Chapter 13
Henry Cavendish (1731–1810): Hydrogen, Carbon Dioxide, Water, and Weighing the World

Abstract Henry Cavendish (1731–1810) was an outstanding chemist and physicist. Although he was not a major figure in the history of respiratory physiology he made important discoveries concerning hydrogen, carbon dioxide, atmospheric air, and water. Hydrogen had been prepared earlier by Boyle but its properties had not been recognized and Cavendish described these in detail including the density of the gas. Carbon dioxide had also previously been studied by Black but Cavendish clarified its properties and measured its density. He was the first person to accurately analyze atmospheric air and reported that the oxygen concentration was very close to the currently accepted value. When he removed all the oxygen and nitrogen from an air sample, he found that there was a residual portion of about 0.8 % which he could not characterize. Later this was shown to be argon. He produced large amounts of water by burning hydrogen in oxygen and recognized that these were its only constituents. Cavendish also worked on electricity and heat. However his main contribution outside chemistry was an audacious experiment to measure the density of the earth which he referred to as "weighing the world". This involved determining the gravitational attraction between lead spheres in a specially constructed building. Although this was a simple experiment in principle, there were numerous complexities which he overcame with meticulous attention to experimental details. His result was very close to the modern accepted value. The Cavendish Experiment as it is called assures his place in the history of science.

13.1 Introduction

Henry Cavendish (1731–1810) was a famous chemist and physicist with broad scientific interests, and in particular he was a meticulous experimenter. He was born in Nice, France where his parents were residing at the time. The family was notably aristocratic and could trace its roots back to Norman times. Henry's father was Lord Charles Cavendish who was the son of the 2nd Duke of Devonshire, and Henry's mother was Anne, a daughter of Henry Grey, 1st Duke of Kent. In spite of these illustrious ancestors, the family was not particularly affluent. Nevertheless during his life, Henry became exceedingly wealthy through bequests, and at his death the estate was worth about a million pounds, an enormous sum in those days. The French

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scientist, Jean-Baptiste Biot (1774–1862) quipped that he was "le plus riche de tous les savants, et probablement aussi le plus savant de tous les riches" (the richest of all learned men, and probably also the most learned of all the rich) [11].

Henry's mother died when he was aged two and he was brought up by his father. In fact he lived with his father until the latter's death in 1783 when Henry was aged 52. He was first educated at the Hackney Academy in London and this is of interest because it was run by dissenters (people who did not conform to the Church of England) and this reminds us that his contemporary, Joseph Priestley (1733–1799), was a fierce non-conformist. Later Henry entered Peterhouse College in Cambridge although, as was common at the time, he did not graduate, possibly because of religious reservations.

The Cavendish family had a strong tradition of public service including extensive political responsibilities. However these topics did not interest Henry and he devoted his life to science. Here his aristocratic connections enabled him to move in the highest circles. At the age of 29 he became a Fellow of the Royal Society of London and he was elected to its Council when he was 34. He was also a trustee of the British Museum, and he became manager of the recently founded Royal Institution of Great Britain when Humphry Davy was working there. Davy worked on respiratory gases especially nitrous oxide.

As a person, Henry Cavendish had many scientific friends but outside this area he was extremely reclusive, perhaps even pathologically so. He remained a bachelor all his life and had an aversion to women. Various anecdotes are told about this. For example he would order his dinner by leaving a note on the hall table, and he had a separate staircase installed in his house so that he could avoid any female servants. His dress was quaintly old-fashioned and he wore an antiquated wig. He refused to sit for a portrait; the only image that we have of him (Fig. 13.1) was surreptitiously sketched by the artist William Alexander.

Cavendish was a very eminent scientist but not a major figure in physiology. However his work is of considerable interest. He was the first person to prepare and understand the nature of hydrogen. He made this by adding acid to metal filings. The gas had previously been produced by Robert Boyle (1627–1691) but he confused it with ordinary air. Cavendish also worked on carbon dioxide, or "fixed air" as it was called. This had previously been prepared by Joseph Black (1728–1799) but his description was brief and Cavendish elucidated its properties. Another important area of research was the properties of water. Joseph Priestley had previously observed that when a mixture of inflammable and common air was exploded with an electric spark, the container "became dewey". Cavendish went on to study the properties of water in detail. Another interest was the composition of atmospheric air which he was the first to accurately determine. He also worked on nitric acid but all his chemistry research was interpreted in terms of the phlogiston theory. This stated that a fire-like element was released during combustion. Having said this, he was one of the first people outside France to recognize the shortcomings of this theory after the crucial studies by Antoine Lavoisier (1747–1794).

Cavendish worked in other areas including experiments on heat. Here he expanded on the work of Black on latent heat. However the major contribution of

Fig. 13.1 Henry Cavendish (1731–1810). This sketch was made surreptitiously by William Alexander. From [16]

Cavendish to science outside chemistry was in the field of gravitational attraction. His major project now known as "the Cavendish experiment" was a meticulous measurement of the gravitational attraction between lead balls in his laboratory carried out with extreme precision [6]. The results allowed him to calculate the average density of the world which he gave as 5.45 times that of water. He referred to this experiment as "weighing the world". As a result, many physicists credit Cavendish with the first accurate measurement of Newton's gravitational constant.

There are three major biographies of Cavendish. The most recent [9] is over 800 pages long and is exhaustive. This is an extension of an earlier book [8] and contains many letters to and from Cavendish. An earlier biography [1] concentrates on his published papers, and a much earlier volume [16] deals extensively with the controversy between Cavendish and Watt on the discovery of the composition of water. A collection of the Cavendish papers is available [10] and several are reproduced on the Internet. Partington [12] has a good discussion of the chemical studies.

13.2 Hydrogen

One of the first publications by Cavendish was titled "Three papers, containing Experiments on factitious Air" [2] and it appeared in the journal *Philosophical Transactions* in 1766. The purpose of this journal was to "register", that is print,

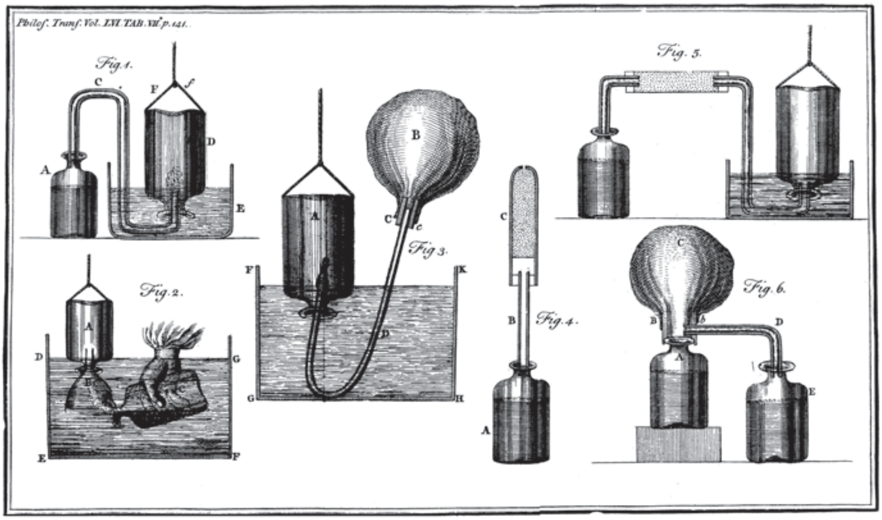

Fig. 13.2 Apparatus used by Cavendish in his studies of hydrogen, carbon dioxide, atmospheric air, and water. From [2]

communications that had been given to the Royal Society. The three papers were presented to the Society on May 29, November 6 and November 13, 1766. *Philosophical Transactions* dealt with all areas of science and the discussions at the Society meetings covered a bewildering array of topics. For example the first paper on inflammable air was preceded by two on a recent solar eclipse, another on the double horns of a rhinoceros, and a third on a very large hernia. Following Cavendish's presentations there was one on men who were 8 ft. tall or more in Patagonia, another on locked jaw apparently cured by electricity, and a third on a swarm of gnats in Oxford. This disconcerting collection emphasizes the lively, effervescent intellectual activity in the Royal Society at the time.

By factitious air Cavendish meant "any kind of air which is contained in other bodies in an unelastic state, and is produced from thence by art" [2]. The term had originally been introduced by Boyle. The first paper was on "Inflammable air" which we know today as hydrogen. Other investigators such as Boyle had previously prepared this gas but had not realized what it was. The detailed studies of Cavendish allowed him to be credited as the first person to recognize its true nature.

Cavendish prepared the gas by the action of acids on various metals. The two acids that he used were spirit of salt (hydrochloric acid) and dilute oil of vitriol (sulfuric acid). He studied three metals, zinc, iron and tin. Various types of apparatus were used in his experiments and these are illustrated in his publication (Fig. 13.2). Cavendish described inflammable air as "permanently elastic" which was a term used to describe all gases at the time. He showed that the volume remained constant in spite of the gas being exposed to water or alkalis. In fact it was so insoluble in water that there was no measurable absorption over a period of several weeks. Finally

Fig. 13.3 Chemical balance used by Cavendish. This was described as "of rude exterior but singular perfection". It is now in the Royal Institution in London. (By permission of the Royal Institution)

he described that it was explosive when it was mixed with common air and exposed to a spark, and he noted that this behavior had been described by others.

An important determination was the density of the new gas. It was easy to measure a given volume by water displacement using the equipment shown in Fig. 13.2. However measuring the weight of a given volume of gas was much more challenging. This was done by placing a known volume of the gas in a bladder as shown in the third image of Fig. 13.2 and weighing it using a sensitive analytical balance. One of Cavendish's balances that still exists today is shown in Fig. 13.3. Other scientists at the time, for example Black, had also developed very accurate balances. Cavendish measured the density of several samples of hydrogen and compared the density with that of common air and water. He reported that the mean density was "8700 times lighter than water". This meant that it was much lighter than air which had "its specific gravity… 7840 times less than that of water". The paper read by Cavendish on May 29 describing his work on inflammable air was warmly received, and the secretary of the Society, Henry Oldenburg, wrote in the Society's Journal Book that "It is impossible to do Justice to the Experiments under the title "Of inflammable air" without citing them wholly" [14].

13.3 Carbon Dioxide

The second of the three papers was read by Cavendish on November 6, 1766 and was about his work on “Fixed air”. We now know this as carbon dioxide and it had previously been produced by Joseph Black although his description was brief. Cavendish produced fixed air by the same methods as used by Black, that is by adding acid to alkalis such as calcium carbonate or magnesium carbonate, or heating these substances, that is what is known as calcination. Cavendish explored the properties of this gas using the same techniques as he had for inflammable air. He reported that it was permanently elastic like inflammable air but in other respects it was different. First it was soluble in water and for that reason he collected it over mercury. He also found that it was not flammable and he reported its density as 511 times lighter than water, or 1.57 times heavier than common air.

Cavendish’s third paper presented to the Society on November 13 dealt with the gases produced by fermentation and putrefaction. The results showed considerable variability as we might expect and these studies are of less interest.

Cavendish’s work on factitious airs earned him the Copley Medal of the Royal Society, its highest distinction. His work was characterized by very careful measurements, and he resisted the temptation to extrapolate beyond exactly what he had found. As an example of his meticulous methods, he kept a sample of fixed air over mercury for “upwards of a year” to see if any change in volume occurred. However his interpretation of his chemical experiments was marred by the fact that he worked within the confines of the phlogiston theory, and therefore the full implications of his discoveries were only seen after Lavoisier had demolished this.

13.4 Composition of Atmospheric Air

In 1783 Cavendish published a paper “An account of a new eudiometer” [3]. This term which had been used by others, particularly Priestley and Lavoisier, is odd. It comes from the Greek εὐδίος (eudios) meaning fine weather, and the instrument was used to measure the “goodness” of air. In effect this was the concentration of oxygen in the air. Previous measurements by Priestley and others had shown considerable variation in the measurement and Cavendish was determined to obtain the correct value. Priestley was the first person to describe the preparation of oxygen.

The method consisted of adding “nitrous gas” (nitric oxide) to air and measuring the reduction of volume. The nitric oxide combined with the oxygen to form nitrogen dioxide (NO_2) which was soluble in water. The nitric oxide was prepared by another method, that is by adding nitric acid to copper. Cavendish experimented by using various proportions of air and nitric oxide to determine the best way of completely removing the oxygen. He also determined the concentration of oxygen by another method, that is by adding inflammable air (hydrogen) to atmospheric air and exploding the mixture with a spark of electricity.

Cavendish's results showed that the concentration of oxygen in air had a mean value of 20.83. This is very close to the value of 20.93 which is accepted today. He also analyzed air collected at high altitude during a balloon ascent by the eccentric American physician and balloonist, John Jeffries. This had essentially the same value.

Cavendish was also able to remove both the oxygen and the nitrogen from an air sample. The nitrogen was removed by adding oxygen and subjecting the mixture to an electric spark which resulted in the formation of nitric oxide. To his surprise he found that a small bubble of gas remained. This was unexplained until about a hundred years later when the gas was shown to be argon by Rayleigh and Ramsey [13]. Cavendish reported that its volume was 1/120 of the total, that is 0.83 %. The modern figure for the percentage volume of argon is 0.93.

13.5 Composition of Water

In 1784 Cavendish published a paper showing that burning hydrogen in oxygen produced water [5]. As mentioned earlier, Priestley had previously observed that when inflammable air was exploded with common air by an electric spark the container "became dewey". This experiment was conducted with Priestley's colleague, John Warltire. They also reported that when the explosion was made in an airtight vessel, it was accompanied by a loss of weight. This was attributed by Warltire to the loss of heat which he thought had weight.

Cavendish repeated the experiment in his usual meticulous way and found no loss of weight which did not surprise him because he did not believe that heat had weight. He reported that about one-fifth of the air lost its elasticity (that is disappeared) and that this had condensed into a dew. He went to produce larger amounts of the dewy substance, showed that it had no taste or smell, and concluded "in short, it seemed pure water" [5].

Cavendish reported his findings to Priestley in about March 1783 but the paper was not published until 1784. Meanwhile James Watt (1736–1819) had published a paper on the composition of water [14] and the result was an unpleasant controversy about priority.

13.6 Electricity and Heat

Like many other contemporary scientists, Cavendish was interested in the properties of electricity and heat. It is now recognized that Cavendish made important contributions to the study of electricity but this was not appreciated in his lifetime because he wrote little about these topics. Subsequently James Clerk Maxwell collected and carefully studied Cavendish's notebooks and manuscripts which were subsequently published in 1879 [10].

Cavendish found, but did not publish, the fact that electrical force diminished as the inverse square of the distance just as the case with gravitation. Previously Priestley had suggested this. Cavendish also appreciated the concept of electrical potential which was called the degree of electrification. He measured this using an electrometer containing two gold leaves. When the device was electrified the two leaves diverged and he measured the angle between them. He recognized that in a good conductor the electrical potential was uniform. He also showed that the flow of electricity, which we now refer to as the current, was proportional to the resistance between two points having different potentials. There was no way of measuring current at that time and Cavendish estimated this by holding the electrodes and noting whether the sensation was limited to his fingers, or whether it ascended to his wrists, or his elbows. He also studied the electrical behavior of the torpedo electric fish and compared the fish's electric shock with that from a series of Leyden jars. He stated that electricity was the result of particles that repel each other and we now know that this is a property of electrons.

The work of Cavendish on heat was similarly described in his notebooks and manuscripts and relatively little was published. He believed that the temperature of a substance was related to the degree of motion of its constituents. For example he stated "Heat most likely is the vibrating of the particles of which bodies are composed". He rejected the notion of heat as a fluid with weight which was a popular theory at the time. This was referred to above in his experiments on the production of water. In a paper on the freezing of mercury [4] he used the concept of latent heat which was later developed by Black although Cavendish did not use this term. As in the case of electricity, his treatment of heat was mathematical. Some of his unpublished work on heat was similar to research conducted later by Black and it is said that Cavendish may have delayed publication to give Black an advantage.

13.7 Density of the Earth

The major topics of this paper are Cavendish's studies of hydrogen, carbon dioxide, atmospheric air, and water because of their physiological importance. A brief note about his research on electricity and heat has also been included. However in the later stages of his life, Cavendish carried out a truly extraordinary experiment which he referred to as "weighing the world". In fact the objective was to determine the density of the earth which was the title of the paper [6]. This audacious experiment was so remarkable and gives so much insight into the meticulous experimental methods of Cavendish that it will be briefly described here. History has recognized its significance so that it is generally referred to as "The Cavendish Experiment".

Cavendish was nearly 67 when he embarked on the project and it was the last paper that he published. The experiment was described at length in elegant English in 65 pages in the journal *Philosophical Transactions*. He began by explaining that a friend, the Reverend John Michell, had started to construct an apparatus to measure the density of the earth but he had died before the equipment was completed.

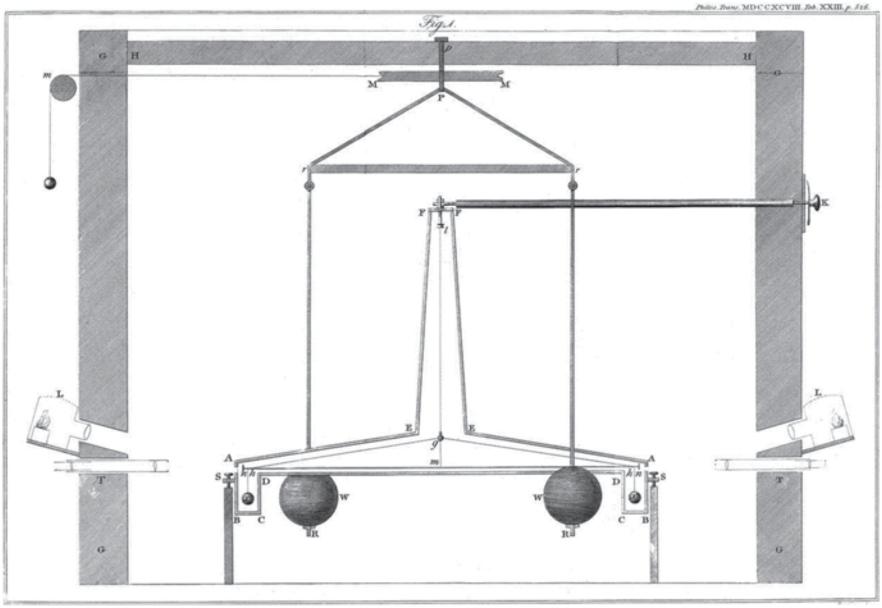

Fig. 13.4 Diagram of the apparatus used by Cavendish to "weigh the world". The apparatus itself is now believed to be in the Royal Institution collection. See text for details. From [6]

Cavendish acquired this and used the same principle but made a number of changes. The basic idea was very simple but carrying it out was extremely challenging. The objective was to measure the gravitational force between two metal balls in the laboratory but the force was vanishingly small being only about 0.02 mg weight (2×10^{-7} N).

Figure 13.4 which is reproduced from Cavendish's report shows the apparatus. The moving part of the experiment was a 6-foot (1.8 m) long wooden rod suspended by a thin wire. At each end of the rod were two lead balls of 2 in. (51 mm) diameter suspended by short wires. This part of the equipment was encased in a narrow wooden box to protect it from air currents. The second part of the apparatus consisted of two massive lead balls each 12 in. (305 mm) in diameter and each weighing about 350 pounds (158 kg). These were suspended from a frame which could be rotated from outside the room. These large lead balls were carefully moved so that they could be placed about 2 in. (5.1 cm) from the small balls. As a result of the gravitational attraction, the rod suspending the small balls rotated slightly and the deflection was measured using a vernier scale and telescopes viewing through the wall of the laboratory room as shown in Fig. 13.4. The room had been specially built of wood away from the house and was 10 ft. (3.05 m) square and 10 ft. high. The walls were said to be 2 ft. (0.61 m) thick. The reason for the special room was to maintain a constant temperature and thus limit convective air currents.

Cavendish found that when the wooden rod was deflected it did not come to rest in a new position but continued to oscillate. He calculated the mean deflection from the extremes of the oscillation. In addition, by timing the period of the oscillations he was able to determine the force required to cause torsion of the wire. There was an elaborate series of calculations that are described in detail in the 65-page paper.

Although the principle of the experiment was simple, there were many complicating factors. These included small variations of temperature that generated convection currents in the air and therefore displaced the wooden rod. Each experiment took several hours to complete. The deflection of the rod caused by the gravitational attraction was only about 0.16 in. (4.1 mm) but Cavendish was able to measure this to an accuracy of better than 1/100 of an inch (0.25 mm) by means of the vernier scale. Interestingly the torsion balance method remains the best way today of measuring the gravitational constant. At about the same time Charles Augustin de Coulomb (1736–1785) also used a torsion balance to measure the electrostatic force of repulsion [7].

The single number that came out of Cavendish's monumental experiment was that the mean density of the earth was 5.448 times that of water. (Oddly enough he actually reported the number as 5.48 because of a simple arithmetic error.) This is close to the modern value. It allows the calculation of the Newtonian gravitational constant G to be 6.74×10^{-11} m^3 kg^{-1} s^{-2} although Cavendish did not do this sum. It differs from the currently accepted value by only 1%. Note that to derive the "weight" of the earth (actually its mass), it is necessary to know its radius. This was first measured by the Greek, Eratosthenes, in about 200 BC.

This prosaic account of the experiment does not do justice to the extreme attention to errors described by Cavendish in his paper, and anyone who is interested should read this. It is available on the Internet. "The Cavendish Experiment" is a fitting denouement to the extraordinary experimental life of this unusual man.

In conclusion, Cavendish was not a major figure in the history of respiratory physiology but he was a scientist of exceptional interest. Although he was a recluse and had many eccentricities, he was a meticulous experimenter. He is best known as the discoverer of hydrogen, and he made important contributions to our knowledge of carbon dioxide and water. His bold experiment to "weigh the world", as he put it, assures his place in the history of science.

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