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VIII.
DISSOLVING UNCERTAINTIES IN WATER: ELECTRIC FISHES, VOLTA'S ALARM BELL, HUMPHRY DAVY, AND A DYNAMICAL SCIENCE[1].

Wide-eyed in the new world of tropical Spanish America in the first years of the nineteenth century, Alexander von Humboldt, the archetype of scientific explorer, watched Indians drive wild horses through water in ponds infested by the dreaded *tembladores,* electric eels (gymnotus)[2]. The horses were badly shocked, terrified, occasionally even stunned and drowned, but the fish became thereby exhausted and could be caught, studied, and even eaten (they tasted disagreeable). These were more formidable than the *torpedo* familiar to fishermen in the Mediterranean[3]; and Humboldt experimented on them, becoming convinced that the shock happened only at the will of the animal. Au fait with the latest Parisian science, he had electrical apparatus with him, and delighted his host: 'Señor del Pozo could not contain his joy … the name of Galvani and Volta had not previously been heard in those vast solitudes'. Aware of work by Henry Cavendish, Humboldt knew the fish was somehow electrical[4].

Conscious of health and safety, we know that electricity and water don't mix; but in the years of revolution and romanticism around 1800 they fruitfully did. There are a number of questions that we can use them to answer, exploring the nature of matter and force: What sort of thing was electricity, and how many kinds were there?, What was water, an element or compound?, and How did research on electricity and water illuminate the mystery of elective affinity, promising to transform chemistry from a kind of exploring into a dynamical, fundamental science?

Electric shocks were familiar to late eighteenth-century natural philosophers, and to the audiences for their lectures and demonstrations. The electric fluid (or fluids), generated by friction in machines where a glass disc or globe rotated against a 'rubber' covered with soft cloth, would charge up a Leyden Jar, a glass vessel covered in tinfoil[5]. A collection of these jars was called a battery, a word that calls up visions of assault and artillery. Indeed, when a jar or battery of them was touched, you got a shock that might be transmitted through a chain of people holding hands and make them jump in unison. Experimenters calibrated themselves to measure electricity, by how severe the shock was. The effect for them was unpleasant; and when Benjamin Franklin drew down lightning with his kite, extremely dangerous[6]. The 'Franklinic' electricity from the machine and the 'animal' electricity from the torpedo fish were soon compared scientifically. In 1775 the reclusive philosopher Henry Cavendish made a model torpedo fish out of wood, leather, sealing wax and tinfoil to establish their identity[7]. Nevertheless, using electric fish experimenters could not reproduce all the effects, such as sparks, of Leyden Jars.

Luigi Galvani, with his work on frogs' legs that twitched in contact with damp metals, gave his name to a branch of unorthodox medicine: listless teenagers might be galvanised into action[8]. Animal electricity was named 'Galvanic' after him. More creepily, corpses of executed criminals were made to twitch, contort themselves and grimace when electrified experimentally. The descriptions are horrible, leading us to the world of Frankenstein[9]:

> the leg was thrown out with such violence as nearly to overturn one of the assistants … the chest heaved and fell; the belly protruded and again collapsed … every muscle in his countenance was simultaneously thrown into fearful action … spectators were forced to leave the apartment from terror or sickness, and one gentleman fainted.

Clearly, electricity was not just something for parlour-tricks, but intimately connected with life, and an important agent in natural processes such as thunderstorms. Then in 1799 Alessandro Volta found that he could produce a steady electric current through the mere contact of dissimilar metals in a 'pile'. The three kinds of electricity, 'Voltaic', 'Galvanic' (or animal), and Franklinic, seemed similar but not quite identical in their effects.

In March 1800 Volta sent a letter in French about his discovery to Sir Joseph Banks, President of the Royal Society of London, rather than to Paris (then the centre of things scientific): and it was published in the Society's *Philosophical Transactions*[10]. Humphry Davy later described Volta's work as an alarm-bell to the experimenters of Europe, waking everybody up[11]:

> demonstrating new properties in electricity … an instrument of discovery in other branches of knowledge; exhibiting relations between subjects before apparently without connection, and serving as a bond of unity between chemical and physical philosophy.

Before it was published, the surgeon Anthony Carlisle and the scientific translator, editor, and writer William Nicholson had been shown the letter and repeated Volta's experiment[12]. Nicholson had improved a device for detecting electric charge in which gold leaves rather than frog's legs were used; but making good contact with the pile was tricky. To improve it, they put a drop of water on the terminal; and found that a gas was emitted. Investigating further, they filled a small tube from the New River aqueduct in London and dipped wires from the 'pile' into the water, finding that gases were given off at each terminal. Piles were soon replaced by troughs with series of metal plates immersed at first in water, later in dilute acid: which were in due course called batteries.

Water and elective affinity

Water was, with earth, air, and fire, one of the classic four elements that in their various combinations made up everything: it was cold and wet in quality. By the late eighteenth century, chemists and mineralogists in Sweden and elsewhere had recognised that there were many different 'earths' containing different metals, familiar and new. At the same time, chemists, particularly Joseph Priestley in Britain, had established that there were various 'airs', as different from each other as metals were[13]. Since neither earth nor air could be true simple 'elements', Antoine Lavoisier in 1789 proposed 'simple substances', the limits of analysis, as the fundamental entities of chemistry instead[14]. Meanwhile in 1784-5 Cavendish had made the astonishing discovery that, in Nicholson's words[15]:

> If a mixture of about two parts, by measure, of inflammable air, with one of vital air, be set on fire, in a strong closed vessel, which may be done by the electric spark, the airs, if pure, will almost totally disappear, and the product will be water …

In 1787, Lavoisier and his associates in France had renamed the gases, in accordance with his new theory of burning[16]: enormous volumes of them, forty litres of inflammable air (hydrogen) and twenty of vital air (oxygen) would give about a tablespoonful of water. The vessel must be strong to stand up to the explosion.

That compression indicated the strength of the 'elective affinity' that bound these simple bodies together so tightly. Reversing this violently-explosive reaction would be hard: heat transformed the water into steam, but not back into its component gases. Isaac Newton had revealed the force that kept the planets in their orbits; and throughout his life, reflecting upon chemistry, sought dynamical understanding there too – writing in his last work (the Queries to the *Opticks,* 1730)[17]:

> There are therefore Agents in Nature able to make the Particles of Bodies stick together by very strong Attractions. And it is the Business of experimental Philosophy to find them out.

Men of science distinguished the attractions of gravity, of cohesion (overcome when solids melted and liquids evaporated), and affinity. Gravity was universal, and so in different degrees (except perhaps for 'permanent gases') was cohesion; but affinity was elective, because (like the people in Goethe's famous novel[18]) some things will combine and others will not, and one substance can be displaced from combinations by another more strongly attracted. Priestley expected a Newton of chemistry who would make it a fundamental and dynamical science, revealing the deep structure of matter, and the forces that modify it[19]:

> Hitherto philosophy has been chiefly conversant about the sensible properties of bodies; electricity, together with chymistry, and the doctrine of light and colours, seems to be giving us an inlet into their internal structure, on which all their sensible properties depend. By pursuing this new light, therefore, the bounds of natural science may possibly be extended beyond what we can now form an idea of. New worlds may open to our view, and the glory of the great Sir Isaac Newton himself, and all his contemporaries, be eclipsed, by a new set of philosophers, in quite a new field of speculation.

Newton would, he believed, be especially astonished by electricity: 'its presence and effects are everywhere'.

Electricity and water come together

Priestley's aspirations were partly realised in what can be called the Second Scientific Revolution of the decades either side of 1800, when in France exact mathematical and experimental reasoning, and careful taxonomy, replaced the broad views and systems of the philosophes; and in Britain and Germany new science was allied with Romantic visions in an age of wonder[20]. Volta's experiment bonded together electricity and chemistry (previously, as Davy said above, 'apparently without connection'): and Davy, recognised by Priestley as his scientific heir[21], did indeed cast a brilliant light upon chemistry, electricity and optics when he made the first electric arc, using charcoal terminals and Thomas Beddoes' large Voltaic battery at the Pneumatic Institution in Bristol. Beddoes is now getting the attention he deserves, as more than Davy's patron: but his interests were primarily medical, where Davy's were in matter and forces[22]. What caused them and others particular excitement was that the current from Volta's little battery in Nicholson and Carlisle's experiment was quietly decomposing water into hydrogen and oxygen, reversing that explosive reaction that Cavendish first witnessed and understood.

In Bristol, Davy and Beddoes were close friends of Samuel Taylor Coleridge and Robert Southey, and Davy also met William Wordsworth and later stayed at Dove Cottage in the Lake District. He knew about the romantic connotations of water: Alph the sacred river, the Ancient Mariner's wide, wide sea, and the vale of the Wye at Tintern Abbey. But he was a man of science, and at the Pneumatic Institution had become well-known for exciting work on the respiration of Priestley's 'factitious airs', especially nitrous oxide: which turned out to be 'laughing gas', an entertaining recreational drug with variable and undignified physiological effects that (although well known, and taught to medical students) did not enter serious medicine for another generation[23]. This research was, like Priestley said his work had been, essentially inductive and experimental: Davy made gases, and tried breathing them, with sometimes alarming (almost fatal) consequences[24]. Much chemistry was done in that exploratory way (like Humboldt's science) right through the nineteenth century. Thus the great physicist J.J. Thomson wrote of his older contemporary William Crookes the chemist[25]:

> In his investigations he was like an explorer in an unknown country, examining everything that seemed of interest, rather than a traveller wishing to reach some particular place, and regarding the intervening country as something to be rushed through as quickly as possible.

Thomson, in his work on the electron, saw himself as the traveller, doing crucial experiments to test a theory and working hypothetico-deductively with complex apparatus in a modern university laboratory: Crookes' science on the other hand was (like Humboldt's) descriptive of the brave new world he found himself entering, and his demonstration-experiments (like Davy's) wonderful to behold. Chemistry was an art or craft, where manual skills were essential, as much as a science[26].

Faced with Volta's battery, however, Davy had a theory. He was from the outset convinced that the continuing electric current could not be generated by the mere contact of the damp metals, but must be the result of chemical change manifested electrically, rather than in flashes, bangs, fizzings or heat. He devised batteries with a single metal and two different liquids, and made other modifications described in a series of letters in the informal and rapidly-published *Nicholson's Journal,* a more formal paper in the Royal Society's much grander *Philosophical Transactions,* and then in the Royal Institution's *Journals*[27]. At the beginning of 1801, when he was twenty-two, he had been headhunted, and appointed as a lecturer at the Royal Institution, founded by Count Rumford and others in London's smart West End to promote practical science[28]. He turned out to be a brilliant lecturer, attracting such large and fashionable audiences that the Institution could support the laboratory in which he would do research. But at first he had to do the 'applied' research his patrons there wanted: on tanning, and on agriculture, where chemical knowledge should be useful to landowners. This work, which earned him in 1805 the Copley Medal of the Royal Society, essentially vindicated and publicised the best practice of the day, bringing scientific understanding where there had just been empiricism: at that time, technology frequently preceded science, rather than following from it as we are taught (following Davy's rhetoric) to expect.

By 1806 he had been promoted to Professor at the Royal Institution, was a Fellow and medallist of the Royal Society, and as a distinguished man of science could decide his own research agenda. He returned to Volta's battery. In the interim, William Hyde Wollaston (a pioneer of platinum chemistry) had in 1801 published in the same volume of *Philosophical Transactions* as Davy's paper an experiment in which water was decomposed by 'Franklinic' electricity, using extremely fine terminals: he sealed fine gold wires into glass, and ground the glass away until he could see a tip of gold through a magnifying-glass[29]. He had inferred that the oxidation of the metal in Volta's battery was the primary cause of the electricity; and that there was some oxidation in the machine. So, although the hydrogen and oxygen bubbled off mixed rather than separately at the terminals or poles, the analogies seemed strong enough for him to conclude that:

> The similarity in the means by which both [Franklinic] electricity and GALVANISM [Voltaic electricity] appear to be excited, in addition to the resemblance that has been traced between their effects, shews that they are both essentially the same, and confirms an opinion that has already been advanced by others, that all the differences discoverable in the effects of the latter, may be owing to its being less intense, but produced in much larger quantity.

Wollaston was nicknamed 'the Pope' because he was deemed infallible as an analyst; and his high reputation lent weight to these conclusions. The distinction of 'quantity' and 'intensity' was important. But no further research seemed to follow clearly from this work; and experimental results, in Britain and on the continent of Europe, were puzzling and inconclusive.

Davy triumphant

Thus around the positive pole, where the oxygen was generated, the water became acidic; while at the negative, where approximately twice the volume of hydrogen bubbled forth, it became alkaline. It was not at all clear what could be going on. In Lavoisier's chemistry, the current orthodoxy, heat or 'caloric' was a weightless fluid that entered into combination with ordinary matter (so that water, for example, was a compound of definite quantities of ice and caloric); it seemed likely that electricity was similar – but might be two fluids, positive and negative. Oxygen and hydrogen might even be compounds of water and positive and negative electricity. A great deal of open-ended experimental research went on, with Humboldt, Georges Cuvier, and Johann Wilhelm Ritter among the distinguished men of science drawn in, coming to very different conclusions from the evidence but unable to develop a testable theory with predictive power: they remained explorers. It was odd that the gases appeared only at the terminals: and Christian Johann Dietrich von Grotthus proposed a 'chain' mechanism. If we imagine a dance in which the men and women, in a line between two poles, keep changing partners to their left, then women will steadily accumulate at one end, and men at the other: so it is, perhaps, with the oxygen and the hydrogen. But in 1806 there was no general agreement: what was revealed was that the proportions were not exactly in the 1:2 ratio by volume in which they combined in refined experiments like Cavendish's; and that there was this curious appearance of acid and alkali. To sort out in a chemical process what is the main reaction, and what are side-reactions (masking it, and therefore of limited interest) is always a problem.

Davy entered the arena that autumn, after his holiday and before the 'London season' of Law Courts, Parliament, theatres and lectures, dinners and balls, began in November. This time he was a traveller, not an explorer[30]. He did not believe in caloric, was convinced that chemical affinity was electrical, and sure that under the right circumstances an electric current decomposing water must simply and precisely reverse the violent reaction that had generated it. He would persist until he got the answer he wanted. He suspected the glass in common use, which was indeed known not to be inert. He redistilled water in silver apparatus, and used vessels of agate and of gold, with terminals made of the platinum that Wollaston (in a process he kept secret) had made available in metallic form; and the Royal Institution's enormous Voltaic battery. The results were closer to what he expected, but there was still some acid and alkali after a time. He found that they were nitrous acid and ammonia; and concluded that they were the result of the oxygen and hydrogen combining at the moment they were released with dissolved nitrogen in the water. Performing the experiment with freshly-boiled water under hydrogen, he triumphantly recorded that no acid or alkali was formed even after twenty-fours hours, and that the gases came off in the exact proportions in which they formed water. He concluded that electricity and chemical affinity were manifestations of one power.

For this paper Davy received a prize from the Parisian Academy of Sciences – where the Royal Society celebrated useful knowledge, the French honoured theory. In the following autumn, he amazed the scientific world with the spectacular experiment of decomposing fused caustic potash using a large electric battery and platinum terminals. Sparks flew around the laboratory, and globules of what at first he called 'potagen' collected around the negative pole. It was lighter than water, and reacted so violently with it that the hydrogen generated caught fire. After discussion with fellow-chemists, Davy concluded that despite these anomalous properties, it was a metal; and that potash was its oxide[31]. The insight gained from studying water thus gave chemists a powerful new analytical tool, as well as the insight into the chemical bond that Jacob Berzelius systematised as 'dualism', the idea that every chemical compound had a positive and negative component[32].

There was one more question: Lavoisier and his associates named 'oxygen' from the Greek for sour (and the Germans still call it Saurstoff) because they believed that it was the acid-generator, present in all of them. Indeed, carbonic, sulphuric and nitric acids contain it; and where metals form two oxides, that with more oxygen will be more acidic. But Davy showed that caustic potash, though highly alkaline, contains more than 25% oxygen; and water, which is neutral, was known to contain a whopping 89%. Davy demonstrated that the chemical reactivity of metals depended upon their electrical state, a positive charge making them reactive and a negative one inert: a principle used in 'galvanising' iron by coating it with more-reactive zinc. He established that 'muriatic' acid from sea-salt was composed of hydrogen and chlorine, containing no oxygen unless there was water around to dilute it[33]. As HCl (using Berzelius' notation) it had no element in common with sulphuric acid, then perceived as SO3. Davy therefore concluded that acidity does not depend upon a component, but upon electrical arrangements among particles. This study of what Davy called 'chlorine', identifying it as an element, and its compound with hydrogen, hydrochloric acid, showed how important water was not merely as a solvent but as a reagent: dryness matters.

Dualism was too simple a story, but the intuition that chemical affinity was electrical was a brilliant insight[34]. The great mathematician Pierre Simon Laplace had extended Newton's work by demonstrating that the solar system was stable, despite the wobbles caused by planets attracting one another gravitationally: there was no need for God to intervene and reset the celestial clockwork. He and his friend the chemist Claude-Louis Berthollet also tried to show that the attractions of cohesion and affinity might be gravitational, or due to forces akin to it[35]. That did not work; and John Dalton had made no assumptions about the glue that might hold his atoms together in their compounds. Davy really had dissolved doubts in water, and chemistry became (at least in principle) like Newtonian physics a dynamical science based upon understanding of forces, not confined to explorers using description and experiment.

Epilogue

What about those electric fishes? Humboldt, an inspirational polymath who stimulated Charles Darwin among others, had high hopes of their importance in understanding life as well as electricity, writing that[36]:

> The discoveries that will be made on the electromotive apparatus of these fish … will extend to all the phenomena of muscular motion subject to volition. It will perhaps be found that, in most animals, every contraction of muscular fibre is preceded by a discharge from the nerve into the muscle; and that the mere simple contact of heterogeneous substances is a source of movement and of life in all organized beings.

In the event, the physiology took longer than the electrochemistry. In Rome, in the spring of 1829, Davy was a very sick man. Following a series of strokes that had made him resign the Presidency of the Royal Society in 1827 and seek health in warmer climates, he was thought to be dying; his brother John (a doctor) and his wife were summoned to his bedside. But he was still experimenting, in the spirit of 1806, trying to get sufficient current from a torpedo to decompose water. He failed, and shortly afterwards died in Geneva on the way home to England. John Davy did further experiments, but Humphry's disciple Michael Faraday in 1833 acquired a live *gymnotus* for the Royal Institution. In experiments meticulously detailed in his *Diary,* boldly handling the creature, he demonstrated what he called the 'identity of electricities', bringing that chapter of this watery and fishy tale to a conclusion[37].

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[1] This was the first in the series of general public lectures 'Reflections on Water' given in Durham University on 4th November 2009, under the auspices of the University's Institute of Advanced Studies and Department of Philosophy, with support from the Society for the History of Alchemy and Chemistry, for which I am very grateful. The occasion also marked the launch of my book, *The Making of Modern Science: Science, Technology and Modernity, 1789-1914,* Cambridge: Polity Press, 2009.

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