

La química en la historia,
para la enseñanza

Henry Cavendish

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Resumen

Henry Cavendish (1731-1810) fue un científico inglés que contribuyó en forma notable a la física y a la química. Sus trabajos sobre el gas inflamable (hidrógeno) llevaron al descubrimiento de la composición del agua y con ello a la caída de la teoría del flogisto. Cavendish midió la densidad de varios gases con alta precisión y desarrolló los conceptos de calor específico y entalpía sin establecerlos en términos matemáticos. Es también muy conocido por el experimento famoso que lleva su nombre, para determinar la densidad de la Tierra mediante una balanza de torsión. Junto con Coulomb transformó los conceptos de electricidad de cualitativos a cuantitativos.

Abstract

Henry Cavendish (1731-1810) was a British scholar who made valuable contributions to physics and chemistry. His work on the combustion of inflammable air (hydrogen) led to the discovery of the composition of water and to the demise of the phlogiston theory. He measured the density of several gases with high accuracy and developed the concepts of specific heat and enthalpy without establishing them in mathematical terms. He is also well known for the famous experiment that carries his name for determining the density of the Earth using a torsion balance. Together with Coulomb he transformed electricity from a qualitative into a quantitative science.

Life and career (Cuvier, 1811; Wilson, 1851; Berry, 1960)

Henry Cavendish was born on October 10, 1731, in Nice, France, the eldest of the two sons of Lord Charles Cavendish and Lady Anne Grey. Anne Grey passed away when Henry was two years old.

His father was a gifted experimental physicist who made some important experimentation on heat, electricity, and terrestrial magnetism, and at the time of Henry's birth he was the administrator of the

British Museum. Charles Cavendish let his son take an active part in many of his laboratory measurements and thus played an important role in shaping Henry's future career as a scientist.

Very little is known of Henry's early years, except that he attended Dr. Newcome's school at Hackney, celebrated in his time for the education of the children of the upper classes in sound classical learning. On December 18, 1749, at the age of eighteen, Cavendish entered St. Peter's College, Cambridge, and matriculated as a Fellow commoner. He remained there until February 23, 1753, a few days before the end of his studies, when he left without taking his degree. The fact that little information available about Cavendish's private life is a reflection about his character; he lived a very secluded life with almost no social activity, devoting nearly all his time to the variegated scientific questions that intrigued him. He was elected to the Royal Society in 1760, participated in almost all the sessions but consequent with his introvert character, asked almost no questions. Cavendish never married, being a well-known misogynist.

Although Cavendish was elected to the Royal Society in 1760, he did not publish anything in the *Philosophical Transactions* until 1766, when his celebrated paper *On Factitious Air* (Cavendish, 1766) appeared. Significantly enough, this paper was considered so important that its author was awarded the Copley Medal, the highest distinction that the Royal Society can confer. As stated by Berry (Berry, 1960) Cavendish was an excellent mathematician, electrician, astronomer, meteorologist, and geologist, and a chemist equally learned and original.

A reading of the (few) papers published by Cavendish shows how he shifted his interest between many seemingly unrelated subjects. His first works (1766-1788) were on the behavior of gases, thermometry, and different heat phenomena, particularly specific heats and latent heats, in which he assisted his father. In the course of this work he did much to improve the accuracy of the ordinary mercury thermometer. The electrical researches in which he achieved well-known results, occupied him between 1771 and 1788. After that date he transferred his chief interests to terrestrial and astronomical subjects. In 1798 he published his notorious paper on the density of the Earth (Cavendish, 1798), often

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known as the *Cavendish experiment*, where he reported a result that has been unsurpassed by any of the later investigations on this subject. Terrestrial magnetism, a subject on which he first began to make observations with his father, continued to occupy his attention at intervals throughout his life. Much of Cavendish's work remained in the form of unpublished papers; eventually these were edited in two volumes, the first one containing the electrical researches and the second the chemical and dynamical ones (Maxwell *et al.*, 1921). Had he published during his lifetime all the researches he completed, his reputation would have been much wider and more varied even than it was.

Cavendish was not only a gifted experimentalist, but he was also a highly competent mathematician, skilled in the use of infinitesimal calculus (Berry, 1960) He became extremely rich after one of his uncles bequeathed him all his fortune; at the time of his death he was the largest holder of Bank stock in England.

Cavendish died on February 24, 1810, at the age of 79, after a few days' illness, and was buried in All Saints' Church, Derby, now Derby Cathedral.

The many eulogies pronounced in his honor reflect the high esteem in which his English and French colleagues held him. In a lecture delivered in 1810 by Sir Humphry Davy (1778-1829) he said: "It may be said of him, what can, perhaps, hardly be said of any other person, that whatever he has done has been perfect at the moment of its production. Since the death of Newton, if I may be permitted to give an opinion, England has sustained no scientific loss as great as that of Cavendish. Like his great predecessor, he died full of years and glory. His name will be an object of more veneration and of glory". Jean-Baptiste Biot (1774-1862) felt that he could truly say that Cavendish was "le plus riche de tous les savants et probablement aussi, le plus savant de tous les riches" (the wealthiest of all learned men and the most learned of wealthy men). Georges Cuvier (1769-1832) pronounced the *Éloge Funèbre* in his honor at the Académie des Sciences (Cuvier, 1811).

Scientific contribution

Some of Cavendish's most important contributions to chemistry and physics will be described in detail now.

1. Arsenic (Maxwell *et al.*, 1921)

Research in this topic was done about 1764, but never published. Its purpose was to determine the differ-

ences between regulus of arsenic (metallic arsenic), white arsenic (arsenious acid, AsO_3), and arsenical acid (AsO_5). This work is important because it contains a method for preparing arsenic acid, which is the one now in use, and because it was done before Carl Wilhelm Scheele's (1742-1786) published his findings on the subject (Scheele, 1775). It also contains a very detailed description of arsenic acids and some of its salts.

Cavendish first proceeded to repeat some of the experiments that Pierre-Joseph Macquer (1718-1784) (Macquer, 1746, 1748) had done to prepare what was called neutral arsenical salt, by heating a mixture of arsenious oxide and potassium nitrate and then crystallizing the product from hot water. His results indicated that this salt was not strictly neutral, as Macquer supposed, since it dissolved alkaline carbonates and showed a weak acid reaction towards syrup of violets. Cavendish then studied the effect of heating arsenious oxide directly with nitric acid. He took notice of the red fumes released (nitrous acid produced by the action of air on nitric acid) and discussed this phenomenon on the basis of the reduction of the acid by heat and inflammable matter. The product of the reaction was evaporated to complete dryness and the residue heated to "almost as great a heat as the furnace would admit of". Cavendish found that "the product weighted about 1/6th part more than arsen, from which it was made". The actual result was, of course, the oxidation of arsenious oxide to arsenic pentoxide. Although he did not realize the real meaning of the reaction (oxygen was yet to be discovered) he remarked: "I think these experiments shew pretty plainly that the only difference between plain arsenic and the arsenical acid is that the latter is more thoroughly deprived of its Phlogiston that the former. The nitrous acid is known to have a great disposition to lay hold of Phlogiston, and there are strong reasons for thinking that the dissolving of metallic substances in that acid is a very powerful method of depriving them of it" (Maxwell *et al.*, 1921).

Cavendish did also a number of qualitative experiments on his arsenic pentoxide and showed that the pentoxide was soluble in water with pronounced acidic properties, and that it not contain nitric acid.

2. Gases

Cavendish's first memoir on gases was entitled *Three Papers Containing Experiments on Factitious Air* and was

published in 1766¹ (Cavendish, 1766). As the title indicates, this paper is divided into three sections; the first one deals with inflammable gas, the second with carbonic acid (CO₂), and the third with the gases evolved during fermentation and putrefaction. All three sections contain the method of preparation of the gases and a study of their reactions. The first section, entitled *Containing Experiments on Inflammable Air*, deals with the action of zinc, iron, and tin on dilute sulfuric acid and hydrogen chloride. Cavendish found that although zinc dissolved in both acids faster than iron or tin, it yielded the same amount of gas, independently of the acid employed. The attack of iron by solutions of sulphuric acid of different concentrations resulted in the same quantity of inflammable air. Tin dissolved best in warm muriatic acid. The three metals dissolved readily in nitrous (nitric) acid and generated air (nitric oxide), which was not inflammable. They also dissolved with effervescence in hot oil of vitriol and discharged “plenty of vapors which smell strongly of the volatile sulphurous acid, and which are not at all inflammable”. Being a supporter of the phlogiston theory, he interpreted these results correspondingly: “Their phlogiston flies off without having its nature changed by the acid, and forms inflammable air but when they are dissolved in nitrous acid or strong oil of vitriol, the phlogiston of the metals unites to the acid used for their solution and flies away with it in fumes, and the phlogiston loses its inflammability.” The sulphurous acid, which is evolved when oil of vitriol is employed, is thus represented as being phlogisticated sulphuric acid. It appears that Cavendish believed that the hydrogen that evolved did not originate from the dilution water but from the metal itself as it underwent solution. Initially he assumed that the heating principle of bodies was phlogiston, which was supposed to fly off during the phenomena of heat and light, and that when metals were plunged in either of these dilute acids, it escaped in the form of an aeriform body, which he called *inflammable air*. Later experiments led him to assume that inflammable air was a combination of the mysterious phlogiston and water (Cavendish, 1778).

Cavendish observed that the volumes of inflammable air generated depended on the nature of the

metal and not upon the acid, and he quoted the volumes of gas obtained from one ounce of each metal. In addition, he pointed out that sulfuric acid had very little action on tin, but that the metal “dissolves slowly in strong spirit of salt when cold; while the assistance of heat it dissolves moderately fast”. He then showed that “all three metallic substances dissolve readily in the nitrous acid and generate air; but the air is not at all inflammable. They also unite readily, with the assistance of heat, to the undiluted acid of vitriol; but very little of the salt, formed by their union with the acid, dissolves in the fluid. They all unite to the acid with a considerable effervescence, and discharge plenty of vapors, which smell strongly of the volatile of the volatile sulphurous acid, and which are not at all inflammable”.

As mentioned before, analysis of Cavendish’s reasoning shows that his initial belief was that the hydrogen originated from the metals and not from the acids. Afterwards, he changed his opinion stating that the gas was actually given off by the water that accompanied the acids.

Cavendish subsequently investigated some of the properties of his inflammable air. He performed many experiments using an electrical spark to fire the gas mixed with ordinary air in varying proportions and noting the loudness of the resulting explosion. Thus “with 7 parts of inflammable to 3 of common air, there was a very gentle bounce or rather puff; it continued burning for some seconds in the belly of the bottle”. His conclusion was that “from these experiments this air, like other inflammable substances, cannot burn without the assistance of common air. It seems, too, that unless the mixture contains more common than inflammable air, the common air, therein, is not sufficient to consume the whole of the inflammable air, whereby part of the inflammable air remains, and burns by means of the common air, which rushes into the bottle after the explosion”. Inflammable gas did not lose its elasticity during storage and sparingly soluble in water and in fixed or volatile alkalis. The next experiments were concerned with attempts to determine the relative density of the gas compared with that of air. Two methods were employed, the first consisted in weighing a bladder when filled with the gas and when empty, and the second was that of loss of weight. The gas was generated by the action of zinc or iron on dilute hydrogen chloride or sulphuric acid within an apparatus from which it escaped after being dried by potassium carbonate. The

¹ According to Cavendish factitious air is any kind of air, which is contained in other bodies in an unelastic state, and is produced from thence by art.

whole apparatus was weighed before and after the reaction had taken place. Cavendish concluded that inflammable gas was about 8,760 times lighter than water, or eleven times more than air.

Cavendish also tried to dissolve copper with hydrogen chloride and found that although the reaction did not generate inflammable air it produced “a gas which immediately loses its elasticity, as soon as it comes in contact with water”. He did not examine the characteristics of this elastic fluid (gaseous hydrogen chloride).

The second section of Cavendish’s paper deals with *Experiments on Fixed Air, or that Species of Factitious Air, Which is Produced from Alkaline Substances, by Solution in Acids or by Calcination*. In this study on carbon dioxide Cavendish made several experiments on the weight of the gas, which was evolved from different carbonates (marble, ammonium, and potassium carbonates) by the action of acids; determined some of the properties of the gas, such as its density and solubility in water and other liquids.

Cavendish also tested the elastic fluid extracted from chalk and alkalis and compared it with the air produced by fermentation and putrefaction and with that found at the bottom of wells, caves, and mines. He found that all these gases had the same properties and were, in fact, identical. He called this gas *fixed air*. He determined the density of fixed air and found it to be a third higher than that of ordinary air, a result that explained why fixed air was found in caves and low places. Furthermore, he discovered that fixed air combined with water and the solution was capable of dissolving limestone and iron, a property that accounted for the formation of stalactites and the presence of iron in mineral waters (Cuvier, 1811).

The concluding section of Cavendish’s paper is entitled *Containing Experiments on the Air, Produced by Fermentation or Putrefaction*. It was already known that carbon dioxide was produced during fermentation and Cavendish tried to determine whether any other gas was evolved simultaneously when fermenting brown sugar and apple juice with yeast. With brown sugar he found “that there is not the least of any kind of air discharged from the sugar and water by fermentation, but what is absorbed by the *sope lees* (a solution of potassium hydroxide), and which may therefore be reasonable supposed to be fixed air”.

Cavendish found that the putrefaction of gravy broth generated a mixture of gases, as only partly the gas produced was absorbed by “*sope lees*”. The soluble part thus consisted of fixed air, while the insol-

uble residue when mixed with common air “took fire on applying a piece of lighted paper, and went off with a gentle bounce”. Based on the loudness of the explosions Cavendish concluded that this sort of inflammable gas was nearly of the same kind as that produced by the action of acids on metals.

From what we know today about fermentation it can be assumed that the inflammable gas that Cavendish obtained after removing the carbon dioxide was a variable mixture of hydrogen, methane, and carbon monoxide.

In two additional papers (Cavendish, 1784, 1785) Cavendish described his findings about the formation of nitric acid when mixtures of nitrogen and oxygen were sparked in the presence of moisture. Most of his experiments were performed in a simple apparatus consisting of a narrow glass tube, bent nearly at a right angle, and containing mercury with the open ends dipping into vessels containing the same liquid. The bend of the tube was uppermost, and the gases, which were to be subjected to the action of the spark, were admitted over the mercury so as to occupy a space within the bend. Liquid such as alkaline solutions could be admitted above the surface of the mercury so as to absorb the products of the reaction. Cavendish made a series of experiments using limewater, which demonstrated conclusively that carbon dioxide was not produced when air was sparked. He also showed that sparking either pure oxygen or pure nitrogen produced no diminution in volume, but a contraction always occurred when a mixture of the two gases was subjected to the action of the spark. In the latter case his experiments yielded an unexpected result: “When the electric spark was made to pass through common air, included between short columns of a solution of litmus, the solution acquired a red colour, and the air as diminished, conformably to what was observed by Dr. Priestley. When lime water was used, instead of the solution of litmus, and the spark continued till the air could be no further diminished, not the least cloud could be perceived in the lime water, but the air was reduced to 2/3 of its original bulk, which is a greater diminution than it could have suffered by mere phlogistication, as that is very little more than 1/6 of the whole. Neither was any cloud produced when fixed air was let up to it; but on the further addition of a little caustic volatile alkali, a brown sediment was immediately perceived. Hence we can conclude that the limewater was saturated by some acid formed during the operation the brown col-

our of the sediment, it most likely proceeded from some of the quicksilver having been dissolved. We may safely conclude, that in the present experiments the phlogisticated air was enabled, by means of the electrical spark, to unite to, or form a chemical composition with the dephlogisticated air, and was thus reduced to nitrous acid, which united to the soap- lees and formed a solution of nitre the soap- lees being then poured out of the tube, and separated from the quicksilver, seemed to be perfectly neutralized as they did not at all discolour paper tinged with the juice of blue flowers. Being evaporated to dryness, they left a small quantity of salt, which was evidently nitre, as appeared by the manner in which paper, impregnated with a solution of it burned”.

Cavendish reported that “when five parts of pure dephlogisticated air were mixed with three parts of common air almost the whole of the air was made to disappear” when sparked over “soap- lees”. This conclusion is of interest and significant because Cavendish was stating definitely that he regarded the atmosphere as consisting of a mixture of nitrogen and oxygen: “It must be considered that common air consists of one part of dephlogisticated air, mixed with four of phlogisticated, so that a mixture of five parts of pure dephlogisticated air, and three of common air, is the same thing as a mixture of seven parts of dephlogisticated air with three of phlogisticated”.

During these experiments Cavendish made another discovery of great importance, which he did not pursue further and remained completely ignored for almost one century, until John William Strutt (Lord Rayleigh, 1842-1919) recognized its significance in connexion with some puzzling results which he had obtained in his determinations of the density of nitrogen. Rayleigh had observed that the density of atmospheric nitrogen was greater than that of nitrogen prepared from its compounds. Although the difference was very small, it was large enough to understand that it could not be due to experimental error. Having abandoned ideas of light impurities in chemical nitrogen, Rayleigh concluded that atmospheric nitrogen must contain a small proportion of a heavy gas, and having recalled Cavendish’s forgotten experiment, continued the work, which led to the discovery of argon and the other inert gases.

In 1778 Cavendish published another paper in which he reported corrected results of his first experiments (Cavendish, 1778).

3. *The water controversy*

Several chemists had noted that the burning of inflammable air deposited dew on the walls of the vessel. In 1766, Pierre-Joseph Macquer (1718-1784) while studying the possibility that a flame of inflammable gas evolved smoke or soot, observed that whenever a glass vessel was held over the burning jet, moisture formed inside the vessel, which he assumed to be water (Macquer, 1766). In the same year, and independently of Macquer, John Warltire observed that when a jet of inflammable gas was allowed to burn under a bell jar, closed below and containing air, until the flame went out, “immediately after the flame was extinguished there appeared through almost the whole of the received a fine powdery substance like a whitish cloud, and that the air left in the glass was perfectly noxious”. Warltire explained this result by the supposition that the gases contained some water diffused through them, and that that this, being condensed, appeared in drops on the sides of the containing vessel. Warltire paid little attention to this result because he was interested in determining whether heat has weight or not. In further experimentation he used a closed copper vessel, holding about three pints, to avoid the risk of injury from explosions. He weighted the vessel before and after the explosion and to his surprise he found that a loss of weight of about two grains always occurred, although the vessel was hermetically closed so that no air could escape by the explosion. He repeated his experiments using glass vessels and again he found the same loss in weight but now he also noticed that the inside of the glass, though clean and dry before, immediately became dewy. To Priestley, these results confirmed his opinion that common air deposits its moisture by phlogistication (Priestley, 1781).

The formation of dew was neglected as an irrelevant effect but all except Cavendish who thought that perhaps the dew was what was left behind as phlogiston was released from inflammable air. Cavendish, intrigued by the loss in weight, decided to repeat Warltire’s experiments using a larger vessel to be sure that the weight loss was not caused by errors in weighing. His results contradicted those of Warltire: “The experiment did not succeed with me; for though the vessel I used held more than Mr. Warltire’s, namely 24,000 grains of water (1 lb = 7,000 grains), and though the experiment was repeated several times with different proportions of common and inflammable air, I could never perceive a loss of

weight of more than one-fifth of grain, and commonly none at all. In all the experiments the inside of the glass globe became dewy, as observed by Mr. Warltire". Cavendish analysed his results and concluded that "423 measures of inflammable air are nearly sufficient to completely phlogisticate 1,000 of common air; and that the bulk of the air remaining after the explosion is then very little more than four-fifths of the common air employed, so that we can safely conclude that when they are mixed in this proportion and exploded, almost all of the inflammable air and about one-fifth of the common air lose their elasticity, and are condensed into the dew which lines the glass".

Additional experiments to identify the nature of the liquid phase led him to conclude that: "by this experiment it appears that this dew is plain water, and consequently that almost all the inflammable air, and about one-fifth of the common air are turned into pure water". The air has disappeared in the ratio two to one (Cavendish, 1784, 1785).

Shortly after Cavendish made public his findings about the burning of inflammable air and the formation of water, James Watt came forward with the claim that he had announced the same result on a previous date, and afterwards, Antoine-Laurent Lavoisier (1743-1794) declared that he had discovered the compound nature of water before, and independently of either. A controversy accordingly arose in which Cavendish and Watt disputed with each other the priority of the discovery while at the same time they rejected Lavoisier's arguments regarding the identification of the composition of water. This dispute not only was not settled during the lifetime of the claimants, every so often it continues to flare again in the literature (Schofield, 1963; Miller, 2002).

This "paternity" controversy was caused a series of fortuitous events. Cavendish reported his findings to Joseph Priestley (1733-1804), who repeated the experiments and reported them to James Watt (1736-1819). In a letter that circulated among members of the Royal Society, Watt gave his interpretation of the experiments. Hearing about Cavendish's experiments and Watt's conclusions from Charles Blagden (1748-1820) on a trip to Paris in 1783, Antoine-Laurent Lavoisier (1743-1794) did experiments of his own and wrote an account of them (Lavoisier, 1781). As noted by Wilson (Wilson, 1851) although the original claims were founded on similar experiments, Cavendish, Watt, and Lavoisier arrived at

their conclusions while performing them for different purposes. Cavendish was investigating the products of combustion; Watt was studying the changes that a vapor may undergo if all its latent heat became sensible; and Lavoisier was seeking in the combustion of inflammable gases for additional proofs of the truth of his view that oxygen is the great acidifying agent.

In June 1783 Lavoisier, after learning that Cavendish had obtained water by burning a mixture of inflammable air and dephlogisticated air understood immediately the remarkable significance of this result and explained it by saying that water was a compound of both gases (Lavoisier, 1781). With this explanation he had the key for the difference between the reaction of a metal or its calx with an acid, by admitting that water participated in the reaction. In the first reaction water decomposed and released its inflammable gas and dephlogisticated air (oxygen). The latter combined with the metal to yield the metallic calx (the term 'oxide' had not been defined yet). The second reaction was simply the combination of the acid with the calx to give the pertinent salt.

Lavoisier's hypothesis about the composition of water was further demonstrated by its decomposition (Lavoisier, 1786). The experiments were witnessed and controlled by a commission appointed by the Académie de Sciences, which included, among others, Claude-Louis Berthollet (1748-1822) and Gaspard Monge (1746-1818). Water was contacted with hot iron filings, which rusted, giving off inflammable air. The weight of the inflammable air plus the weight gain of the rusted filings was shown to be equal to the weight of the water consumed. The commission's report included the following statements: "One of the parts of the modern doctrine the most solidly established, is the formation, decomposition, and recomposition of water. And how can we doubt it, when we see that in burning together fifteen grains of inflammable air and eighty-five of vital air, we obtain exactly one hundred grains of water, in which, by decomposition, we find again the same principles and in the same proportions. If we doubt of a truth established by experiments so simple and palpable, there would be nothing certain in natural philosophy".

This interpretation was accepted gradually but it was, however, powerless to convince Priestley, who remained faithful to the phlogiston theory until his death. The phlogiston theory was now on its way out to be replaced by Lavoisier's new chemistry.

4. Heat

Cavendish did research on different aspects of the thermodynamics of sensible and latent heat, at intervals over a period of some thirty years of his scientific activities. The range of his studies included thermometry, dilation of gases, specific heats, latent heats of fusion and vaporization, and the properties of freezing mixtures. He published only his findings on thermometry and freezing mixtures; the rest remained recorded in his laboratory notes (Maxwell *et al.*, 1921; Cavendish, 1783, 1786, 1788).

Measurements of temperature by observations of the thermal expansion of liquids before Cavendish's time had been widely made, but had scarcely attained any degree of precision (Wisniak, 2000). Various liquids were used as thermometric substances, such as alcohol (spirit of wine), linseed oil, and mercury. The use of fixed points, particularly those of the melting point of ice and the boiling point of water, in the construction of thermometric scales appear to have originated before 1701, when Newton published a short note on the subject, entitled *scala graduum caloris*.

In November 1773 the Council of the Royal Society decided that daily observations should be made at their house with the barometer, thermometer, rain gage, wind gage, and hygrometer. Cavendish was appointed to direct and supervise the observational work, and this led to the publication of his paper entitled *An Account of the Meteorological Instruments Used at the Royal Society's House* (Cavendish, 1776b). This paper was divided into four sections, the first of which dealt with the thermometers, the second with the barometer, rain gage, wind gage, and hygrometer, the third with the variation compass, and the fourth with the dipping needle.

Cavendish realized immediately that when the bulb of a thermometer was submerged in a hot liquid the difference in temperatures between the bulb and the stem of the instrument could lead to a significant error in the true temperature. He stated that the only accurate method was to take care that all parts of the thermometric fluid be heated equally: "for a thermometer dipped into a liquor of the heat of boiling water will stand at least 2° higher, if it is immersed to such a depth that the quicksilver in the tube is heated to the same degree as that in the ball, than if it is immersed no lower than the freezing point, and the rest of the tube is not much warmer than the air. The only accurate method is to take care that all parts of the quicksilver should be heated

equally. For this reason, in trying the heat of liquors much hotter than or colder than the air, the thermometer ought if possible to be immersed almost as far as the top of the column of the quicksilver in the tube" (Cavendish, 1788). He understood that his was not an easy operational feature so he drew a table of corrections to be applied to the observed readings. His table was based on the coefficient of expansion of mercury, which he expressed by stating: "quicksilver expands 11500th part of its bulk for each degree of heat".

Cavendish also drew attention to the precautions that had to be taken when fixing the boiling point of water in mercury thermometers; at a meeting of the Royal Society on April 18, 1766 he used a number of thermometers to give a practical demonstration on the best conditions for fixing the boiling point of water.

Cavendish measured the vapor pressure of water between 52° and 172° F using the constant volume method and obtained results very close to those that Victor Regnault (1810-1878) would obtain almost 50 years later (Regnault, 1847). Afterwards, he proceeded to measure the coefficient of expansion of atmospheric air, nitrous air (nitric oxide), fixed air (carbon dioxide), heavy inflammable air (presumably a mixture derived from the destructive distillation of wood, or from heated coal), dephlogisticated air (oxygen), phlogisticated air (nitrogen), and inflammable air (hydrogen). It was well known long time before the time of Cavendish that air expands to a much greater extent than solids and liquids do under the influence of heat; some quantitative determinations had been made by various experimentalists but there was no agreement between their results. Cavendish's method was based on varying the pressure of the gas so as to maintain the volume constant, a procedure that in 1847 Regnault would claim to be the most accurate (Wisniak, 2001). The resulting values of the thermal coefficient of expansion were mostly about 1/370 for one degree Fahrenheit (1/205 in the centigrade scale). From this Cavendish concluded that different gases had the same thermal coefficient of expansion.

The experiments by which Cavendish was led to the discovery of specific and latent heat appear to have originated in connection with the question as to whether the mixing of equal quantities of water at different temperatures would result in the final temperature being the arithmetical mean of the two. It was widely held that such would not be the case. For

example, according to Jean André De Luc (1727-1817) when equal weights of water at 212°F and 32°F respectively were mixed, the final temperature was only slightly lower (119°F !) than the hotter one. Cavendish was able to show that when known weights of water at different temperatures are mixed together, the heat lost by the hotter liquid is strictly equal to the heat gained by the colder one. Here, without realizing it, he was anticipating the concept of enthalpy.

In the course of this work Cavendish discovered that when different substances at different temperatures were mixed, the above simple rule no longer held, that is, the final temperature was not determined in the same way as when quantities of the same substance at different temperatures were mixed. Substances accordingly were found to differ as regards their thermal capacity. Cavendish described this property as “the effect of substance in heating or cooling others”, which is the same thing as specific heat, or the thermal capacity per unit mass.

By these trials Cavendish justified the truth of his proposition “that on mixing hot and cold water the quantity of heat in the liquors taken together should be the same after the mixing as before, or that the hot water should communicate as much heat to the cold water as it lost itself”. He then proceeded to try the effect of mixing unlike liquids initially at different temperatures. He described these experiments with the following significant note: “One would naturally imagine that if cold mercury or any other substance is added to hot water, the heat of the mixture would be the same as if an equal amount of water of the same degree of heat had been added, or in other words that all bodies heat and cool each other when mixed together equally in proportion to their weights. The following experiments will show that this is far from being the case”. His first experiments led to the general result that “hot water is cooled near as much by the addition of one part of cold water as by that of 30 parts of mercury of the same heat”. Repetition of the experiments with other substances led him to the general conclusion that “it would seem, therefore, to be a constant rule that when the effects of any two bodies in cooling one substance are found to bear a certain proportion to each other, that their effects in heating or cooling any other substance will bear the same proportion to each other. The true explanation of these phenomena seems to be that it requires a greater quantity of

heat to raise the heat of some bodies a given number of degrees by the thermometer, than it does to raise other bodies the same number of degrees”.

Between 1783 and 1786 Cavendish published three papers related to the freezing of pure substances and mixtures, in particular mercury, nitric acid, sulphuric acid, and spirit of wine (Maxwell *et al.*, 1921, Cavendish, 1786, 1788). These papers were commentaries about observations made in North America by officers of the Hudson Bay Company on the effect of strong natural cold on the above mentioned substances. The observations were made under Cavendish's guidance and financed by him. In a way, these experiments were a sequel of Cavendish's previous work on the correct calibration of the mercury thermometer. From the times of the alchemists it was universally believed that mercury could not be frozen at the lowest temperature so far attainable. It was believed that mercury owed its apparent permanent fluidity to some anomalous peculiarity. Then, on December 1759, Braun of St. Petersburg, when using a mixture of snow and nitric acid observed that the mercury in the thermometer sank to such a depth that by extrapolation from 0°F the observed depths represented temperatures of several hundred degrees below 0°; some measurements corresponding even to -556°F (!). In this situation Braun found that the mercury was completely solidified. His measurement of the temperature was, however, completely erroneous because he did not take into account the contraction of mercury during cooling and, also, that mercury, contrary to water, contracts during solidification; he simply assumed that the descent of the mercury in the stem took place while the mercury was in the liquid state. Thomas Hutchins, who was to become Governor of Albany Fort at Hudson's Bay, performed additional experiments during the winter there and also found that mercury could be frozen. Cavendish understood Braun's errors and requested from Hutchins to perform additional experiments in which mercury was frozen not in the tube of the thermometer, but in a separate vessel, in which the thermometer was immersed, and taking adequate measurements to avoid the freezing of the whole mass of mercury. From his early experiments on latent heats Cavendish was already aware that the temperature remains constant during a change in phase. In this manner it was found that the freezing temperature of mercury was somewhere between 39° to 40° F below zero (Cavendish, 1783). In the latter publication Cavendish remarked

that the cause of the rise in temperature that takes place during freezing is to be thought in the general principle “that all, or almost all, bodies by changing from a fluid to a solid state, or from the state of an elastic to that of an inelastic fluid, generate heat; and that cold is produced by the contrary process” (Maxwell *et al.*, 1921).

5. Density of the Earth

Newton’s theory of gravitation explained the motion of terrestrial objects and celestial bodies by postulating that pairs of massive objects attracted each other with a force proportional to the product of the two masses and inversely proportional to the square of the distance between them. In his book *Principia* (Newton, 1687) Newton reported the relative densities of the Sun, Jupiter, Saturn, and the Earth as 100, 94.5, 67, and 400, respectively, so that if the density of the Earth were known the densities of the Sun and the two planets could be calculated. On the basis of the known density of rocks at the surface of the Earth and rocks from mines, Newton guessed that the average density of the Earth is 5 to 6 times the density of water (Newton, 1687). After Newton, and at different times, British and French scientists attempted to weigh the Earth by observing the gravitational force on a test mass from a nearly large mountain. The experimental procedure involved measuring the line of a pendulum hung near a mountain and comparing it to the line expected if the mountain was not there. These effects were hampered, however, by a very imperfect knowledge of the composition and average density of the rock composing the mountain. The interference of nearby masses on the free oscillation of a pendulum was well known from Newton’s time; he was aware that the time of vibration of a pendulum varied according to the latitude, and indeed observations on the length of the seconds pendulum in different parts of the world had been made in his time. The length of the seconds pendulum was also shown to decrease with an increase in height, but this was not in agreement with the inverse square law of the distance as reckoned from the center of the Earth.

The determination of the structure and composition of the interior of the Earth was one of the many subjects that interested Cavendish. In an exchange of letters with his friend John Mitchell (1724-1793) they discussed the possibility of devising an experiment to weigh the Earth. Mitchell suggested an arrangement similar to the one used by Charles

Coulomb (1736-1806) for measuring the electrical force between small charged metal spheres, that is, using a torsion balance to detect the very small gravitational attraction between metal spheres. Mitchell built a first prototype of the equipment but died (1793) before he was able to conduct the experiments.

The apparatus eventually was moved to Cavendish’s laboratory where he rebuilt most of it. His balance was constructed from a 6-foot wooden rod suspended at his middle point by a long metal fiber and carrying two 2-inch diameter lead spheres at each extremity; this dumbbell had a period of about 7 minutes when it was disturbed. The rod was thus capable of vibrating in a horizontal plane. Two 350-pound lead spheres, brought close to the enclosure housing the rod provided the attraction effect. In this way vibrations were set up between the attractive force and the torsion of the wire and equilibrium was determined between the turning moment and the moment of torsion.

Cavendish was aware that the force with which the balls would be attracted by the weights was very small (not more than one fifty-millionth part of their weight) so that air currents set up by changes of temperature could easily vitiate the measurements. Accordingly, he mounted a finely ruled scale near the end of the dumbbell, which could be read to one-hundredth of an inch resolution. He enclosed the apparatus in a mahogany case, placed the whole arrangement in a shut room, and observed the motion of the arm from the outside, by means of a telescope. Observations were made of the natural period of the pendulum and its displacement from rest by the attraction of the external lead spheres, twisting the pendulum first in one direction and then in the other. In addition, the observations were performed with the attractive spheres in three positions, which Cavendish designated as positive, negative, and midway position, respectively.

Cavendish’s paper contains a detailed account of the calculation method, as well as of the necessary corrections; he made seventeen experiments and arrived at the result that the density of the Earth should be 5.48 greater than that of water (Cavendish, 1798). In 1841 Francis Baily (1774-1844) reviewed Cavendish’s calculations and found a small mistake of simple arithmetic that decreased the expected density of the Earth from 5.48 to 5.45 (Berry, 1960). The present accepted value of the average mean density of the Earth is 5.52 times the density of water.

Cuvier was so impressed by the elegance of

Cavendish's method that he wrote: "Archimedes needed a fulcrum in order to move the Earth, but Cavendish needed none to weight it". Cavendish equipment and experiment are so clever and simple to build and perform that it is usually part of the standard experiments performed in many teaching physics laboratories; it is known under the name "the Cavendish experiment".

6. Electricity

Up to the seventeenth century all the knowledge about electricity was basically what the Greeks knew at the time of Tales of Miletus (625-547 BCE), that when amber was rubbed it acquired the ability to pick up light bodies. There was also no clear distinction between electricity and magnetism. Although the electrostatic machine developed by Otto von Guericke (1602-1686) in 1660 was well known, its workings were far from being understood. A crucial step took place in 1745-1746 when Ewald Georg von Kleist (1700-1748) and Pieter van Musschenbroek (1692-1761) discovered the Leyden jar. This discovery led to a flurry of experimentation during which many more facts were added about electrical phenomena. The fundamental differences between conductors and insulators became better known, as well as the phenomena of electrification by induction and by friction. At the time when Cavendish began his work on electrostatics there was a fairly considerable knowledge of the qualitative features of the subject. As stated in the *Encyclopedie* (Diderot, 1751) of Denis Diderot (1713-1784), although physicists did not agree on the cause of electricity, they agreed on the existence of electrical matter, concentrated more or less in electrified bodies. Movement of this particular matter produced the effects observed, but the explanations of the same disagreed. Two rival theories had been put forward for explaining the familiar phenomena of electricity, the two-fluid and the one-fluid theories.

The two-fluid theory, associated with the names of Charles François de Cisternay Du Fay (1698-1739; a great lieutenant of Louis XV and superintendent of the royal gardens at Versailles) and Robert Symmer (1707-1763), arose as a result of the differences which had been observed when materials such as glass on the one hand, and amber and other resinous bodies on the other, were electrified by friction. According to Du Fay: "Thus there exists two electricities of distinct nature, to wit that of transparent and solid bodies like glass, crystal, etc., and that of

bituminous or resinous bodies like amber, copal, sealing wax, etc. Both kinds repel all such as are of the same electricity as their own, but, on the contrary, attract all such as are of different electricity. I shall call the one resinous electricity and the other vitreous electricity."

The one-fluid theory appears to have originated with Benjamin Franklin (1706-1790), who regarded all electrical phenomena in terms of a body being either over or undercharged. For Franklin, electrical matter consisted of particles extremely subtle, since it could permeate common matter with no difficulty. Common matter was a kind of sponge of the electric fluid. In common matter there was as much of the electrical as it would contain within its substance. If more was added then it would lie on the surface and form what Franklin called an electrical atmosphere. A body having an electrical atmosphere was said to be electrified. According to Franklin's theory, a positively charged body was regarded as having a redundancy of electricity, while a deficiency of electricity was synonymous with its being negatively charged. The state of an uncharged body was accordingly regarded in terms of there being no excess or defect of the electric fluid (Franklin, 1751). In terms of the two-fluid theory an uncharged body was supposed to contain both fluids in a condition comparable with that of a product resulting from their mutual neutralization, and electrification was regarded as a consequence of the separation of the two fundamental fluids. In summary, according to Franklin, Du Fay's two fluids were actually two aspects of the same force: excess and a deficiency of the electric fluid, which he named positive and negative electricity.

Franklin's theory of the existence of an electric atmosphere was unable to provide a satisfactory explanation to the experimental fact that bodies charged negatively (having less than the common quantity of electricity) repelled as well as those that have more. This difficulty was removed when in 1759 Franz Maria Ulrich Theodosius Aepinus (1724-1802) proposed the hypothesis that when molecules of common matter were deprived of their normal electricity they repelled each other exactly like the particles of electrical matter. Aepinus was led to this explanation by his discovery of piezoelectricity (when tourmaline crystals are heated they develop opposite electric charges at the ends of their polar axes). The discovery of electric poles also convinced Aepinus that there must be a close connection between electric and magnetic induction.

The one and two-fluid theories were capable of providing some understanding of the fundamental principles of electrostatics, and particularly of the phenomena of attraction and repulsion. Aepinus and Cavendish supported the one fluid theory, while Charles Coulomb (1736-1806) seemed to have preferred the two-fluid theory, which was later developed mathematically by Siméon-Denis Poisson (1781-1840).

Franklin had defined the concept of electrical charge or amount of electricity, but neither him nor his successors had been able to measure it. Most of the concepts were still qualitative. It was left to Cavendish and Coulomb to transform electricity into a quantitative science.

Cavendish published only two papers on the subject of electricity (Cavendish, 1771, 1776a), the rest of his many findings remained as unpublished manuscripts. The first paper (Cavendish, 1771) was almost completely theoretical. Cavendish started from the theory of Aepinus assuming that electricity was caused by an elastic fluid (electric fluid) interspersed between the particles of bodies and surrounding the bodies themselves in the form of an atmosphere. Although this atmosphere was located at a very small distance from the body, its attractive and repulsive power extended to very considerable distances. The particles of the electric fluid repelled each other and attracted particles of all other matter with a force inversely proportional as some less power of the distance than the cube. The particles of all matter also repelled each other, and attracted those of the electric fluid with a force varying according to the same power of the distances. Cavendish gave two fundamental definitions regarding bodies being positively or negatively electrified: (1) the notion of degree of electrification of a conductor, which he later denominated the compression of electricity (today: electric potential); when the fluid within any body was more compressed than in its natural state he called the body positively electrified; when it was less compressed he called it negatively electrified, and (2) when any body contained more of the electric fluid than it did in its natural state, he called it overcharged, and vice versa.

Cavendish put forward the following arguments to demonstrate that the law of the inverse square of the distance governed electrostatic attraction and repulsion: if electric attraction and repulsion were inversely proportional to some higher power of the distance than the cube, a particle could not have

been sensibly affected by the repulsion of any fluid, except what was placed close to it. If the repulsion was inversely as the cube of the distance, a particle could not be sensibly affected by the repulsion of any finite quantity of fluid, except what was close to it. But as the repulsion was supposed to be inversely as some power of the distance less than the cube, a particle could be sensibly affected by the repulsion of a finite quantity of fluid placed at a finite distance from it. His reasoning that there could not be electrostatic force within a closed spherical contained was based on Newton's gravitational theory. He then showed that it is "likely that it is inversely as the square", for only on that assumption one could explain the absence of electrical force inside a hollow sphere, or the surface charges of sphere and plane parallel plates, and the phenomenon of electric induction.

Further unpublished work (1772-1773) described Cavendish's ingenious experiment to demonstrate that all points inside an electrified hollow sphere are electrically neutral so that the "redundant fluid" (electrical charge) is lodged entirely on its surface. He also provided the definition of electrostatic capacity: the charges of two conductors that are electrified to "the same degree" are proportional to the capacities. The capacity could be measured directly by discharging the conductors by means of a test plane. Cavendish also discovered that the capacity of condensers of equal dimensions varies according to the substance employed to separate the plates. The latter result, which would later be rediscovered by Michael Faraday (1791-1867), would lead to the definition and measurement of the dielectric constant.

A large part of Cavendish's experimental work on electricity was concerned with measurements of the capacity of conductors and a comparison of the electrical conductivities of various bodies (Maxwell *et al.*, 1921). According to his results "iron wire conducts roughly 400 million better than rain or dishwater; that is, the electricity meets no more resistance in passing through a piece of iron wire 400,000,000 inches long, than through a column of water of the same diameter only one inch long. Seawater conducts 100 times, and a saturated solution of sea salt about 720 times, better than rain water." Much of his work was concerned with finding the ratios of the charges of various bodies of different shapes and sizes to that of a sphere 12.1 inches in diameter, all bodies being equally electrified (charged to the same potential). These findings carried

with them the concept, which would later be known as Ohm's law. ▣

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