


Ryan D. Tweney is Professor of Psychology at Bowling Green State University, Bowling Green, Ohio 43403. He has worked extensively on cognitive models of scientific thought, most recently on the application of such models to an understanding of Faraday’s Diaries, and is completing a book on this topic.

He is coauthor, along with D. Gooding, of “Michael Faraday’s ‘Chemical Notes, Hints, Suggestions and Objects of Pursuit’ of 1822”.

FARADAY’S SEARCH FOR FLUORINE

Harold Goldwhite, California State University - Los Angeles

In a relatively concentrated and intense period of experimentation, from January 1834 to December 1835, Michael Faraday attempted to prepare elemental fluorine. He was not successful in those attempts. This article presents the background to Faraday’s work, the status of fluorine in 1834, the details of Faraday’s experimentation, and an assessment of the chemistry involved. It also speculates on Faraday’s motivation in undertaking this endeavor.

In 1771 Carl Scheele, repeating and reinterpreting an experiment first reported by Marggraff in 1764, demonstrated that reaction between fluorspar (calcium fluoride) and sulfuric acid liberated a peculiar acid which was combined with lime in the fluorspar (1). This “flussaure” was always accompanied by deposits of silica in the receiver, for Scheele used glass retorts for his experiments, and he opined that flussaure might contain silica. In 1781 it was shown that the source of the silica in Scheele’s experiments was the glass vessels (2). When Lavoisier advanced his new system in the Traité élémentaire in 1789, he described Scheele’s acid as “l’acide fluorique” and, following his oxygen system of acids, asserted that it contained oxygen combined with an as yet unknown radical, “fluoricum” (3).

While Humphry Davy was engaged in clarifying the ele-
mentary nature of chlorine (4), the French physicist A. Ampère drew his attention, in two letters sent in late 1810 and in 1812, to the many similarities between hydrochloric and hydro-fluoric acids. A passage from Ampère's first letter to the master electrochemist makes some striking points (5):

It remains to be seen whether electricity would not decompose liquid hydrofluoric acid if water were removed as far as possible, hydrogen going to one side and oxyfluoric acid to the other, just as when water and hydromuriatic acid are decomposed by the same agent. The only difficulty to be feared is the combination of the oxyfluoric acid set free with the conductor with which it would be brought into contact in the nascent state. Perhaps there is no metal with which it would not combine, but supposing that oxyfluoric acid should, like oxymuriatic acid, be incapable of combining with carbon, this latter body might be a sufficiently good conductor for it to be used with success as such in this experiment.

In the second letter to Davy, Ampère proposed the name “le fluor”, or fluorine, for the new radical by analogy with the recently adopted name of chlorine for oxymuriatic acid.

During 1813 and 1814 Davy pursued fluorine but with no success (6):

I undertook the experiment of electrizing pure liquid fluoric acid with considerable interest, as it seemed to offer the most probable method of ascertaining its real nature, but considerable difficulties occurred in executing the process. The liquid fluoric acid immediately destroys glass and all animal and vegetable substances, it acts on all bodies containing metallic oxides, and I know of no substances which are not rapidly dissolved or decomposed by it, except metals, charcoal, phosphorus, sulfur, and certain combinations of chlorine. I attempted to make tubes of sulfur, of muriates of lead, and of copper containing metallic wires, by which it might be electrized, but without success.

I succeeded, however, in boring a piece of horn silver [i.e., native silver chloride] in such a manner that I was able to cement a platina wire into it, by means of a spirit lamp, and by inverting this in a tray of platina filled with liquid fluoric acid I contrived to submit the fluid to the agency of electricity in such a manner that in successive experiments it was possible to collect any elastic fluid that might be produced.

But to no avail. Davy’s hydrofluoric acid was not anhydrous, and the only decomposition products collected were hydrogen and oxygen from the water it contained. Davy’s attempts to prepare fluorine chemically, by treating heated metal fluorides with a stream of chlorine gas, were equally unproductive (7). This was the situation in the 1820s and early 1830s.

One of the leading chemical characteristics of chlorine, noted by all early workers, was its ability to function as a supporter of combustion, in some respects analogous to oxygen. The story of Davy’s tour of Europe, accompanied by the young Faraday, from 1813 to 1815 is a familiar one, and so is that of Davy’s brilliant series of investigations made with his portable laboratory during that tour, which indicated the elementary nature of Courtois’ dark crystals, more or less simultaneously with Gay Lussac, and the similarity between this novel iodine and chlorine. The excitement of these discoveries by his mentor made a strong impression on the young Faraday. We find him writing to Benjamin Abbott, his closest friend, from Geneva in July 1814 (8):

Before I leave iodine I must ask you & also desire you to inform me of the state of your sentiments respecting chlorine whether you class that substance & fluorine with oxygen ...

After Davy and Faraday returned to England in 1815 Faraday began to broaden his horizons, and undertook in 1816
a course of lectures on chemistry to the City Philosophical Society, a group of young men bent on self-improvement. In his fifth lecture, on the supporters of combustion, he suggested that “It is probable that none of these bodies, oxygen, chlorine, iodine & fluorine, are really simple in their nature” (9). Here we see Faraday following Davy in his rejection of Dalton’s chemical atomism. Incidentally, Faraday was steadfast in this opposition and we find him writing to Charles Babbage in April 1837 that (10):

The simple substances known are fifty three to which if you add fluorine or the X which must stand in its place the number will be 54. I hope the progress of discovery will be rather to diminish than increase the number.

Faraday’s interest in the halogens, stimulated by his early contact with Davy’s work on chlorine and iodine, showed up in a number of his early chemical investigations. In his first contribution to Philosophical Transactions, in 1821, he described the first reported binary compounds of chlorine and carbon, which he obtained in the course of his investigations of the reactions between olefiuant gas (ethylene) and chlorine. He isolated and characterized two new compounds, the crystalline perchloride of carbon (hexachloroethane) and the liquid protochloride of carbon (tetrachloroethylene) (11). In 1822 he worked with the crystalline hydrates of chlorine and observed liquid chlorine in the same year (12). The progression from chlorine to fluorine may have been an attractive one to him. Faraday’s diary allows us to follow the course of his experimental attempts to prepare fluorine (13). Amongst the wide range of his exploratory electrochemical investigations in mid-January 1834, he tried the electrolysis of aqueous solutions of potassium fluoride, both without and with the addition of sulfuric acid. In the latter case he noted the action of hydrogen fluoride on the glass of his apparatus and also (14):

“N electrode 0.67 ci: this hydrogen ... P Electrode only 0.20 ci:; which was oxygen. Still the Platina Electrode was not apparently acted upon and the glass in the neighborhood was. From which, and from the small quantity of oxygen, I conclude that Fluorine had been evolved at the Electrode and dissolved in the water without decomposing it, but something in the manner of chlorine and iodine. If not so, then the platina ought to have been corroded or else the full equivalent of oxygen set free.

A week later a similar experiment in platinum apparatus gave him a solution which bleached a solution of indigo, and he took this for “additional proof of the production of an aqueous solution of fluorine ... in its bleaching power of analogy with chlorine” (15).

Chemical attempts to prepare fluorine followed (16). By analogy with Scheele's original preparation of chlorine, Faraday mixed “Flour Spar and Ox. Manganese well powdered” in a platinum crucible with sulfuric acid, but only hydrofluoric acid was evolved. Potassium fluoride substituted for the fluor spar gave similar results, but when “Fluate Potassa, Red lead and Oil Vitriol” were heated in the same crucible the fumes smelt “as if a little Euchlorine with it”. However, red lead and oil of vitriol with no added fluoride seemed to give a similar smell. Nevertheless, the slight possibility that the lead compound might be producing a little fluorine induced Faraday to continue working with lead salts. He prepared lead fluoride by reaction between potassium fluoride and lead nitrate, and noted that it fuses unchanged at red heat in platinum. Preliminary attempts to make silver fluoride led Faraday to conclude that it must be soluble in water (as indeed it is) and he did not initially isolate it. Lead fluoride became the focus of Faraday’s subsequent electrolytic experiments.

In platinum apparatus that would be dubbed microscale today, Faraday electrolyzed fused lead fluoride (m.p. 822°C) and observed (17):

Much good action at N. foil; lead reduced and Platina alloyed and fused. At P. Electrode effervescence much; vapours transparent, pungent etc.

When he used a plumbago (graphite) positive electrode there was evolution of a pungent gas or vapor, but no action on the plumbago (17). An elegant new apparatus allowed Faraday to observe the vapor more carefully (18):

Although the gas or vapor at the P. electrode came off irregularly and soon mixed with air in and about the tube, I was able to make the
following observations. It must I think have been fluo-

erine. It was colorless and transparent. It did not produce fumes in the air like hydro fluoric acid, but when an open glass was held over the end, thus, fumes at the aperture above were produced ... The transparent fluorine va-

pors pungent to the mouth and nostrils. They reddened litmus paper but did not bleach it ... A little copper leaf tarnished in the fumes. Silver leaf also tarnished ... but I could dissolve no fluoate off from it.

The experiments continued for a month. Faraday isolated silver(I) fluoride, but it did not break down thermally, as he had hoped, to give fluorine. He observed decomposition but concluded that it was due to the presence of water in the silver fluoride, a salt that is hard to dehydrate fully. Electrolysis of molten lead fluoride in another new apparatus confirmed his earlier observations, and his opinion that he had prepared fluorine, but added nothing new to his observations (19). The topic was put aside for a time in mid-February 1834.

Faraday came back to it in January 1835. He essayed new ways of making lead fluoride, and noted that lead chloride and lead fluoride, when fused together, apparently form a mixed compound - "probably a useful mixture in voltaic decompositions for fluorine". After a month's work on the chemistry of lead and silver fluorides, and after preparing a large batch of lead fluoride that was probably purer than his earlier samples, he was ready to resume electrolyses. His Diary entry of 19 February 1835 is confidently headed "Fluorine" (20). Another new electrolysis vessel was devised, but this time (21):

... there were very little signs of any gaseous or vaporous matter being produced in the retort ... By far the greatest portion of the electricity passes as through an undecomposable conductor, a metal for instance; but there appears to be a little action, for lead is rendered at the cathode and the platina wire is corroded at the anode. In this state this body [fused lead(II) fluoride] presents an extraordinary case between ordinary electrolytes and ordinary good conductors ... I must look out for a fluoride not having the peculiar properties this possesses. Try several.

His passing comment on the intermediate conductivity of lead fluoride represents one of the first recorded observations of the phenomenon of semiconductors.

Fluorine from lead fluoride was proving elusive, and Faraday was quick to suggest what had been the problems in his earlier experiments (22):

As the first fluoride of lead [January-February 1834] gave gas at P. Electrode when electrolyzed, suspected now this was from nitrate or oxide present left in from nitrate when washed. Added a little pure oxide of lead to this pure fluoride of lead, and now gas was evolved at the Anode. But this probably oxygen from the oxide. This confirms my view.

He continued to explore the chemistry of fused lead fluoride, noting that it apparently reacted with charcoal, and possibly even with diamond. On minimal evidence he suggested that a "fluo-carbon had been formed, analogous to fluo-silicon and acting in the same manner on water". He repeated the experiment with lead fluoride and plumbago on a larger scale, but the results were inconclusive (23).

In October 1835 Faraday was still looking for suitable fluorine precursors. He examined routes to platinum fluorides and gold fluorides, but found nothing encouraging (24). Then in November 1835, he started his last concentrated attack on the problem (25):

I required a solution equivalent to hydro fluoric acid in which I might render platina, Gold, etc. positive by the Voltaic battery: for this purpose I added strong sulphuric acid to the strong solution of fluoride Pm. [potassium] ... No fumes of H. f. acid were produced (unless large quantities were used), nor did the solution taste as sour as I expected.

Faraday's apparatus for reacting lead fluoride and graphite in an attempt to prepare "fluo-carbon" (32).
Many different metals were tried as electrodes in this solution: platinum, gold, palladium, silver, iron, tin, antimony, copper, and zinc. No fluorine was obtained, but Faraday was led to speculate on the properties of his unobtained element (25):

Supposing fluorine obtained and held in platina vessels. Would it not abstract hydrogen from water at common temperatures? Would it not inflame in hot steam? Would not a mixture of fluorine and steam burn spontaneously or be ignited by a flame or an electric spark? Would not fluorine serve as an abstractor of hydrogen, and so be opposed to bodies generally as abstractors of oxygen.

By the end of 1835 Faraday had apparently decided to move to more promising areas: "I cannot go on at present with the fluorine experiments". When he reprinted his earlier publications on electrochemistry in the first volume of his Experimental Researches in Electricity in 1839 he quoted (26):

Hydrofluoric acid and fluorides. Solution of hydrofluoric acid did not appear to be decomposed under the influence of the electric current: it was the water which gave way apparently. The fused fluorides were electrolysed; but having during these actions obtained fluorine in the separate state, I think it better to refer to a future series of these researches, in which I purpose giving a fuller account of the results than would be consistent with propriety here.

but he added, in December 1838, for the reprint, the following significant footnote:

I have not obtained fluorine: my expectations, amounting to conviction, passed away one by one when subjected to rigorous examination; some very singular results were obtained.

Faraday himself pointed to some of his earlier spurious sightings of "fluorine" as probably due to oxygen from traces of oxide or nitrate in his samples. That may have been part of the problem, but the earliest lead fluoride electrolyses he conducted were in equipment open to the air. Lead(II) fluoride has a substantial vapor pressure at its melting point of 822°C; its vapor is readily hydrolyzed to produce lead oxide and hydrogen fluoride (27). Consequently the vapors above Faraday's molten lead fluoride in equipment open to the air redened litmus and inevitably produced oxide, a source of oxygen in the electrolysis. It is significant that in his final experiments, in closed apparatus, there was very little gas evolution. The electrochemistry of pure molten lead fluoride in vacuo does not appear to have been explored. Since lead(IV) fluoride exists, as do well-characterized hexafluoroplumbates(IV) (28), it seems possible that the redox process in molten lead(II) fluoride might give elemental lead and lead(IV) fluoride which, in lead(II) fluoride, might be present as $\text{Pb}^{2+}\text{PbF}_6^{2-}$ (equivalent stoichiometrically to a novel lead trifluoride).

The episode with fluorine demonstrates many of Faraday's skills as an experimenter: the visualization of an important problem; the breadth of the attack on it; the range of ingenious equipment and experiments devised for that attack; the repetition to check on reliability and reproducibility; the rapid grasp of anomaly, and the suggestions of reasons for it; and the decision to abandon an unprofitable area when the returns were not up to his expectations. It sounds like (and is) a check-list for any aspiring scientist. Faraday's early views on "philosophical deduction", enunciated in his final lecture to the City Philosophical Society, stood him in good stead (29):

The man who is certain he is right is almost sure to be wrong; and he has the additional misfortune of inevitably remaining so. All our theories are fixed upon uncertain data, and all of them want alteration and support. All I wish to point out is ... the continual guard against philosophical prejudices which should be preserved in the mind. The man who wishes to advance in knowledge should never of himself fix obstacles in the way.

Let me close with a speculation. Among all Faraday's electrochemical experiments, the attempt to prepare fluorine is in some ways an oddity. Faraday did, of course, carry out many other qualitative experiments to determine products of electrolyses, and was certainly a pioneer in fused salt electrolysis, but the attack on the fluorine problem was unusually sustained, and Faraday seems to have been uncharacteristically optimistic in his view of his early results. It seems to me that he wanted to believe he had prepared fluorine, and I am drawn to speculate on why this was so. One reason may have been the significance of the result. During most of the 19th century, the isolation of elemental fluorine was a, or perhaps the, major challenge to inorganic chemists. Moissan's eventual success in 1886 gained him international recognition. Faraday was aware of the recognition that discovery of new elements (through the application of electrochemistry) could bring to an investigator, for he had Davy's example before him. I believe Faraday would not have been indifferent to the acclaim that would have greeted him as the discoverer of fluorine.

References and Notes

5. A. Ampère to H. Davy; reprinted and translated by F. D.


10. M. Faraday to C. Babbage, Royal Institution, 7 April 1837, reference 8, p. 313.


---

**OBSERVATIONS ON FARADAY AS ORGANIC CHEMIST MANQUE**

Derek A. Davenport, Purdue University

Faraday’s work in pure chemistry has been treated somewhat condescendingly by commentators. Partington dismisses it in less than a page and Williams’ rather fuller treatment is consigned to an omnibus chapter titled “The Fallow Years” (1, 2). There is perhaps some justice in this. If we exclude the work on liquefaction of gases as being *sui generis* non-chemical and if we yield that on “Relations of Gold and Other Metals to Light” to the uncoagulated and as yet unnamed colloid chemists (3), we are forced to concede that even those chemical papers Faraday chose to reprint in *Experimental Researches in Chemistry and Physics* (4) are, for the most part, minor work. Faraday’s touching footnote to the first of these, “Analysis of Native Caustic Lime”, could with equal humility have been appended to several others (5):

I reprint this paper at full length. It was the beginning of my communications to the public, and in its results very important to me. Sir Humphry Davy gave me the analysis to make as a first attempt in chemistry at a time when my fear was greater than my confidence, and both far greater than my knowledge; at a time also when I had no thought of ever writing an original paper on science. The addition of his own comments and the publication of the paper encouraged me to go on making, from time to time, other slight communications, some of which appear in this volume. Their transference from the “Quarterly” into other Journals increased my boldness; and now that forty years have elapsed and I can look back on what the successive communications have led to, I still hope, much as their character has changed, that I have not, either now or forty years ago, been too bold.

There are six papers, however, that taken together provide a striking exception to this generalization: “Two New Compounds of Chlorine and Carbon, etc.”; “New Compound of Chlorine and Carbon”; “Hydriodide of Carbon”; “New Compounds of Carbon and Hydrogen”; “Pure Caoutchouc”; and “Mutual Action of Sulphuric Acid and Naphthaline”. These reveal that in the years between 1820 and 1826, Faraday had mastered those arts - synthesis, separation, purification, characterization, analysis - necessary to the emerging subdiscipline of organic chemistry. Indeed, it is doubtful that any of his contemporaries could claim greater achievement in that area. Even so he abandoned the subject in 1826, never to return, and if we are to judge by his letters to Liebig and Dumas, among others, he subsequently evinced little interest in the extraordinary efflorescence of organic chemistry that took place during the rest of his life.

“On Two New Compounds of Chlorine and Carbon, and on a New Compound of Iodine, Carbon, and Hydrogen” (6) describes the preparation and characterization of perchloride

Harold Goldwhite is Professor of Chemistry at California State University, Los Angeles, CA 90032. He writes a monthly column, “This Month in Chemical History”, for SCALACS, the Journal of the Southern California Section of the American Chemical Society, and is currently serving as Secretary-Treasurer of HIST. He is interested in early 19th century inorganic chemistry and in the chemistry of the Manhattan Project.