a category of their own but were listed under “natural philosophy.”

When chemists spoke of wanting their science to be like natural philosophy, they usually had in mind useful mathematical laws of chemistry deduced from experimental facts.¹⁷⁴ Black thought that chemistry lacking first principles was “not yet a science,” and that the present task of chemists was to form a “general law” by induction, following Newton’s *Opticks* as a model; they should avoid all “pretensions of a full system.”¹⁷⁵ Cavendish looked for regularities, not for a complete system of chemistry, in implicit agreement with Black. His work on equivalent weights can be seen as implying a general law. His hypothesis that *all* metals including the perfect metals and mercury are deprived of their phlogiston when they are dissolved in acids is a potential law. In his most sustained series of chemical experiments, he looked for the cause of the diminution common air in *all* the ways it can be phlogisticated and for what becomes of the air, and he thought he found the answer, again a law. He showed little if any interest in reforming the nomenclature of chemistry or deciding on the chemical elements, matters which would have come up in any proposal of a full system of chemistry. His chemical researches were systematic in a different sense. Recognizing the implication of Black’s work, that for chemistry to advance it was necessary to study factitious airs, he made a systematic examination of the properties of distinct factitious airs, the subject of his first publication in chemistry.

Given Cavendish’s appreciation of the importance of theory to scientific advance together with his ability in making theories, it may seem strange that he did not take a more constructive interest in the theoretical side of chemistry. If chemistry lacked first principles, as Black said, and if for this reason it was insufficiently developed to consider making a theory of chemistry as a whole, Cavendish might have considered making a theory of the part of chemistry he knew best, pneumatic chemistry. Priestley had that in mind when he said that his goal was a “*general theory* of all the kinds of air,” only the experimental evidence was lacking.¹⁷⁶ Cavendish might have agreed about the evidence, but in any case he showed no inclination to attempt Priestley’s theory. He looked for general results with the help of

¹⁷³Cavallo (1781, 157).

¹⁷⁴Duncan (1970, 26).

¹⁷⁵Quoted in Brock (1992, 271).

¹⁷⁶John G. McEvoy (1968, 117).

affinities within the framework of the phlogiston theory, which he did not have to invent but only modify.

Lavoisier was inferior to Cavendish in experimental skill, but he was superior in his “ability to relate parts to the whole, and so erect a large theoretical structure.”¹⁷⁷ There is no way of knowing exactly why Cavendish did not do something, but it is worth noting that in the two comprehensive theories he worked out, for electricity and heat, he began with a hypothesis about the cause of the phenomena, which he then elaborated mathematically. Chemistry in his day did not offer him a comparable opportunity to exercise this skill.

Exactitude

When after completing his paper on the theory of electricity, Cavendish found that Aepinus had published a theory based on nearly the same hypothesis, he justified publishing his own because he had developed it much further and, as he said, “I flatter myself, in a more accurate manner.”¹⁷⁸ When his first paper, on factitious air, was read to the Royal Society, he was thanked for his “Accurate paper.”¹⁷⁹ In the year he published his last chemical paper, a colleague referred to him as “that most accurate philosopher.”¹⁸⁰ “Possessing depth and extent of mathematical knowledge” Humphry Davy said that Cavendish “reasoned with the caution of a geometer upon the results of his experiments.”¹⁸¹

One key to Cavendish’s accuracy was his understanding of instruments, which in turn rested on his understanding of the science underlying them. This is shown by advice he gave on how to operate an air pump (Fig. 14.14). John Smeaton claimed that his improved air pump gave rarefactions of 1000 or 2000 times instead of the previous limits of under 150. Implicit confidence was placed in his claim until the instrument maker Edward Nairne discovered a fallacy, which he recognized after obtaining incredible rarefactions of 100,000. By making comparisons with other standard gauges, Nairne saw that the error lay in Smeaton’s new gauge, a pear-shaped bulb holding mercury, but not knowing the reason for it, he performed an experiment with the air pump before Smeaton and other interested fellows of the Royal Society. One of them was Cavendish, who recognized that the discrepancy between the gauges was due to water vapor. He explained that to get the gauges to agree the air pump must be as free as possible of all traces of water, since Smeaton’s gauge did not measure vapor pressure in addition to air pressure as other gauges did. When Nairne took this precaution, the gauges agreed, and the rarefaction proved to be a believable 600. Cavendish’s explanation was based on his father’s experiments, which showed that whenever the pressure of the atmosphere on water is reduced to a certain level, which depends on temperature, the water is immediately turned into vapor and is as immediately turned back into water upon restoring the pressure.¹⁸²

¹⁷⁷Frank Greenaway (1776/1970, xii).

¹⁷⁸Henry Cavendish (1771, 33).

¹⁷⁹6 Nov. 1766, JB, Royal Society 25:927.

¹⁸⁰James Keir, quoted in Joseph Priestley (1788, 327).

¹⁸¹Humphry Davy (1812, 37).

¹⁸²This clarification of the air pump in 1776 was described by Nairne in a paper and by Charles Hutton in his entry “Air” in *Mathematical and Philosophical Dictionary* (1795–1796, 1:56–57).

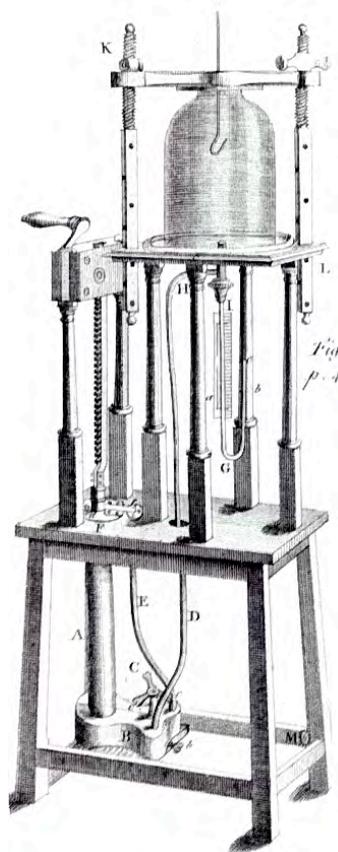


Figure 14.14: John Smeaton's Air-Pump. The left-hand figure shows A barrel, B cistern, C handle of cock, D pipe communicating from cock to receiver, E pipe between cock and valve, G siphon gauge. The right-hand figure shows the new gauge, a glass holding about a half pound of mercury, held up by the brass piece DE and open at A; the graduated tube BC is closed at C. While the receiver is being exhausted, the gauge is suspended in it. When the pumping is done, the gauge is lowered so that its open end is immersed in a cistern of mercury. The air is then let in, driving mercury up into the gauge until the air remaining in it is of the same density as the external air. The rarefaction of the air in the receiver can then be read off from the number of divisions occupied by the air at the top. Cavendish noted that the air trapped in the gauge contains water vapor; compressed by the mercury, the vapor at a certain point is turned into liquid water, eliminating the partial vapor pressure and thus allowing readings of unprecedented rarefactions. In other gauges of the time, this phenomenon did not occur. The gauge is described by its inventor, John Smeaton (1752b, 421); illustration of the air-pump opposite, 424. Cavendish's analysis of the pair-gauge is given by Edward Nairne, *PT* 67 (1777): 622.

When someone objected to his explanation of the difference between the gauges, Cavendish said that the objection would be credible except for a “circumstance” he neglected to mention: “while any air is left in the receiver the pressure therein will be greater than if it contained only the vapor of water.”¹⁸³ The circumstance was the principle of partial pressures, which Cavendish used in various calculations, but which would only become generally known in the next century with the work of John Dalton.¹⁸⁴

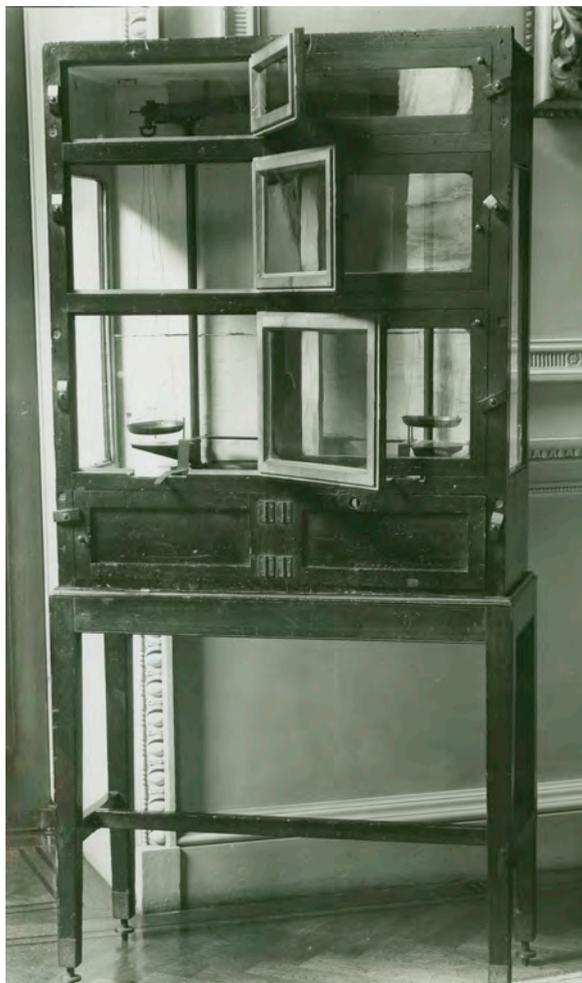


Figure 14.15: Chemical Balance. Built by “Harrison,” this instrument is the earliest of the great precision balances of the eighteenth century. Reproduced by permission of the Royal Institution of Great Britain.

¹⁸³The person Cavendish addressed is not named. Cavendish Mss IV, 4.

¹⁸⁴S.A. Dymont (1937, 473).

The instrument that typifies Cavendish's exactness in chemistry is the balance. We have mentioned that Cavendish owned the first of the great precision balances of the eighteenth century (Fig. 14.15). The beam of his balance was not suspended, as it was in earlier balances, but rested on a hardened steel knife edge standing on a steel plate. It was made of a wide flat iron bar, triangular in form, and $19\frac{1}{2}$ inches long. Suspended from its ends by thin wires attached to brass universal joints were weighing pans measuring about 1 foot across. There was a threaded rod with a nut on each arm of the beam to adjust the center of gravity of the beam to compensate for unequal weight in the arms. The index instead of being at the center of the beam was placed at one end and oriented horizontally, increasing the size of the movement of the beam over a graduated arc. The balance was enclosed in a rough wooden case with glass windows standing on a table. It was capable of weighing to an accuracy of 5 milligrams.¹⁸⁵ There is no date on it, but the maker's name is known to be "Harrison," who may have been William Harrison, who was employed by Cavendish. This Harrison had worked under Jesse Ramsden, who built the one other great precision balance in Britain, owned by the Royal Society.¹⁸⁶ Cavendish's preference in chemistry for weighing is explained by what Blagden said about this form of measurement: "quantities can be determined to much greater exactness by weight than by any practicable way of measurement."¹⁸⁷ The determination of weights, William Nicholson wrote, was "half the business of the chemist."¹⁸⁸ Wilson singled out Cavendish's weighing as the one certainty among the debated events of the "water controversy."¹⁸⁹

In addition to Cavendish's and the Royal Society's early precision balances, there was a third one, owned by Lavoisier. His balance had the same innovative features as the other two, though they were realized differently.¹⁹⁰ With the help of the precision balance, chemistry was becoming a science exact enough to attract an astronomer. When Lavoisier learned of Cavendish's experiments on water, he made his own with the assistance of Laplace.¹⁹¹ So caught up in chemistry was Laplace that Blagden asked a French colleague if what he was told was true, that Laplace "had renounced his mathematical studies, & was applying himself solidly to chemistry."¹⁹² When Laplace read Cavendish's paper on water, he wrote to Blagden that Cavendish's experiments were "infinitely important," made with the "preci-

¹⁸⁵ Ernest Child (1940, 79). Maurice Dumas (1972, 134, 222–223). Precision balances first appeared in assaying offices, in the 1770s.

¹⁸⁶ From a list of Henry Cavendish's servants at his death in 1810, we know that his instrument maker's name was William Harrison, who was sixty-one at that time. It could be another Harrison. Cavendish's balance is attributed to Thomas Harrison in Mary Holbrook (1992, 169). It is attributed to John Harrison by Maurice Dumas, who says that only a clock-maker would have had the skill to make it (1972, 134, 222).

¹⁸⁷ Charles Blagden (1790, 325).

¹⁸⁸ William Nicholson, in his translation of notes by French chemists to the French edition of Richard Kirwan (1789, viii).

¹⁸⁹ Wilson (1851, 363).

¹⁹⁰ Dumas (1972, 225–226).

¹⁹¹ Lavoisier could be careless at times. When he and Laplace burned oxygen and hydrogen to obtain water, they did not keep track of the exact quantities of the gases, assuming that the weights of the gases and of the water formed from them were equal. According to Blagden, who witnessed it, Lavoisier and Laplace's first experiment on the production of water was "good for nothing as to determining the proportions of air & water," and their only dependable result was the test of the purity of water; they intended to repeat the experiment with the "necessary precision," but the account of this first experiment was read before the Academy of Sciences anyway. Charles Blagden to Joseph Banks, 25 June 1783, BM(NH), DTC 3:56–58. Henry Guerlac (1975, 78).

¹⁹² Charles Blagden to Claude Louis Berthollet, 8 Dec. 1789, draft, Blagden Letterbook, Royal Society 7:377.

sion and finesse that distinguish that excellent physicist.”¹⁹³ This may be taken as a tribute from one astronomer to another, both of whom were working in chemistry. What Laplace said of Cavendish’s work others who commented on it said too: it was distinguished for its exactitude.

Measuring and weighing, the recording of objects in numbers, presuppose standards. In his work with the eudiometer, Cavendish introduced a “standard” of goodness (oxygen) based on the goodness of common air, which was itself a standard; as he had shown, the composition of common air is constant, the criterion of a standard. In his experiments on electricity, he introduced a standard for capacitance, that of a conducting globe of a certain diameter. In his experiments on freezing solutions, he determined the specific gravities of acids of various strengths, which he specified by the weights of a standard substance, marble, dissolved by a unit weight of the acids. In his experiments on specific heats, he introduced pure water as a standard substance; using a specified weight of water as reference, he calculated the equivalent weights of substances in terms of their heating effect.

Cavendish introduced the word “equivalent” in chemistry, though the concept went back to the turn of the eighteenth century, to Wilhelm Homberg’s quantitative experiments on the neutralization of alkalis by acids.¹⁹⁴ In his experiments, Homberg ignored the weight of gases absorbed and given off, a deficiency which Black pointed out in his work on *magnesia alba*.¹⁹⁵ James Keir corrected Homberg’s table of the equivalent weights of acids referred to salt of tartar with numbers he took from Cavendish’s 1766 paper on factitious air.¹⁹⁶ In that paper Cavendish introduced marble as a standard equivalent weight: he first determined the proportion of fixed air in marble, and then with reference to 1000 grains of marble he found the equivalent weights of fixed air in several other alkalis, volatile sal ammoniac, pearl ashes, and salt of tartar. Following is an example of Cavendish’s determination of equivalent weights and of their use in explaining chemical reactions. By combining a sample of the alkali volatile sal ammoniac (solution of ammonium carbonate in alcohol) with the acid spirit of salt (hydrochloric acid), Cavendish determined two weights: 1661 grains of the sample saturated as much acid as 1000 grains of marble did. In this case, 1661 grains and 1000 grains were equivalent weights of the two alkalis. He determined that 1000 grains of marble contained $407\frac{1}{2}$ grains of fixed air, and that 1661 grains of volatile sal ammoniac contained 885 grains of fixed air. These numbers show that volatile “sal ammoniac contains more fixed air, in proportion to the quantity of acid that it can saturate, than marble does, in the proportion [...] 885 to $407\frac{1}{2}$.” This result accounted for a “remarkable phenomenon,” Cavendish said. To a solution of the alkali chalk in the acid spirit of salt he added a solution of volatile sal ammoniac, producing a considerable effervescence, which “surprised” him since the acid was perfectly neutralized by the chalk. The explanation was that volatile sal ammoniac contained more fixed air in proportion to the quantity of acid that it could saturate than chalk did (chalk taking the place of marble in the previous example). In the solution, the volatile sal ammoniac united to the acid (it having greater affinity to the acid than the chalk did), losing its fixed air, part of which united to the chalk that was separated from the acid, and part of which “flew off in an elastic form,” since the chalk was not able to absorb

¹⁹³Pierre Simon Laplace to Charles Blagden, 7 May 1785, Blagden Letters, Royal Society, L.181.

¹⁹⁴Marie Boas Hall (1972). J.R. Partington (1961–62, 3:44–45).

¹⁹⁵Black (1898, 17–18).

¹⁹⁶Partington (1961–62, 3:320).

all of the fixed air.¹⁹⁷ Equivalent weights were weights with which the chemist could make physically meaningful comparisons.

Cavendish applied the concept of equivalents throughout natural philosophy. In his theory of heat, he proposed an experiment to measure the mechanical “equivalent” of heat, the term he used.¹⁹⁸ In his study of compounds of tartar, he determined the “equivalent” weights of several alkalis.¹⁹⁹ In his experiments on the specific heats of various substances, he stated the results in terms of the “equivalent” weight of water. In his experiments on the heats generated by mixing acids and different alkalies, each of the alkali solutions had as much alkali as “equivalent” to a specified weight of marble.²⁰⁰ In his experiments on electrical resistances, he prepared solutions of neutral salts in which the amount of acid in each was “equivalent” to that in a solution of sea salt of a certain concentration.²⁰¹ By the use of the balance together with standards and equivalents, Cavendish gave to his work its characteristic stamp of exactitude.

In several experimental fields, Cavendish introduced the law of reciprocal proportions, which he called “a constant rule” of nature. He began the account of his electrical experiments with the rule that when two charged bodies are successively connected to a third body, the proportion of the charges in the two bodies is the same as the proportion of the charges of the third body successively connected to one and the other body. If he said that the charge of a thin circular plate is to the charge of a globe of the same diameter as 1 to 1.57, he meant that if the two bodies were successively connected to a trial plate, the two charges on the trial plate would bear the same proportion, 1 to 1.57.²⁰² This was the justification of the trial plate, the instrument he used throughout his experiments on the charges of bodies. He established a similar rule about the heating effects of two bodies on each other and on a third body, the justification of the principal instrument in his researches on specific and latent heats, the mercury thermometer.²⁰³ He did not take his reciprocity rules in heat and electricity as self-evident but carried out experiments to prove them. In his chemical work on freezing mixtures Cavendish assumed without comment the rule of reciprocal proportions, later proposed by Richter.²⁰⁴ The rule was a precondition of “strict reasoning” about nature, the habit of thought behind Cavendish’s reputation for exactitude.

¹⁹⁷Cavendish (1766, 93).

¹⁹⁸McCormmach (2004, 134–135).

¹⁹⁹Cavendish Mss II, 2(b). Unnumbered pages at the end.

²⁰⁰Cavendish Mss III(a), 9:82.

²⁰¹In addition to neutral salts, Cavendish prepared solutions of fixed alkali and acids. Maxwell found that when the amounts of the salts and acids are expressed in pennyweights, they are very nearly equal to their equivalent weights in modern chemistry, where the equivalent weight of hydrogen is taken as 1. The remarkable agreement is not just in ratios but in absolute numbers, which comes from Cavendish’s practice of using as a standard the equivalent weight of marble, the modern value of which is 100. By taking 100 pennyweights of marble as the standard, the equivalent weights of the other salts and acids come out as Cavendish stated them. Henry Cavendish (1879h, 329–330; 1879k, 360–361). Maxwell’s commentary, *ibid.*, lxii–lxiii.

²⁰²Henry Cavendish (1879b, 114–115).

²⁰³Henry Cavendish (1921c, 340).

²⁰⁴Wilson pointed out Cavendish’s use of the “law of reciprocal proportion.” A certain quantity of sulfuric acid saturates a given quantity of a particular alkali, and a different certain quantity of nitric acid saturates the same quantity of alkali. This quantity of nitric acid dissolves 33 parts of marble. It follows from the rule that the above quantity of sulfuric acid also dissolves 33 parts of marble. Cavendish estimated the strength of acids by the quantity of marble they dissolved, but because in the case of sulfuric acid, the quantity of marble it dissolved was not an accurate method, he estimated its strength by comparing it with nitric acid, which was accurate. This is why he took the roundabout way, making use of reciprocity. Wilson (1851, 465).

It is clearer to us than it was to Cavendish's contemporaries that his direction in chemistry would prevail. British resistance to Lavoisier's anti-phlogistic chemistry was partly based on distrust of his claims for quantitative accuracy and even of the relevance of those claims to the disputed issues in chemistry, and as well of his geometric model of reasoning in chemistry.²⁰⁵ Cavendish's direction may not have had unanimous support, but his marked preference for quantitative methods represented an influential opinion both in Britain and abroad. Black, it is said, was not so much a chemist as a natural philosopher, who looked for general laws and made use of quantifying instruments, the balance and the thermometer. Lavoisier applied to chemistry the methods of experimental physics, with its reliance on instruments of measurement; without measuring and weighing, he said, "neither physics nor chemistry can any longer admit anything whatever."²⁰⁶ Precision was not yet of decisive importance, but the recognition of an indispensable role for weighing and measurement in chemistry insured that it was coming.

As indicators of the trend, we note several examples of measuring and weighing in the late eighteenth century and the beginning of the nineteenth century, a time when about a third of chemical publications were quantitative.²⁰⁷ The examples have been mentioned earlier in different contexts. Carl Friedrich Wenzel, director of Freiburg foundries, having observed that acids and bases combine in constant proportions published a table of equivalent weights in 1777.²⁰⁸ In 1781–83 Kirwan made specific gravities of compounds and their ingredients a measure of their affinities, and he made equivalent weights a measure of the affinities of acids for bases, in his opinion the foundation of "chymistry, considered as a science."²⁰⁹ Richter's weights of bases required to neutralize a given quantity of an acid were published in tabular form in 1802. Following Lavoisier's *Treatise* in 1789, much of the research in chemistry was directed to determining by weight the constituents of compounds with ever greater accuracy. J.L. Proust presented the law of definite proportions in 1797. Dalton published the law of multiple proportions in 1804, and the next year he first mentioned in print his atomic theory of chemistry, which made atomic weights a way of distinguishing substances quantitatively. In 1809 Gay-Lussac determined the law of definite proportions for volumes of reacting gases. From the end of the eighteenth century, physical constants and measurable properties of substances entered standard chemical textbooks.²¹⁰ Quantitative differences took on increasing importance in differentiating and combining substances, always a principal objective of chemistry. Cavendish lived long enough to see his approach successfully pursued by many chemists.

Concern with accuracy was at the same time concern with error. Cavendish would seem to be preoccupied with error, but he was practicing good science as it was increasingly done. Francis Wollaston wrote to Herschel, "I believe we both of us have the advancement of science too much at heart to decline acknowledging an error." Errors could be looked at as opportunity. Herschel thought that a theory by John Michell was fundamentally in error but also that it was "of the utmost importance, its being contrary to facts being a point of

²⁰⁵Jan Golinski (1992, 130–152).

²⁰⁶A.L. Donovan (1975, 201, 215, 220–221; 1993, 49). Brock (1992, 117).

²⁰⁷H. Gilman McCann (1978, 143–146).

²⁰⁸Ihde (1964, 96).

²⁰⁹Richard Kirwan (1781, 8–9; 1783, 34, 36, 38).

²¹⁰Guerlac (1961, 197, 199, 203–205, 211).

almost as much consequence as its agreeing with them.”²¹¹ James Hutton said that errors are not grounds for skepticism; on the contrary, they “contribute for establishing the certainty of science, when these are properly corrected.”²¹² “Errors may lead to truth,”²¹³ Dalrymple said simply. Cavendish took precautions to reduce, not unrealistically to eliminate, the “error of the observer,” the “error of the instrument,” and overall the “error of the experiment.” His work in chemistry belonged to a common world of scientific practice, which valued accuracy, considered errors, introduced standards of measurements and practice, and improved instruments.

Cavendish’s direction in science may have had sources outside of science as well. The caution with which he moved through his life has a parallel in his analysis of the circumstances of experiments, a point we take up in the last chapter. There may have been an additional source arising from his place in society. Measurement has long been a trademark of authority and sovereign power. Measures are legislated, and standards that secure them are kept by a central authority. Governments impose uniform measures ensuring an orderly commerce by providing all parties with a common language. Scientific organizations desire uniform measures for similar reasons, and the same measures are used in the activities of civil society and in scientific work. The desirability of exactness in weighing was recognized in commerce and in science in Cavendish’s time. As a member of the ruling class, Cavendish might have instinctively imbued his work with the common language of authority: number, weight, and measure.²¹⁴

²¹¹Francis Wollaston to William Herschel, 22 Mar. 1789, Royal Astronomical Society, Herschel Mss W 1/13, W. 193. William Herschel to Samuel Vince, 15 Jan. 1784, *ibid.*, W 1/1, 92–95, on 93.

²¹²James Hutton (1794, 6).

²¹³Howard T. Fry (1970, xiii).

²¹⁴Witold Kula (1986, 18). Kisch (1965, 8).