# Sir William Crookes

## INVESTIGATIONS ON IRIDIUM CRUCIBLES AND THE VOLATILITY OF THE PLATINUM METALS

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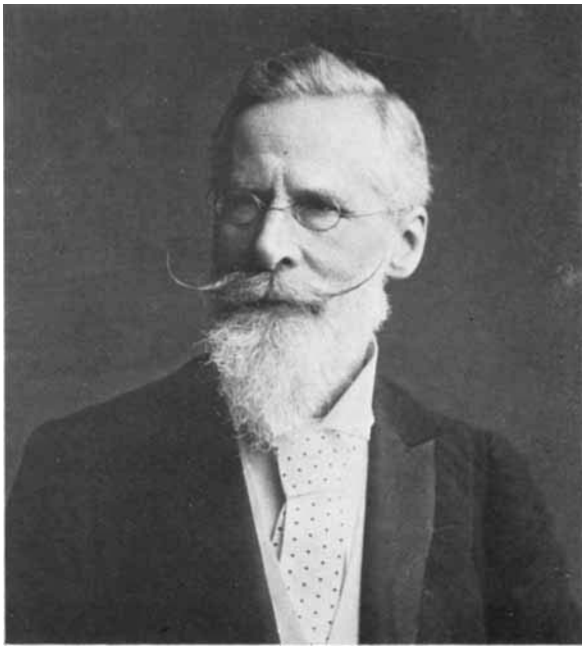
**Johnson Matthey & Co Limited**

William Crookes was born on June 17th, 1832, and after attending courses in chemistry at the College of Science, remained for three years as an assistant under Professor Hoffman. He then taught for nearly a year as lecturer in chemistry at Chester Training College, and was known as "Professor" ever afterwards. He had some private means, and in 1858 came to London and set up as a consultant with a small private laboratory at his home at 20 Mornington Road, near Regent's Park.

In December 1859, he founded the weekly journal *The Chemical News* and remained as editor for the next sixty years. *The Chemical News* prospered from the first and was widely read. It provided excellent summaries of important technical and scientific publications throughout the world and, through its correspondence pages, a forum for many notable – and often amusing – discussions.

Only fifteen months later Crookes had a piece of good fortune when he was able to announce on March 30th, 1861, the discovery of a new element which he later christened Thallium. The discovery is often described as the result of a spectroscopic examination. In fact, Crookes very simply – though no less to his credit – observed an unexpected, and hitherto unreported, bright green flash in the course of a flame test when a small sample of the seleniferous residues from sulphuric acid manufacture at Tilkerode, in the Hartig mountains, was supported on a



**Sir William Crookes, O.M., F.R.S.**
**1832–1919**

*President of the Royal Society from 1913 to 1916, Sir William Crookes died fifty years ago this month at the age of 87. Most of his working life spanned an era in which a man could take very nearly the whole of science as his province. It was thus almost inevitable that the platinum metals should have been included among his many interests, and his observations on the loss of weight of the platinum group metals when heated in air have indeed been quoted as authoritative for nearly half a century*

*In this detail from a painting by H. Jamyn Brooks at the Royal Institution the front row shows, left to right, Mr A. J. Balfour (then Prime Minister), Sir William Crookes, Crichton Browne, Lord Rayleigh, George Matthey, Ludwig Mond and Oliver Lodge. The occasion was the demonstration by Dewar in 1904 of the properties of liquid hydrogen*

platinum wire in a gas flame. The material was left over from earlier work on sulpho-selenides in which he had engaged at the College of Science. Crookes was a good experimenter, and he followed up his initial observation by isolating the new element and investigating its properties. A sample was inevitably shown at the Great Exhibition of 1862 and recognition very quickly followed (too quickly, some declared) by his election as a fellow of the Royal Society in November 1863.

His determination of the atomic weight of thallium, reported in 1873, was a first-class piece of work and the figure he obtained, 203.642, equivalent to 204.03 when corrected to modern values, compares very favourably with the 1961 International value of 204.37.

His flair for careful observation continued to serve him well. He devised the radiometer – though his explanation of its action was soon discredited – he described the Crookes dark space in the cathode discharge tube – but was less than profound in his theoretical views on electrical discharges through gases – he separated Uranium X, he devised the spintharoscope, and he developed Crookes glass to protect the eye against the ultra-violet. In his later years, like Sir Oliver Lodge, he explored the mysteries of spiritualism. Lord Kelvin is said to have remarked of him that "Crookes started more absolutely new hares than any other man among his scientific contemporaries".

All his work was done in his private laboratory in his house, first in Mornington Road and after 1880 at 7 Kensington Park Gardens (which he claimed to be the first in England to be lighted by electricity) and much of it was financed by grants from the Royal Society. In his later years he was involved in a variety of commercial enterprises.

He was prominent in every area of scientific activity in London for nearly sixty years and was widely honoured. He was elected President of the Institution of Electrical Engineers in 1890, of the British Association in 1898, and of the Royal Society in 1913. He was awarded the Order of Merit in 1910. No scientific meeting of note failed to welcome him, and in scores of paintings and photographs of scientific gatherings of the period his distinguished bearded figure is prominent in the foregound.

The early issues of *The Chemical News* devoted a remarkable amount of space to the platinum metals. The first three issues serialised a translation of a classic paper by Deville and Debray, "On platinum and its associated metals", which includes a description of a long-forgotten use of the lime furnace for the fire-refining of platinum. The base metals are slagged off, gold and palladium vaporised and collected in an earthenware tube, and osmic acid finally trapped in a vessel full of ammonia. Part of the osmium is deposited on the tube walls in the metallic state. Later issues included a reprint of a paper by Woolcott Gibbs, describing the treatment of osmiridium residues from Californian gold and from Siberia, and a translation of Claus' classic paper "On certain properties of the platinum metals, particularly ruthenium".

It was not until 1908 that Crookes published any original observations on the platinum metals, but in a communication read in May of that year to the Royal Society he was the first to "draw the attention of chemists to the great advantages of using crucibles of pure iridium instead of platinum in laboratory work".

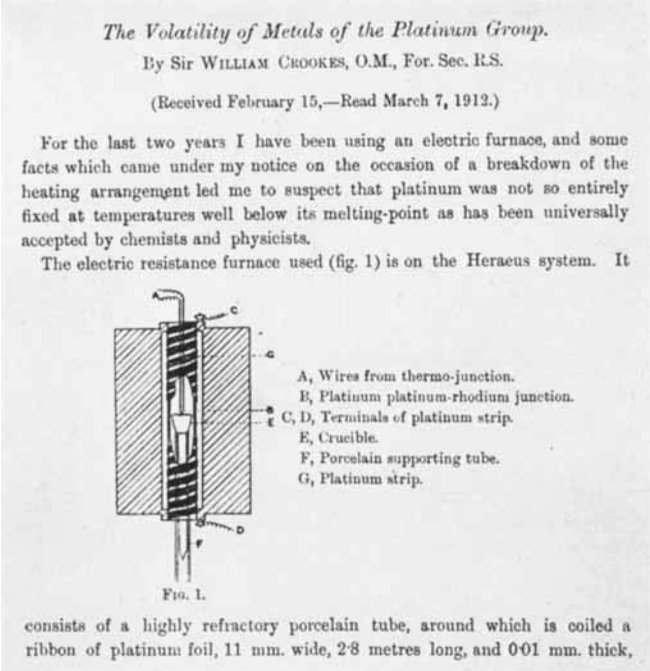
The crucibles were supplied by "Messrs Johnson and Matthey" and one of these has been preserved to this day. Crookes noted that the iridium crucibles resisted fusion of many fluxes, including caustic soda, and were not attacked by molten lead, zinc, nickel, gold and iron. Temperatures are not recorded. One paragraph introduces without comment a quite unexpected characteristic. "Copper melted in the crucible for some time", Crookes wrote, makes it "hot rotten, i.e. it is brittle when hot. But if the copper is well burnt off at a high heat the iridium reverts to its original condition". No explanation is given as to how copper could be "burnt off".

One other passage reveals a common misconception. "Heated for some hours over a Bunsen burner insufficiently supplied with air the iridium crucible is unaffected and the deposit of carbon easily burns away, leaving the surface of the metal uninjured. All chemists know how seriously a platinum crucible is attacked in these circumstances". In fact, a clean platinum crucible is quite unattacked, though it may be disastrously embrittled if it contains certain compounds (particularly arsenates or phosphates) which are reduced in the yellow flame and alloy with the platinum to form brittle phases. Many chemists even today attribute the trouble to attack on platinum by carbon.

These details apart, in advocating the use

*One of the iridium crucibles made for Crookes in 1908 by Johnson Matthey*

*The first page of Crookes' paper on "The Volatility of Metals of the Platinum Group" read to the Royal Society in March 1912, showing the platinum-wound furnace in which his investigation was carried out*


*The Volatility of Metals of the Platinum Group.*

By Sir WILLIAM CROOKES, O.M., For. Sec. R.S.

(Received February 15,—Read March 7, 1912.)

For the last two years I have been using an electric furnace, and some facts which came under my notice on the occasion of a breakdown of the heating arrangement led me to suspect that platinum was not so entirely fixed at temperatures well below its melting-point as has been universally accepted by chemists and physicists.

The electric resistance furnace used (fig. 1) is on the Heraeus system. It



FIG. 1.

consists of a highly refractory porcelain tube, around which is coiled a ribbon of platinum foil, 11 mm. wide, 2·8 metres long, and 0·01 mm. thick,

of iridium (and rhodium) crucibles for certain chemical operations, Sir William Crookes was far in advance of his times. It is only within the last decade that any serious application has been made of iridium crucibles, although they are now employed widely for growing laser crystals and also for melting special glasses.

The measurements reported by Crookes to the Royal Society in March 1912 of the loss of weight of the platinum metals when heated in air are better known. They stemmed from his observation of the "fine glistening dust" deposits of platinum on the porcelain tube of a furnace wound with platinum ribbon. The furnace had failed through localised thinning of the winding after operating at 1500°C, and under the microscope the deposits appeared as "beautifully formal hexagonal plates with a brilliant metallic lustre and perfect crystalline form".

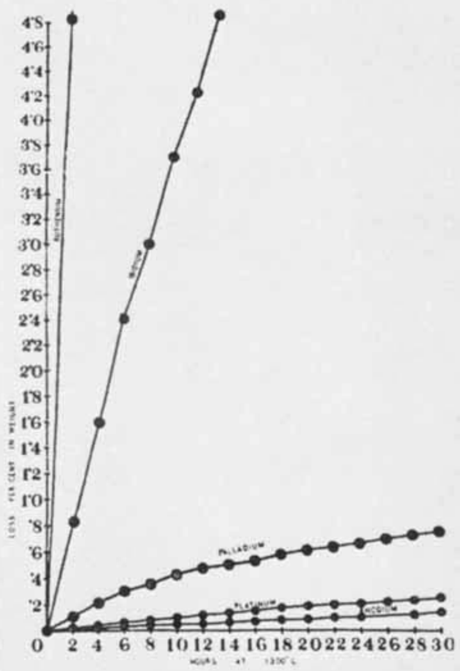



FIG. 9.

*Crookes' results for the losses in weight of the platinum metals when heated in air at 1300°C. It will be seen that the loss is expressed as a percentage of the weight, not of the unit area of surface, in spite of the differences in size and form of the specimens*

*The weight losses of palladium and iridium in air at 900°C. No loss was recorded for platinum or rhodium at this temperature*

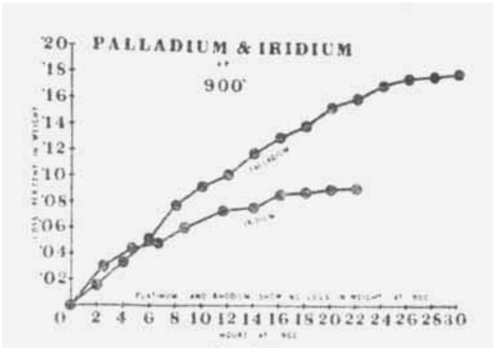



Fig. 10.

Crookes accordingly set out to determine the loss of weight of the various platinum metals, using as his specimens a platinum crucible weighing 150 grains, an iridium crucible "as hard as steel" of about the same weight, a polished plate of palladium weighing 58 grains, a rhodium specimen (presumably as sheet) weighing 32 grains, and a "highly polished plate" of ruthenium. The weight and dimensions of the ruthenium are not specified; and it is of interest to reflect that there must be few, even today, who have seen highly polished ruthenium sheet. The choice of grains instead of grammes as units of weight is explained in a footnote: "I have used my standard platinum grain weights for nearly fifty years, and they are too valuable to discard in favour of gramme weights, which would demand many months' work on them to bring them to the state of accuracy into which I have now got the grain weights".

In devising the arrangements for heating, Crookes was concerned to avoid the possibility as he said of "the action known as 'air washing' (particles from a white-hot semi-molten surface being mechanically carried away by a current of impinging air)". Today it is not clear why the surfaces should have been thought to be "semi-molten" at 1300°C, the highest temperature used. Accordingly, the heating was carried out in a vertical resistance-heated tube furnace, closed at the top and "nearly closed at the place where the crucible stood and almost completely obstructed at the lower end". In this way, "the platinum was in almost still air".

The experiments were made at 1300°C and 900°C, the samples being removed for weighing every 2 hours, the total time of heating being 30 hours. The results are shown in Figs. 9 and 10 of his paper, reproduced here, and have been widely quoted ever since. The relatively high losses of platinum at the higher temperature almost certainly surprised Crookes, but he rejected the possibility that these could be due to a volatile oxide on the evidence that the crystals deposited on the walls of a platinum-wound furnace were metallic platinum. The concept of oxygen acting as a carrier to transport platinum from a hotter source (where platinum oxide concentration is high) to a cooler surface (yet above the decomposition temperature of the oxide) was of course not available to him.

It was a little unfortunate, perhaps, that the upper temperature chosen was 1300°C. At this temperature it is true that the vapour pressure of $PtO_2$ in air is rather higher than that of $RhO_2$ so that rhodium surfaces lose weight less than platinum ones. This led to a belief that at high temperatures in general rhodium is the less volatile in air; actually above 1300°C the vapour pressure of $RhO_2$ increases very rapidly and soon greatly exceeds that of $PtO_2$.

With iridium, rhodium and ruthenium it was obvious visually that oxidation occurs and Crookes endeavoured to ascertain whether iridium would volatilise in a vacuum at 1300°C. Experimental difficulties, however, prevented him from reaching a definite conclusion.

Crookes was certainly among the first to study the behaviour of the platinum metals when heated in air to high temperatures, though in this as in other directions he was an experimenter rather than a philosopher.