Sir Humphry Davy on Platinum

A FOOTNOTE TO THE BICENTENARY CELEBRATIONS

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Sir Humphry Davy was born in Penzance on December 17th 1778 and to celebrate the bicentenary of his birth the Royal Institution, where he was Resident Professor from 1802 to 1813 and Honorary Professor for the following ten years, organised a number of lectures and an exhibition illustrating his life and work.

Davy is probably best known to chemists for his isolation of potassium and sodium, and later the alkaline earth elements, by means of the then new methods of electrochemistry, and to the general public for his invention of the miner's safety lamp—the latter completed in only two weeks of intense investigation. Many other aspects of Davy's genius, his many decisive experiments, his remarkable series of lectures to crowded audiences at the Royal Institution—to which he gave the character it has ever since retained—and his romantic nature and love of poetry, were all reviewed during the Symposium held during December, but an important but less appreciated phase of his chemical investigations underlies one of the most significant applications of platinum in modern industry.

Davy had excellent opportunities of securing platinum for his experiments. In 1807—the year in which he first electrolysed fused potash in a platinum spoon connected to the positive terminal of a battery—he was elected one of the Joint Secretaries of the Royal Society (he had been elected a Fellow in 1803) his colleague being William Hyde Wollaston. Their association developed into a real friendship, and Davy was able to obtain his requirements from Wollaston, who had only recently succeeded in refining native platinum on a scientific basis and in making malleable platinum available commercially. In addition

Sir Humphry Davy
1778–1829

When Davy began his researches at the newly founded Royal Institution the new field of electricity had just opened, while the laws of chemical combination had yet to be firmly established. In the first of his six Bakerian Lectures to the Royal Society in 1806 he introduced a new concept into chemistry—the relation of electrical charge to chemical affinity, and much of his later work was in electrochemistry, but in his major researches on flame that led to the invention of the safety lamp he also discovered the phenomenon of heterogeneous catalysis over platinum

From the portrait by Sir Thomas Lawrence in the possession of the Royal Society.

to their association in the Royal Society Wollaston was among the managers of the Royal Institution, and in the Davy archives preserved there a note gives his appreciation of Wollaston, describing him as

"I think jealous and reserved in the earlier part of his life, but latterly he became far more agreeable and confiding and was a warm and kind friend and a pleasant social companion"

In 1812 Davy published his "Elements of Chemical Philosophy", the first section comprising a remarkable summary of the history of chemistry. His comments on platinum later in the book are indicative:

"Platinum is a most valuable metal; as it is not oxidisable, nor fusible under common circumstances, and only with difficulty combinable with sulphur, and not acted upon by common acids, it is admirably adapted for the uses of the philosophical chemist, and may be advantageously employed in all cases where gold is applied, unless the use is connected with the colour or malleability of the metal"

One other finding of importance in connection with platinum, made a few years later than the major discovery about to be described, was the change in resistance of a platinum wire with increasing temperature, the basis of course of the modern resistance thermometer. In a paper given to the Royal Society in July 1821 on "Further Researches on the Magnetic Phenomena Produced by Electricity, with some new experiments on the properties of electrified bodies in their relation to conducting powers and temperature" (1), Davy wrote

"The most remarkable general result that I obtained by these researches, and which I shall mention first, as it influences all the others, was, that the conducting power of metallic bodies varied with the temperature, and was lower, in some inverse ratio, as the temperature was higher. Thus a wire of platinum of 1/220, and three inches in length, when kept cool by oil discharged the electricity of two batteries, or of twenty double plates: but when suffered to be heated by exposure in the air, it barely discharged one battery"

Among his inspired forecasts were the concepts that

"Matter may ultimately be found to be the same in essence, differing only in the arrangement of its particles"

and that the elements might be arranged in the order of their natural resemblances; for example

"Platinum is analogous to gold, silver and palladium; and palladium is connected by distinct analogies with tin, zinc, iron and manganese"

But the most vital discovery concerning platinum arose during Davy's classic researches on flame arising from an appeal made to him after a disastrous explosion in a coal mine, followed by a number of other similar explosions in the same area of Northumbria. In a paper read to the Royal Society on January 23, 1817 (2), Davy described "the discovery of a new and curious series of phenomena".

"I was making experiments on the increase of the limits of the combustibility of gaseous mixtures of coal gas and air by increase of temperature. For this purpose, I introduced a small wire-gauze safe-lamp with some fine wire of platinum fixed above the flame, into a combustible mixture containing the maximum of coal gas, and when the inflammation had taken place in the wire-gauze cylinder, I threw in more coal gas, expecting that the heat acquired by the mixed gas in passing through the wire-gauze would prevent the excess from extinguishing the flame. The flame continued for two or three seconds after the coal gas was introduced; and when it was extinguished, that part of the wire of platinum which had been hottest remained ignited, and continued so for many minutes, and when it was removed into a dark room, it was evident that there was no flame in the cylinder.

It was immediately obvious that this was the result which I had hoped to attain by other methods, and that the oxygene and coal gas in contact with the wire combined without flame, and yet produced heat enough to preserve the wire ignited, and to keep up their own combustion. I proved the truth of this conclusion by making a similar mixture, heating a fine wire of platinum and introducing it into the mixture. It immediately became ignited nearly to whiteness, as if it had been itself in actual combustion, and continued glowing for a long while, and when it was extinguished, the inflammability of the mixture was found entirely destroyed.

A temperature much below ignition only was necessary for producing this curious phenomenon, and the wire was repeatedly taking out and cooled in the atmosphere till it ceased to be visibly red; and yet when admitted again, it instantly became red hot . . .

I have tried to produce these phenomena with various metals; but I have succeeded only with platinum and palladium; with copper, silver, iron, gold and zinc, the effect is not produced."

Thus did Davy discover the phenomenon of heterogeneous catalytic oxidation, and although he obtained the same result with ether, alcohol and other vapours it was left to others to carry further the study of this profoundly important effect. Edmund Davy, his cousin and one-time assistant in the Royal Institution and later Professor of Chemistry at Cork, went on to prepare finely divided platinum catalysts that were active at room temperature (3) while Michael Faraday—sometimes described as Davy's greatest discovery and his major contribution to science—who was assisting Humphry Davy in the experiments just described, went on much later to the study of catalysis, having been mystified by the peculiar reaction of platinum with the oxygen and hydrogen produced in his experiments on the electrolytic decomposition of water (4).

Davy himself gave little further attention to the phenomenon and made only one passing reference to it in a somewhat obscure place. In 1818 he had published a book "On the Safety Lamp . . . with Some Researches on Flame", but in 1825 he was moved to publish a second edition because his experience, as he wrote in the preface

> "having shewn that the precautions which it was intended to describe either are not known or are not attended to, I have thought it might assist the cause of humanity to advertise the book a second time" (5)

This edition contained several appendices, and in Appendix No. 2 he returned to the subject and to the later work of Döbereiner with finely divided platinum such as Edmund Davy had used (6) and of Dulong and Thenard, who had shown that palladium and iridium could behave catalytically at room temperature while nickel, cobalt, rhodium, silver and gold were active only at higher temperatures (7). Davy continued:

> "It is probable that the rationale of all these processes is of the same kind. Whenever any chemical operation is produced by an increase of temperature, whatever occasions an accumulation of heat, must tend to give greater facility to the process; a very thick wire of platinum does not act upon a mixture of oxygen and hydrogen, at a heat below redness; but if beat into thin laminae, it occasions its combustion at the heat of boiling mercury, and, when in the form of the thinnest foil, at usual temperatures. I cooled the spongy platinum to 3° of Fahr., and still it inflamed hydrogen nearly of the same temperature, issuing from a tube cooled by salt and ice.
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> I thought that common radiant heat or light, might be necessary to the effect; but the cooled metal and the gases acted with the same phenomena in darkness.
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> It may be supposed that the spongy platinum absorbs hydrogen, or that it contains oxygen; but neither of these hypotheses will apply to the fact that I first observed, of the ignition of fine wires in different mixtures of inflammable gases and air, at temperatures so far below ignition.
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> A probable explanation of the phenomenon, may, I think, be founded upon the electro-chemical hypothesis which I laid before the Royal Society in 1806; and which has been since adopted and explained, according to their own ideas, by different philosophers."

Immediately after the publication of this second edition Davy became ill and exhausted, and after four years of wandering in Europe he died in Geneva at the early age of 50 on May 29, 1829.

A century and a half later some of the questions raised by Davy's discovery have still not been satisfactorily answered despite intensive research, especially during the past twenty-five years or so. Ignorance of the finer points of reaction mechanism has not, however, proved to be a hindrance to the large-scale usage of catalysed reactions depending upon platinum or its allied metals in modern chemical industry.

References

1 Humphry Davy, *Phil. Trans. Roy. Soc.*, 1821, **111**, 425

2 Humphry Davy, *Phil. Trans. Roy. Soc.*, 1817, **107**, 77

3 Edmund Davy, *Phil. Trans. Roy. Soc.*, 1820, **110**, 108

4 Michael Faraday, *Phil. Trans. Roy. Soc.*, 1834, **124**, 55

5 Humphry Davy, "On the Safety Lamp for Preventing Explosives in Mines, Houses Lighted by Gas, Spirit Warehouses, or Magazines in Ships etc., with Some Researches on Flame", 1825, Appendix 2, pp 148–151

6 J. W. Döbereiner, *Ann. Chim. Phys.*, 1823, **24**, 91

7 P. L. Dulong and L. J. Thenard, *Ann. Chim. Phys.*, 1823, **23**, 440; see also A. J. B. Robertson, *Platinum Metals Rev.*, 1975, **19**, (2), 64