THE PLATINUM METALS

By A. R. POWELL, F.R.S.

IN April 1803 there appeared in the window of a mineralogist's shop in Soho an anonymous leaflet offering for sale a new metal called palladium. In the following year William Hyde Wollaston announced his discovery of another new metal which he called rhodium, and he afterwards admitted in a letter to *Nicholson's Journal* (dated February 1805) that he was the discoverer of palladium and the author of the anonymous advertisement. To celebrate the triple jubilee of Wollaston's announcement of the discovery of palladium, the Institution of Metallurgists is organizing an exhibition of the platinum metals at Grosvenor House, Park Lane, London, W.1, in the week beginning October 19. This exhibition, which will be opened by H.R.H. the Duke of Edinburgh, will illustrate the history of the platinum metals during the past 150 years, the great part they have played in the development of the chemical and electrical industries, and their modern scientific, technical and aesthetic uses. The exhibition will be open free to the general public during October 22-24 between the hours of 10 a.m. and 8 p.m.

Wollaston is now rightly regarded as the greatest pioneer in the platinum metal industry, since he was the first to bring a trained analytical mind to the problem of obtaining malleable platinum. The first account of the existence of platinum in the New World was published by Don Antonio de Ulloa in 1748, and the metal was first recognized as a new element by the Swedish assayer, Scheffer, in November 1751. In the following fifty years many workers in Europe studied the new metal and endeavoured to bring it into a coherent malleable form. W. Lewis, A. S. Marggraf, C. von Sickingen and Delisle were among those who published important observations on the metal; but it was not until about 1786 that Pierre-François Chabaneau, working in Spain in collaboration with the brothers de Elhuyar, succeeded in solving this problem; the methods they used, however, remained a close secret until the early years of this century, when an account of them was discovered among some old archives in Seville.

Working independently in Great Britain, however, Richard Knight discovered "a new and expeditious process for rendering platinum malleable" which he published in the *Philosophical Magazine* in 1800. Whether this publication was the incentive which prompted Wollaston to turn his attention from medicine, in which he graduated at Cambridge, to the study of the platinum metals is not known with certainty; but the fact remains that in this year he abandoned his medical practice and devoted the greater part of his energies to investigating the platinum metals. At this time the refining of the native alluvial platinum grains from Colombia was based on purely empirical observations. Wollaston, however, set himself the task of studying the chemical procedures of refining in a scientific manner, and the first fruits of this work were the discovery of palladium and rhodium. Almost simultaneously his friend, Smithson Tennant, working in Cambridge, discovered iridium and osmium and published his work in 1804. It was not, however, for another forty years that the Russian, Karl Klaus, working at the University of Dorpat, found the last of the platinum group of

metals, ruthenium, in the osmiridium residue remaining after the aqua regia extraction of Russian platinum mineral. Ruthenium occurs only in very small proportions in Colombian platinum mineral, and this fact probably explains why it was not detected by Wollaston or Tennant.

Wollaston thus may be said to have been the first to undertake a systematic investigation of the complex problems involved in the refining and fabrication of the platinum metals. Not only did he succeed in devising scientific methods for their purification, but he also worked out procedures for the consolidation of platinum sponge into ingots of consistently high quality, and for many years carried on a profitable business in supplying platinum ware for use in the laboratory and in the concentration of sulphuric acid. The details of his methods of fabrication were kept secret until 1828, when he revealed them in the Bakerian Lecture to the Royal Society only about a month before his death on December 22.

By this time the beginnings of the present large platinum industry may be said to have been laid. In Britain, Percival Norton Johnson, assisted by his brother-in-law, Thomas Cock, had undertaken the business of platinum refining and fabrication which is now carried out by the firm of Johnson, Matthey and Co., Ltd. In Russia, the discovery of platinum in the Urals in 1819 was followed by the setting up of a platinum refinery at St. Petersburg under the direction of P. A. Sobolevsky. In France, Bréant and Couturier started work in 1812 and had a very flourishing business in supplying platinum ware to Western Europe between 1820 and 1837; they were succeeded by Desmoutis, who was joined by Quennessen about fifteen years later. In Germany, the great Heraeus business was founded in 1851, and the Deutsche Gold und Silber Scheide-Anstalt in 1873 under the name of Roessler.

In the past hundred years or so, the major uses of platinum and the platinum metals have been based on the high melting point and general chemical inertness of the metals. Platinum crucibles for chemical laboratory work were in demand from a very early date; much of the Spanish output made under the direction of Chabaneau went to make platinum apparatus for the great European chemists, and the work of meeting this demand was carried on by Wollaston, and later by Bréant and Couturier. Platinum began to be used for making jewellery in the eighteenth century, the work of the French goldsmith Janety being especially famous. Undoubtedly the first use of platinum on a large scale was for coinage; between 1828 and 1846 nearly half a million ounces of platinum were coined in Russia as 3-, 6- and 12-rouble pieces, and this currency was withdrawn only because a serious fall in the price of platinum caused fears of extensive counterfeiting.

The first use of platinum in the chemical industry was for making boilers for concentrating the dilute sulphuric acid made by the lead-chamber process; for this purpose Wollaston fabricated, between 1805 and 1818, no less than sixteen large boilers each weighing between 322 and 477 oz. Even to-day platinum boilers are in use for the preparation of the purest concentrated acid for analytical purposes. Probably the next important industrial use of

platinum was as a catalyst, supported on magnesium sulphate or asbestos, for the manufacture of sulphuric acid by the contact process; vanadium catalysts have, however, largely supplanted platinum for this purpose owing to their lower price and inertness towards impurities which poison the platinum, but platinized silica gel is still used in some contact acid plants where a high quality of acid is required and relatively pure sulphur dioxide is available.

To-day platinum and platinum alloys are extensively used for melting high-grade optical glass and for making fibre glass, for precious metal thermocouples for the measurement of high temperatures, for electrodes for making persulphates for the manufacture of hydrogen peroxide, and for spinnerets for the production of artificial fibres. The electrical industry, too, is a very large user of the platinum metals in the form of contacts of all kinds, and as resistors for electric furnaces for operating above 1,000° C.

The catalytic properties of the platinum metals are also being exploited more extensively. Platinum and platinum-rhodium alloy gauzes are exclusively used for the manufacture of nitric acid by the ammonia oxidation process of Ostwald, and only recently it has been discovered that platinum dispersed on an alumina, silica or a silica-alumina base can be used in the vapour phase re-forming of the lighter petroleum fractions to produce high-octane motor spirit with superior anti-knock properties. Palladium, too, is finding wide applications as a hydrogenation catalyst in numerous organic syntheses. Recent American work has shown that palladium deposited on alumina is a very active catalyst for the reduction of anthraquinone to the corresponding hydroquinone, which can then be oxidized with air back to the quinone with the formation of hydrogen peroxide, a reaction first developed in Germany during the recent war for the manufacture of hydrogen peroxide for V2 rockets.

Although the platinum metals, with the exception of osmium, are highly resistant to oxidation at room temperature, ruthenium, palladium, rhodium and iridium, even in the massive form, tarnish readily on heating to temperatures above 500–600° C.; but the last three become bright again at temperatures of the order of 1,100–1,200° C. owing to the volatilization or decomposition of the oxide; ruthenium, however, continues to oxidize with increasing rapidity with rise in temperature owing to the formation of the highly volatile tetroxide. Platinum alone of this group remains untarnished on heating in air up to its melting point; but nevertheless it appears to be oxidized at high temperatures in air with the formation of an unstable volatile oxide which decomposes to the metal at slightly lower temperatures; this is the cause of the bright spangles of platinum often seen on the refractory surfaces close to the platinum windings of small resistance furnaces which have been operated for long periods. That an oxidation process is the cause of this phenomenon is proved by the fact that no such volatilization occurs in a vacuum or in reducing or inert atmospheres, and if the refractory surface is kept fairly cool the platinum is deposited in a black form which contains several per cent of oxygen.

Russia and Colombia remained the chief sources of the platinum metals until about the period of the First World War, when the large increase in the output of nickel and copper from the Sudbury mines in Canada combined with improvements in the

refining process resulted in large amounts of the platinum metals becoming available in the residues from the Mond process of refining nickel and, later, in the anode slimes from the electrolytic refining of the nickel and copper. The amount of the platinum metals produced from this source rapidly increased during the next decade until it reached an average of about 250,000 oz. per annum, at which figure it has remained.

In the middle 1920's large deposits of platinum ores were found in various parts of the Transvaal, principally in the Potsgieetersrust, Lydenburg and Rustenburg areas, but by about 1930 only the Rustenburg area remained as an active producer. The output from this area has risen steadily until it is now about as large as that from Canada. The Merensky reef, which surrounds the Bushveld igneous complex in the centre of the Transvaal, is the principal source of the platinum metals; here they occur chiefly in combination with sulphur, arsenic and antimony in a norite rock heavily impregnated with chromite and containing nickel and copper sulphide minerals. In addition to sperrylite (platinum diarsenide), first found in the Sudbury nickel ores, and laurite (ruthenium sulphide), the South African platinum ores contain the new minerals, cooperite (platinum monosulphide), braggite (platinum-palladium-nickel sulphide) and stibiopalladinite (palladium antimonide). The platinum metals occur in these ores roughly in the proportion: platinum 100, palladium 55, rhodium 6, ruthenium 13, iridium 1, osmium 1.

Small alluvial deposits of platinum were discovered in Abyssinia in the late 1920's and much larger deposits in the Goodnews Bay district of Alaska in 1936. The Alaskan alluvial concentrates are remarkable in that they contain a high proportion of iridosmine, which has an unusually high content of iridium and a low content of osmium (only about 10 per cent). The Tasmanian alluvial deposits of osmiridium are now practically worked out; but considerable quantities of osmiridium, associated with native platinum and laurite, are recovered from the heavy black sands which collect on the corduroy tables during the treatment of the gold blanket ore from various mines in the Witwatersrand area of the Transvaal; the precious metal concentrates obtained from this source contain up to 20 per cent of ruthenium with 30–40 per cent of osmium and 25–30 per cent of iridium, but are practically free from rhodium.

UNCERTAINTY, EXPECTATION AND DECISION IN BUSINESS AFFAIRS

DURING the recent meeting of the British Association in Liverpool, Section F (Economics) held a symposium on "The Logic, Philosophy and Psychology of Business Decision-making under Uncertainty", the main focus for discussion being Prof. G. L. S. Shackle's book, "Expectation in Economics" (second edition; Cambridge University Press, 1952). A day and a half were given to the discussion. Prof. Shackle, and many other economists, feel that the process by which a business-man reaches a decision depends very little, if at all, upon the rational assessment of probabilities which orthodox theory in the past assumed. But, of course, once