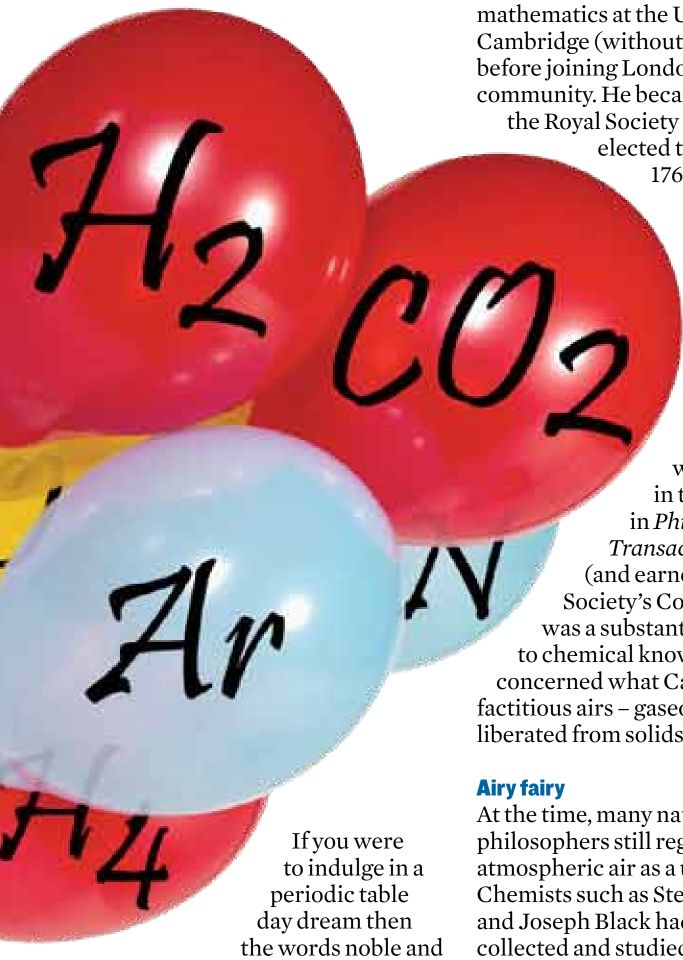
Airs and graces

Henry Cavendish was instrumental in unveiling the components of the air that we breathe. Mike Sutton looks back at his life



If you were to indulge in a periodic table day dream then the words noble and inert, linked to argon and its neighbours, may conjure images of lordly idleness. Such an association would be appropriate, if somewhat ironic. The first person to detect inert gases was indeed an aristocrat, but one who obsessively pursued an active career and was acclaimed as the greatest English scientist since Sir Isaac Newton.

Henry Cavendish (1731–1810) was grandson to two dukes – Devonshire on his father's side, Kent on his mother's. As the younger son of a younger son he was off the main line of inheritance, but still had a very adequate personal income. Other young men in his position might have gone into the church, the army or parliament, become patrons of literature and the arts, or simply led lives of pleasurable indolence. Cavendish, however, devoted himself to physics and chemistry.

His father, Lord Charles Cavendish, was an amateur scientist and a fellow of the Royal Society. He ensured that his son acquired a modern education by sending him to the forward-thinking Dr Newcome's Hackney Academy, rather than to the public school Eton. Cavendish then spent 3 years studying mathematics at the University of Cambridge (without taking a degree) before joining London's scientific community. He became a fellow of the Royal Society in 1760 and was elected to its council in 1765.

Cavendish took an active interest in mathematics, astronomy, meteorology and physics. But his first scientific publication, which appeared in three parts in *Philosophical Transactions* in 1766 (and earned him the Royal Society's Copley medal), was a substantial contribution to chemical knowledge. It concerned what Cavendish called factitious airs – gaseous substances liberated from solids by heat or acids.

Airy fairy

At the time, many natural philosophers still regarded atmospheric air as a unitary element. Chemists such as Stephen Hales and Joseph Black had previously collected and studied other 'airs', but their chemical nature was not well understood. Cavendish, however, developed ingenious new ways to capture and store gases released during chemical reactions, enabling him to measure precisely their volumes and weights.

Part one of Cavendish's 1766 paper concerned the inflammable air – hydrogen, as we now call it – which was liberated by dissolving metals in acids. Others, including Robert Boyle, had collected and burned the gas, but Cavendish was the first to study it quantitatively, estimating it to be 11 times less dense than common air. He showed that fixed weights of zinc, iron or tin released the same quantity of the gas, regardless of whether they were dissolved in spirit of salt (hydrochloric acid) or dilute oil of vitriol (sulfuric acid).

So Cavendish reached the reasonable (but erroneous) conclusion that inflammable air was a constituent of zinc, iron and tin and liberated by acids. He seems to have suspected that the 'air' might actually be pure phlogiston, the fiery matter which early modern chemists like Ernst Stahl (1660–1734) believed to exist in all combustible substances. However, he also considered the possibility that it was a more complex substance in which phlogiston played some part.

Part two of Cavendish's paper concerned fixed air (carbon dioxide). Heating chalk or limestone to produce quicklime (needed for making mortar and cement) was known to release an 'air' which could cause death if inhaled. Black studied it in the 1750s while investigating the medicinal properties of magnesia alba (basic magnesium carbonate). He showed that the fixed air produced by heating limestone was identical to the 'air' released when mineral acids reacted with chalk and other calcareous substances, and to the 'air' generated during alcoholic fermentation.

Cavendish repeated Black's experiments with greater precision, collecting the fixed air over mercury since it was soluble in water. He calculated its density as 1.57 times that of common air – reasonably close to the correct figure of 1.65 – and measured with moderate accuracy the quantity of gas produced by the action of acids on mineral carbonates and bicarbonates. For example, he found that 1000 units of marble (calcium carbonate) contained 407 or 408 units by weight of carbon dioxide; the actual figure is 440.

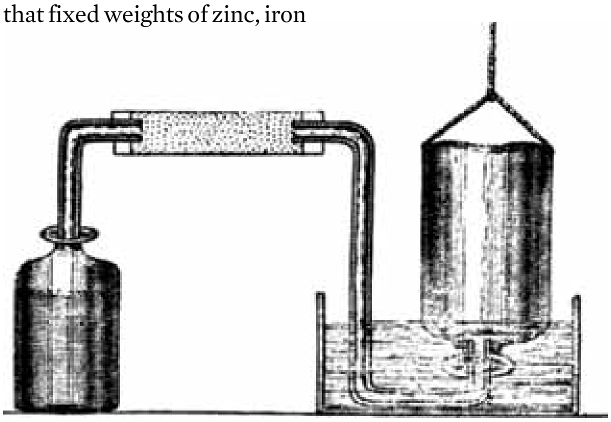
Part three of Cavendish's massive work examined the 'airs' released by fermentation, and by decaying animal and vegetable material. A Scots-Irish chemist and surgeon called David MacBride had identified carbon dioxide in the vapours emitted by putrefying organic matter. But it was Cavendish who showed that they also contained another inflammable air, different from the one produced by adding acids to metals. This heavier inflammable air appeared to consist mainly of marsh gas (methane).

Cavendish also compiled a lengthy manuscript which could

In short

- **Henry Cavendish's meticulous lab work helped to open scientists' eyes to the existence and properties of hydrogen, carbon dioxide and nitrogen**
- **He proved that the dew formed when hydrogen was exploded with oxygen was water**
- **He also isolated argon, which then remained unidentified for over 100 years**
- **He had an obsessive eye for detail and often considered his work unworthy of publication**

Cavendish apparatus for making and collecting hydrogen



potentially have become part four of his paper series. In it, he recorded experiments on other inflammable airs produced by heating organic solids such as wood shavings and hartshorn (red deer horn). Dissatisfied with inconclusive results, Cavendish characteristically abandoned this line of work, leaving it unfinished and unpublished. In fact, after producing one more chemical paper on the mineral content of pump water, Cavendish was to turn his back on chemistry for several years to focus instead on physics.

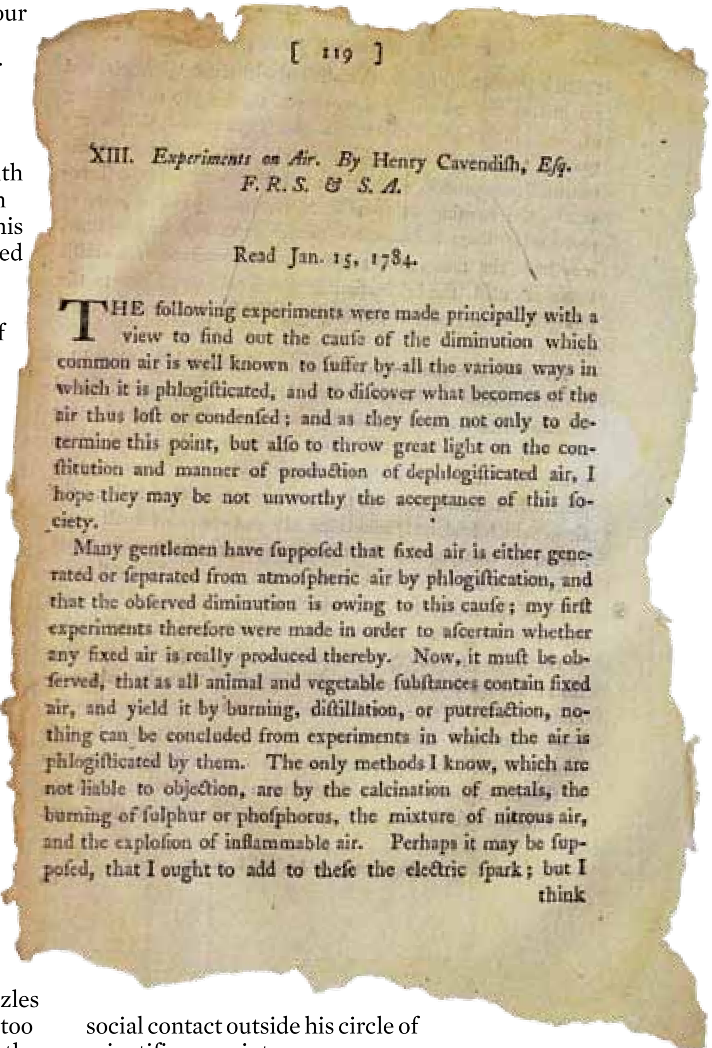
Physical pursuits

Cavendish published little during his physics period, despite performing countless experiments and covering copious pages with notes. Biographers attribute this to his near-obsessive perfectionism.

Cavendish certainly set himself high standards – his model was Newton's book *Principia Mathematica*. His extensive manuscript writings indicate that he hoped to deal with heat and electricity as authoritatively as Newton had handled gravitational attraction and inertial motion. Unfortunately, the puzzles Cavendish grappled with were too complex to be unravelled using the resources then available.

It took another century of effort by some outstanding experimenters and theorists to gain the comprehensive understanding of thermodynamics and electromagnetism that Cavendish sought. Some of his discoveries, if published, would have been valuable additions to scientific knowledge. But rather than present the world with work that was incomplete, he preferred to continue experimenting in private.

Such reticence was characteristic of Cavendish. One colleague noted that he had 'a most reserved disposition and particularly shy habits', while another recorded that he spoke 'with great difficulty and hesitation, and very seldom'. Often ill at ease with his fellow men of science, he was even more uncomfortable with his domestic servants – particularly the women. He instructed them to remain out of his sight at all times, and ordered his dinner by leaving a note on the hall table. Unsurprisingly, he never married, and always tried to avoid social contact outside his circle of scientific acquaintances.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XIII. *Experiments on Air. By* Henry Cavendiſh, *Eſq. F. R. S. & S. A.*

Read Jan. 15, 1784.

THE following experiments were made principally with a view 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, and to diſcover what becomes of the air thus loſt or condenſed; and as they ſeem not only to determine this point, but alſo to throw great light on the conſtitution and manner of production of dephlogiſticated air, I hope they may be not unworthy the acceptance of this ſociety.

Many gentlemen have ſuppoſed that fixed air is either generated or ſeparated from atmoſpheric air by phlogiſtication, and that the obſerved diminution is owing to this cauſe; my firſt experiments therefore were made in order to aſcertain whether any fixed air is really produced thereby. Now, it muſt be obſerved, that as all animal and vegetable ſubſtances contain fixed air, and yield it by burning, diſtillation, or putrefaction, nothing can be concluded from experiments in which the air is phlogiſticated by them. The only methods I know, which are not liable to objection, are by the calcination of metals, the burning of ſulphur or phoſphorus, the mixture of nitrous air, and the exploſion of inflammable air. Perhaps it may be ſuppoſed, that I ought to add to theſe the electric ſpark; but I think

PHILOSOPHICAL TRANSACTIONS

Cavendish's 1784 paper in *Philosophical Transactions* on the synthesis of water

Breath of fresh air

In 1781 Cavendish returned to chemistry with renewed energy. During the previous decade, Carl Scheele in Sweden and Joseph Priestley in England had discovered another new gas, oxygen. It was given various names, reflecting different theoretical interpretations of its origins and behaviour, but the one which eventually stuck was coined by a Frenchman, Antoine Lavoisier. Cavendish made a significant contribution to this unfolding drama.

Seventeenth century natural philosophers had shown that an enclosed body of atmospheric air could sustain animal life (or flames) for only a limited time but it remained unclear whether breath and fire contaminated the air, or consumed some vital portion of it. Scheele – an apothecary with a genius for chemical research – isolated this vital component in the early 1770s. He first called it vitriolic air, probably because he made it by heating manganese dioxide with oil of vitriol. But after obtaining the same gas from other substances without using acid – including saltpetre (potassium nitrate) and mercuric oxide – he renamed it fire air, because it accelerated combustion. Unfortunately for Scheele, publication of his discovery was delayed until 1777 and by then Priestley had already independently made the same discovery.

'He always tried to avoid social contact outside his circle of scientific acquaintances'

Priestley – a Unitarian minister, a lecturer at the Warrington Academy, and a fellow of the Royal Society – had scientific interests as broad as Cavendish's. He began studying fixed air in 1770 while living close to a brewery where it was readily obtainable, and he later published a pamphlet on the manufacture of artificial mineral water which launched the fizzy drink industry.

In 1772 Cavendish and Priestley discussed repeating research done by Hales, which involved adding aqua fortis (nitric acid) to various minerals and metals. When Priestley did the experiment he identified another gas which he called nitrous air (nitric oxide). In contact with atmospheric air, the nitrous air formed a reddish gas (nitrogen dioxide), which dissolved in water to leave a gaseous residue that no longer supported life or fire. He seized on this as a quantitative method for estimating the 'goodness' (oxygen content in our terms) of atmospheric air. Then, in 1774, Priestley produced what we now call oxygen by heating mercury's red oxide.

Cavendish and Priestley, like most of their contemporaries, still accepted the phlogiston theory of combustion. It seemed to them that Cavendish's inflammable air (hydrogen) must be (or must contain) phlogiston, while Scheele's fire air was starved of it. This seemingly explained why they combined explosively when stimulated by a flame or electric spark. But then Lavoisier proposed that combustion was not the loss of phlogiston but the gain of something (oxygen), supporting his claim by meticulously weighing the ingredients and products of combustion reactions.

However, it was not until Priestley visited Paris in 1774, and told Lavoisier about his own discovery of dephlogisticated air, that the French savant realised exactly what was gained during the process of combustion. At first he called the new gas eminently respirable air, but later named it oxygen, combining two Greek words meaning

acid-begetter to recognise the fact that many oxides were acidic when dissolved in water. Similarly, Lavoisier called Cavendish's inflammable air hydrogen – the water-begetter.

Feeling gassy

In 1781 another paper of Priestley's encouraged Cavendish once again to study gases. Priestley and his assistant John Warltire had exploded mixtures of atmospheric air and hydrogen with electric sparks and noticed dew forming inside the vessel. Cavendish, with his usual thoroughness, proved conclusively that this dew was pure water, produced by combining inflammable air with the dephlogisticated air (oxygen) which made up one fifth of atmospheric air. (He called the other four-fifths of the atmosphere phlogisticated air – air so saturated with fiery matter that it could absorb no more. We call it nitrogen.)

Cavendish told several investigators about his synthesis of water, and news of it soon reached Lavoisier who repeated the experiment. Before Cavendish's 'Experiments on air' papers had appeared in the *Philosophical Transactions* for 1784 and 1785, Lavoisier had incorporated it (without acknowledgement) into one of his own papers. English scientists were quick to protest and Lavoisier duly made amends.

Cavendish statue over the entrance to the original Cavendish laboratories in Cambridge, UK

'His final contribution to chemistry – discovering argon – was ignored for many years'

Another priority dispute began when the engineer and scientist James Watt accused Cavendish of plagiarising his research on the composition of water. This misunderstanding was apparently provoked by a malicious correspondent. After seeing Cavendish's paper Watt acknowledged that their theories were different and withdrew the accusations.

Cavendish was initially unconvinced by Lavoisier's account of combustion, pointing out that to identify oxidation so closely with acidity was a mistake, since some acids contain no oxygen. For some years, Cavendish continued to call oxygen dephlogisticated air, but gradually accepted the new nomenclature as it came into general use. Meanwhile, his final contribution to atmospheric chemistry was ignored, and remained so for many years.

By repeatedly sparking atmospheric nitrogen with excess oxygen in a closed container over water, Cavendish converted it into a soluble oxide. (In his language, the dephlogisticated air deprived the phlogisticated air of its phlogiston, converting it to acid.) He then absorbed the surplus oxygen with liver of sulfur (potassium sulfide). But an irreducible gaseous residue remained, occupying approximately 1/120th of the original volume. He published this observation in 1785, but was unable to explain it. It was not until 1894 that Lord Rayleigh and William Ramsay identified the residue as argon – the first of the noble gases to be discovered. As usual, the noble Cavendish was well ahead of his time.

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Further readng

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