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SONS OF GENIUS: CHEMICAL MANIPULATION AND ITS SHIFTING NORMS FROM JOSEPH BLACK TO MICHAEL FARADAY*

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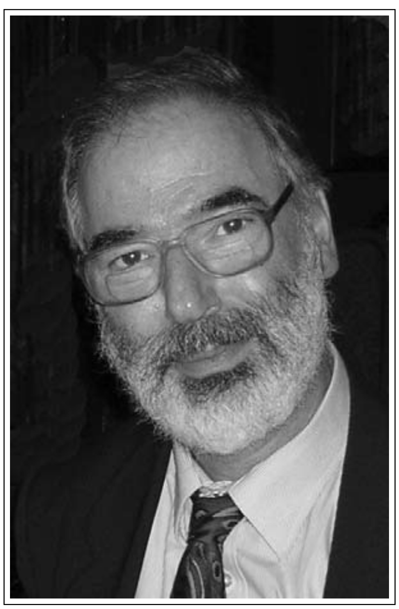


Trevor Levere

Chemistry, for all the growth in theoretical chemistry, is *the* laboratory science. Some laboratory chemists have the chemical equivalent of the gardener's green thumb; some have raised practice to an art; while others have demonstrated less skill, or have arrived at their results in such a way that their experiments were unreproducible by others. I want to look at some prominent chemists from around the 1750s to 1830, to see how far their writings and published results give us an indication of what made for good practice. Good practice changed a lot in the decades around the Chemical Revolution: acceptable margins of error, accuracy and precision, replicable experiments leading to reliable results—much that we take for granted had to be invented. I shall begin with Joseph Black and end with Michael Faraday. Both were brilliant lecturers and masters of demonstration experiments. Black's public experiments always succeeded, and his publications show a very clear grasp of experimental error. Before Faraday began his electrochemical researches, he worked mainly in analytical chemistry and wrote a book on *Chemical Manipulation*. Faraday explained that he wrote it (1):

> …as a book of instruction, no attempts were made to render it pleasing, otherwise than by rendering it effectual; for … if the work taught clearly what it was intended to inculcate, the high interest always belonging to a well made or successful experiment, would be abundantly sufficient to give it all the requisite charms ….

Joseph Black, like Faraday, inspired his audiences with the charms of chemistry. In the 1750s he had carried out researches on magnesia alba, basic magnesium carbonate. He obtained his results by weighing solid magnesia before heating it and the residue after heating; he concluded that the loss in weight was equal to the weight of gas evolved, and he determined the latter's chemical properties. He described and justified each step of the process, the consequences of omitting any operations, the proportions of reactants, and the need for repeated washing and decanting—as many as twelve washes where perfectly pure substances were required.

Black was wise to obtain the weight of the gas by weighing solids; the process of weighing and measuring gases was a very chancy business in the 1750s. Judging by the crudeness of his surviving glassware supplied by a local bottle factory, he would have had a hard time measuring gases directly. He gave his results to one part in 250, which is very close to what John Stock's modern examination of Black's balance has shown was possible: the balance is accurate to one part in 200 (2).

Joseph Priestley discovered more gases than any other eighteenth-century chemist. He measured gas volumes to two or sometimes three figures. He was aware of the problem of impure substances and of the loss of gas through leakage. His quantitative results were sometimes as good as Black's, sometimes a little (but never a lot) worse. And although some of his apparatus was made for him at the Wedgwood factory, much of it was what one could find in a kitchen or shed.

Priestley, like Black, obtained respectable and acceptable results with simple instruments. Thirty years later than Black, and a decade after most of Priestley's pneumatic experiments, the wealthy and reclusive Henry Cavendish, surely one of the most meticulous experimenters ever, obtained impressive results with simple apparatus, and astonishing results with sophisticated apparatus. The results of his researches on gases were more accurate than those of his contemporaries by an order of magnitude. In 1783 he published an account of a new eudiometer for measuring what we would call the oxygen content of a sample of air. By Cavendish's time, what began as a marginal experiment in chemistry applied to medicine had developed into a key experiment in chemistry. Cavendish worked with nitric oxide, which combined with oxygen to produce the dioxide, which was then absorbed in water; the diminution in volume gave an indication of the goodness of the air, its oxygen content. Previous chemists had measured this volumetrically; it was easier to measure the volume of a gas than its weight, because gases were so much lighter than the vessels that contained them. Cavendish bucked the trend by weighing gases under water, thereby avoiding the problem of moisture adhering to the sides of the reaction vessels. He had a balance vastly superior to Black's, made for him by John Harrison, inventor of the marine chronometer. Cavendish was soon carrying out observations to 1/10 grain, a ten-fold increase in accuracy and sensitivity over Black's—we are up to one part in 2,500.(3) Jesse Ramsden, arguably the finest instrument maker of the eighteenth century, made a balance that was used by Cavendish and others in the Royal Society of London in the 1780s, and that was sensitive to a hundredth of a grain, a further ten-fold increase in accuracy (4). Although he provided more details of experimental procedure than anyone before him (the best ratio of gases, the shape and size of the vessels used, the rate of mixing the gases, the purity of the airs involved, the importance of using distilled water, and much besides), he observed that (5):

> There are several contrivances which I use, in order to diminish the trouble of weighing the vessels; but I omit them, as the description would take up too much room.

He did, however, assert that his gravimetric method required less dexterity than the volumetric methods used by others. He checked to see if atmospheric air varied from day to day; he tested samples collected on sixty different days and found differences of less than 0.013 (5):

> Though this difference is but small, yet as each of these means is the mean of seven or eight trials, it is greater than can be expected to proceed from the usual errors of experiment.

Consistent results, obtained by repeating experiments, were nothing new; but Cavendish's standards were higher than those of his predecessors and most of his contemporaries, who would have been very happy with such small discrepancies.

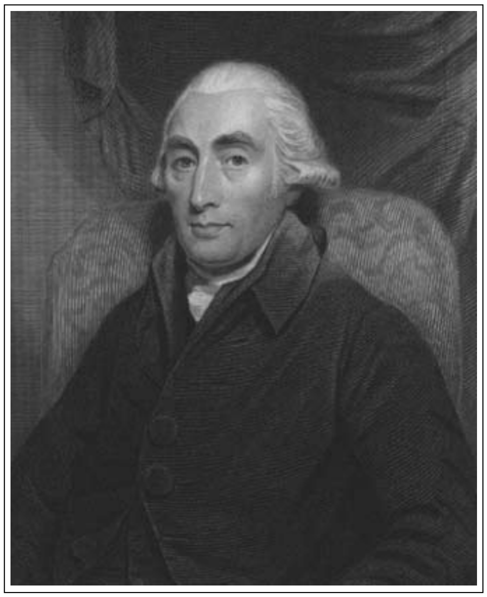
Cavendish also determined the oxygen and nitrogen content of the atmosphere, after removing carbon dioxide. There was a small bubble of air left unabsorbed, not more than 1/120 part of the whole. Anyone who used Cavendish's apparatus and who looked carefully would have detected a very small residual bubble; but no one else in the eighteenth century recorded such an observation (6). In 1894 William Ramsay and Lord Rayleigh announced their discovery of argon, the first inert gas (7). No one, to my knowledge, detected the inert residue in the ninety years between Cavendish and Ramsay (8).

It was, as Black and Cavendish knew, essential to work with pure substances, but the way to obtain them was often obscure. In the mid-1790s, Thomas Beddoes, a former pupil of Joseph Black, was the leading English figure in the development of medicine using various gases for therapeutic purposes. He advocated the use of oxygen for respiratory disorders and recommended manganese treated by mineral acids to prepare the oxygen. The purity of the manganese used was crucial. Beddoes sought a pure mineral source, rather than purifying impure ores himself. Erasmus Darwin, Charles Darwin's grandfather, perhaps the bulkiest and the foremost physician in England, was a close friend of the engineer James Watt (9); he followed pneumatic treatments closely and used manganese supplied by Watt. It was not uniformly reliable. Darwin informed him that one of his patients (10):

> has breathed …pure oxygene [daily] for … 2 or 3 weeks, till he tried the last parcel of manganese, which was sent from your people; the air from which gave him a burning feel[ing in] his lungs with something like suffocation, which obliged him to desist...

Darwin blamed impure manganese. Watt was a good but not great laboratory chemist, who also practiced pneumatic medicine on his employees. The same could be said about Beddoes. While lecturing at Oxford, Beddoes experienced difficulties in performing demonstration experiments. He wrote to Black (11):

> What I find most difficult is to repeat some of those apparently simple exp^{s}. which in your hands are so striking and so instructive. I have not yet learned how to show the gradual approach towards saturation by throwing slowly a powdered salt into water. What salt do you use? & how do you perform the exp^{t}? How do you contrive to make that capital exp^{t} which shews the burning of iron in deph^{d} air? I mean to attempt it, but am told that the vessel has been frequently in other hands burst with great violence?



Joseph Black

Beddoes was no Black; one account of his lectures complains that he was (12):

> …so singularly awkward in the mechanical part of his experiments that they generally failed, and he was then compelled to proceed in his discourse on the hypothesis that the result had been the reverse of that which the eyes of his audience would have led them to believe.

Beddoes's demonstration experiments sometimes failed; those carried out by Lavoisier in the 1780s were successful. Lavoisier, the presiding genius of the Chemical Revolution, had encouraged his instrument makers to construct what was the most dramatic and, in the case of his best balance, the most sensitive chemical apparatus of the eighteenth century. Modern estimates put the accuracy of his great balance made by Fortin, formerly engineer to the King, at 1/400,000, an accuracy that cannot be beaten by the best mechanical balances today (13). His gasometers were masterpieces. He used them to demonstrate the composition of atmospheric air and of water. His demonstration experiments were on the grand scale. In using his gasometers, Lavoisier worked volumetrically. When working with gases by volume and solids by weight, for example in the oxidation of mercury, he measured the volumes of gases, corrected these for temperature and pressure, and then converted these to weights, via densities. That sounds straightforward; but he noted that gases were sometimes lost through leakage from the apparatus and sometimes contaminated by the accidental entry of atmospheric air. He often dismissed such leakage and contamination as trivial. Predictably, this could lead him astray. He reported in his *Traité* of 1789 that atmospheric air was composed of 27% of oxygen and 73% nitrogen by volume (14)—a poor result, so poor that chemists elsewhere had a hard time replicating it. Water was 16% hydrogen by weight, a pretty poor result again, since water is about 11% hydrogen. Lavoisier was working in the certainty (shared by all chemists) that the weight of reactants was equal to the weight of products, and once he had obtained a result manifesting this equality, he *knew* that this was the right result, superior to one obtained by taking the average of a large number of experiments; at most, he would rely on a small number of experiments. He sometimes published his results to six, seven, or even eight figures. These figures were the result of computation, converting from one system of measurement to another, and Lavoisier explained this—but his explanation was and is easily overlooked.

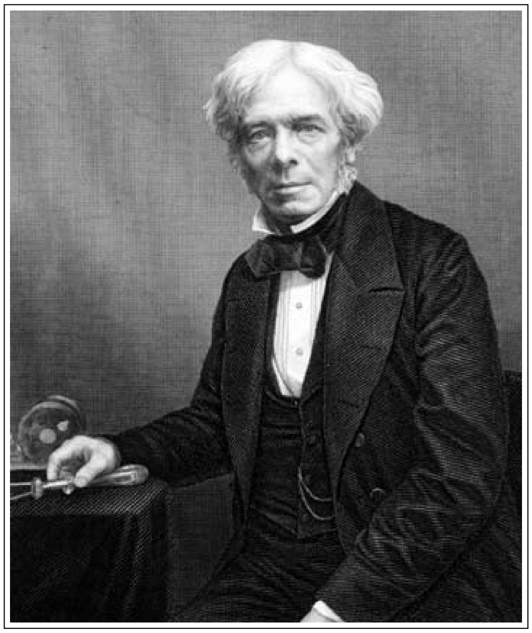
William Nicholson, editor of *A Journal of Natural Philosophy, Chemistry and the Arts* and author of textbooks and a dictionary of chemistry, was scathing about publishing long strings of numbers (15). In his dictionary, Nicholson gave an account of balances, from which (16):

> …the student may form a proper estimate of the value…of the theoretical deductions in chemistry that depend upon a supposed accuracy in weighing, which practice does not authorize. In general, where weights are given to five places of figures, the last figure is an estimate, or guess figure; and where they

> are carried farther, it may be taken for granted that the author deceives either intentionally, or from want of skill in reducing his weights to fractional expressions, or otherwise.

He examined the stages involved in Lavoisier's experiment of the synthesis of water by the continuous combustion of hydrogen and oxygen and concluded that the estimation of hydrogen was at best good to three figures, and of oxygen to four (17).

Lavoisier was, in spite of these strictures, a skilled experimenter and brilliant theoretician; and his published and unpublished results were mostly good and repeatable by others. But there were other chemists who knew what the results *should* be, and whose results were not repeatable. Usselman has charitably called them careless chemists. Thomas Thomson was one such (18). His weakness was his conviction that Prout's hypothesis was true: all atomic weights had to be integral multiples of the atomic weight of hydrogen. Thomson was convinced that the very numerous investigations he described fully confirmed Prout's hypothesis (19). He had taken great pains to obtain the right results, sometimes repeating an experiment eight or ten times before he was satisfied. In the case of nitrogen, he started with nitrates and nitric acid. One set of results gave him the atomic weight of nitrogen as exactly 14 times that of hydrogen. Another set of experiments gave him a slightly different figure. It was clear to him that the latter set of experiments was in error (20):



Michael Faraday

> Had I obtained from 8.65 grains of nitre 4.004 cubic inches of azotic gas, instead of 4 cubic inches, this error would not have existed. But my apparatus was not delicate enough to measure the gas evolved 80 exactly—I may, in reality, have obtained 4.004, cubic inches, without perceiving the slight difference in volume.

And so he was able to explain away the small discrepancy in the results of one set of experiments. When he came to hydrochloric acid, containing one atom of hydrogen and one atom of chlorine, he showed that the atomic weight of chlorine was exactly 36 times the atomic weight of hydrogen. He cited Gay-Lussac's measurement of the vapor density of chlorine, which differed slightly from his own (21):

> If the temperature (as is most likely) was a few degrees above 60, his experiments would coincide exactly with my own.

Such reasoning enabled him to accept Prout's hypothesis as absolute (22). Contemporary chemists, including Berzelius, were far from convinced.

Berzelius, Davy, Faraday, and, as Rocke and Usselman have shown, Liebig (23) were among Thomson's near contemporaries who were meticulous in obtaining reproducible results that others could verify by repeating their experiments. Liebig and Thomson both had a teaching-research laboratory, although Liebig's was successful and Thomson's failed. Davy and Faraday each gave brilliant public lectures on chemistry. Faraday uniquely wrote a manual on the practice of experimental chemistry. Reading that manual gives us the opportunity to be guided by a great chemist through the full range of operations and apparatus in the early nineteenth century.

Up until the late eighteenth century, chemistry had been predominantly a science of qualities, although noting quantities; after the chemical revolution, chemical quantities were as important as qualities. The central instrument for quantifying chemistry was the balance. Faraday devoted 44 pages to its use. The precision balance was the most complex instrument that he discussed, and he explained that active chemists would need one, as well as two common balances, one for large and one for small weights (24):

> …for the weights with which it is necessary to work are almost without limit, and cannot be estimated by the same instrument.

The precision balance should be able to ascertain differences of the 1/50,000 or 1/60,000 part of the weight in the scale

Faraday devoted 116 pages to "pneumatic manipulation, or management of gases", a field where, as we have seen, experimental skills and therefore experimental results had varied widely. But Faraday was not concerned merely with sensitive apparatus and complex operations. At the other extreme were brief accounts of the uses of such simple items as corks and filter paper. Glass blowing was a crucial skill for chemists, at a time when there were few suppliers of chemical apparatus, and when most chemists were their own glass blowers; he gave a detailed account of "bending, blowing, and cutting of Glass." All his descriptions and prescriptions are clear, concise, and elegant. But Faraday insisted that one could not become a chemist by merely reading his book (25):

> No valuable experimental knowledge can be obtained at so cheap a rate. Practice is essential to that facility, without which nothing dependant upon the hands can be done well.

And so he provided a course of "inductive and instructive practices." Faraday was a virtuoso in performing experiments, and a superb teacher of chemical practice.

By the time Faraday wrote, the canons of good laboratory practice had shifted significantly from those of a quarter century before. Volumetric analysis had become precise, and getting results as good as Cavendish's was a reasonable goal for competent chemists. Weighing gases directly and accurately had replaced Black's indirect method. Gone was Lavoisier's insistence that single experiments sufficed if reactants and products could be shown to have exactly the same weight; Lavoisier's method unwittingly showed that weights could balance and yet, given compensating errors, could be seriously awry. Reasonable limits of error were defined and refined; Nicholson's criticisms of Lavoisier showed this process at work, as did Cavendish's insistence that it was necessary to be able to repeat an experiment several times to demonstrate consistency and to arrive at an acceptable result. Cavendish had provided a model for identifying causes of error and modifying experimental procedures to minimize them. Black had been scrupulous about the need to obtain pure substances by repeated washing, distillation, solvent extraction, and more. Davy's first Bakerian lecture, on some chemical agencies of electricity, was a model for eliminating contamination from the atmosphere, from reagents, and from reaction vessels. Chemists increasingly described their experiments and their apparatus in sufficient detail for others to repeat them, and sought to avoid unnecessary complexity in the design of experiments. By Faraday's time, chemical methods had been transformed from those in normal use at the start of the chemical revolution.

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