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Davy hits the headlines (again)

The following is an account of how a historical perspective has influenced both the course of some recent research and also its reception.

On 11 February 2016, SHAC's spring meeting was on "High pressure in the interwar period". Topics naturally included the Haber process for the high pressure conversion of nitrogen and hydrogen gases to ammonia. Haber received the Nobel chemistry prize of 1918 for his work, which solved the problem for mankind posed by the "worldwide economic necessity of supplying bound nitrogen to the soil", now that natural mechanisms were inadequate on account of population growth and demographics, globalisation (in modern parlance), and industrial demand for nitrogen [1]. At the time, his solution, by "fixing" *atmospheric* nitrogen, appeared sustainable (again in modern parlance), unlike continued use of sodium nitrate from Chilean saltpetre, found in "the high-mountain deserts of Chile". Today, Haber-produced ammonia is key to world agricultural production.

Alan Dronsfield, a member of both the Historical Group and SHAC, spoke at the meeting about Haber's work and its antecedents, noting for instance that Davy had in 1807 reported the electrochemical fixation of atmospheric nitrogen.

Also a member of both the Historical Group and SHAC, I was in the audience – and was very struck by Alan's reference to Davy. Alan pointed me towards the key reference [2] and to later endeavours to fix nitrogen electrochemically by Swiss workers in 1922 [3].

Davy had reported the production of ammonia and nitric acid when water containing dissolved air was electrolysed between gold electrodes with a potential of *ca* 100 V. The Swiss workers electrolysed dilute sulfuric acid between a platinum black cathode and a platinum wire anode using lower potentials but under 200 atmospheres of nitrogen and obtained ammonia. Yields were low, though higher yields were obtained from 1998 to 2014 with nickel, palladium, and platinum electrodes.

The fact that nitrogen can be fixed electrochemically is not surprising from a thermodynamic point of view. Consider the following potentially useful overall reaction (occurring in the presence of excess water) –

$$N_2 + 2.25\ H_2O \rightarrow 0.75\ NH_4NO_3 + 0.5\ NH_3 \qquad \text{(R1)}$$

– in which 2 mol N in the 0 oxidation state disproportionate into 0.75 mol N in the +5 state and 1.25 mol N in the -3 state. First, one can reasonably imagine an electrochemical cell in which overall reaction (R1) is achieved:

reaction at the cathode: $N_2 + 6\ e^- + 6\ H^+ \rightarrow 2\ NH_3$; (R2)
reaction at the anode: $1.5\ NH_3 + 2.25\ H_2O \rightarrow 0.75\ NH_4NO_3 + 6\ e^- + 6\ H^+$. (R3)

((R1) is of course the sum of (R2) and (R3).) Secondly, the potential required to drive this reaction, if it could be performed reversibly, can be estimated from tabulated thermodynamic data as *less than 1 V*.

But without the right catalysis, the kinetics of the half-cell reactions (R2) and (R3) are unfavourable.

For almost a century, then, atmospheric nitrogen has been fixed primarily by manufacturing nitrogen gas and hydrogen gas and combining these to form ammonia by use of the Haber process. The Ostwald process is used for oxidising the ammonia into

nitric acid, so that, in turn, ammonium nitrate can be produced, including for direct use as a fertiliser. But the energy demand is high, and has been said to account for 3 % of world carbon dioxide emissions contributing to man-made climate change.

In May 2016, I was visited by my friend from Oxford days, Professor Robert Crabtree of Yale Chemistry Department [4]. The eventual result was a joint "perspectives" paper [5] in which key possibilities discussed were (i) the solar-powered electrolytic production of aqueous ammonium nitrate solution on farms where it could be directly applied to fields, and (ii) the use of *molecular electrocatalysts* rather than catalytic *electrodes* such as platinum.

Davy was cited in the paper, and this excited journalistic interest beyond our expectation. Robert was given the prominent "Opinion/comment" page in the RSC monthly magazine *Chemistry World* [6], which gave him an opportunity to promote our perspectives paper. The editorial staff clearly liked the Davy angle: the headline was "Deriving Mr Davy" and Gilray's "bathroom humour" satire of Davy demonstrating at a Royal Institution lecture [7] was reproduced. The story was then picked up by a journalist for *Chemical & Engineering News* [8], the American Chemical Society's weekly magazine. The headline was "Nabbing nitrogen from the air to make fertilizer on the farm", but the very first sentence began "British chemist Humphry Davy ..."

Davy made the newspapers such as *The Observer* in his own time [9], and to this day is "good copy".

References

1. Fritz Haber, "The synthesis of ammonia from its elements", Nobel Lecture, 2 June 1920, http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1918/haber-lecture.pdf. See especially pages 327-328. This award was unpopular in former Allied countries. Haber had personally supervised the first use of poison gas (chlorine) on the Western Front in the First World War. Nitric acid made from ammonia is used also for manufacture of explosives.

2. Humphry Davy, *Phil. Trans. R. Soc. Lond.* 1807, **97**, 1-56. This reports Davy's Bakerian Lecture "On some chemical agencies of electricity" of 20 November 1806.

3. Fr. Fichter and Richard Suter, *Helv. Chim. Acta* 1922, **5**, 246-255.

4. Robert Crabtree was an undergraduate at Oxford and did his DPhil at Sussex, then moving to the CNRS in France and to Yale. He was recently elected to the National Academy of Sciences.

5. Michael Jewess and Robert H Crabtree, *ACS Sustainable Chem. Eng.*, 2016, 4, 5855-5858.

6. Robert Crabtree, *Chemistry World*, February 2017, 70.

7. James Gilray (1756-1815), "Scientific researches! – New discoveries in pneumaticks! – or – an Experimental lecture on the powers of air" (colour print, Hannah Humphrey, 1802). To view the print, with identification of the individuals and scientific equipment shown in the print, go to http://www.britishmuseum.org/research/collection_online/collection_object_details.aspx?objectId=1478966&partId=1&people=6329&peoA=6329-1-9&page=1.

8. Stephen K Ritter, *Chemical & Engineering News*, 1 May 2017, **95 (18),** 22-23.

9. Harriet Lloyd, “Davy’s lectures in the press”, SHAC spring meeting, Cambridge, 15 June 2015.

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