Short Communications

A simple method for the dissolution of platinum metals

Dissolution of the platinum metals and their alloys is frequently a difficult operation. Although platinum and palladium yield to aqua regia, rhodium presents more difficulty and ruthenium and iridium are quite intractable. GILCHRIST[1] has reviewed the commonly used methods. The traditional approach which involves extraction of platinum and palladium with aqua regia, followed by repeated oxidative alkaline fusions, is tedious and unsatisfactory. The method developed by WICHERS, SCHLECHT AND GORDON[2] is effective but involves heating aqueous hydrochloric acid solutions to temperatures up to 300° in sealed glass tubes. Incidental to a study of the spectrophotometric characteristics of the platinum metal elements in molten salt media, we have observed molten potassium pyrosulfate containing potassium chloride to be an excellent medium for attacking the metals and their alloys. Although the method was not studied extensively, it proved so useful that it was felt worthwhile to describe it briefly in order that others with similar problems might have the opportunity to adapt and apply it to their own needs.

The oxidizing strength of fused potassium pyrosulfate increases with increasing temperature, and at 600° chloride ion appears to be oxidized slowly to chlorine. When the platinum metals are fused with a mixture of potassium chloride and pyrosulfate, they dissolve rapidly. Presumably the chlorine formed acts on the metals directly, and the presence of chloride ion removes and stabilizes the products as chloride complexes.

Experimental

Dry potassium pyrosulfate was prepared by heating the commercial product in a Pyrex flask at about 600–700° until cessation of active bubbling indicated that the water had been driven off. The melt was then poured out into the depressions on a porcelain spot plate which gave, on cooling, a supply of pellets of convenient size. The samples in the form of foil, powder, or fine granules were sealed in small Vycor tubes together with approximately 5-g portions of the dried pyrosulfate and 0.5-g portions of dried potassium chloride. The tubes were conveniently fabricated in the shape of small test tubes, about 10 cm long, from standard Vycor 13 mm o.d. tubing having a wall thickness of approximately 1.2 mm, and should have a volume about three times that of the melt. The Vycor tubing is easily worked with an oxyhydrogen torch. The sealed tubes were placed in a standard crucible furnace, electrically heated and maintained at approximately 600° by a thermocouple-activated temperature controller. At this temperature, about 10 mg of sheet iridium could be dissolved in about 15 min; rhodium was acted upon with similar speed. Compact samples reacted more slowly, and it was found convenient to leave the tubes in the furnace for several hours to ensure complete solution. Platinum and palladium dissolve very rapidly; in fact, palladium may be dissolved without the addition of potassium chloride.

The behavior of ruthenium metal is somewhat more complex. In the absence of chloride, ruthenium is attacked by potassium pyrosulfate only at temperatures above 600°, whereupon it is converted partially to volatile ruthenium tetroxide and partially to a mixture of black substance believed to be ruthenium dioxide, insoluble in the melt and in water, together with a soluble species of unknown oxidation state. When chloride ion is present, ruthenium dissolves rapidly in the melt but the reaction products depend upon the temperature. At 600° in a sealed tube, a mixture of pyrosulfate and chloride converts the metal to a mixture of products including a brown solution probably containing ruthenium(IV), a black precipitate which is probably ruthenium dioxide, and traces of ruthenium tetroxide. At 500° under the same conditions, ruthenium dissolves rapidly and completely to form what is probably ruthenium(IV).

Gold metal is not attacked by potassium pyrosulfate alone. Gold salts decompose to metallic gold when fused with potassium pyrosulfate. In the presence of potassium chloride, however, gold metal is dissolved to give a yellow solution which is stable in the sealed tube. If a melt containing gold and chloride ion is allowed to stand open to the air, gold metal will precipitate after the chloride has volatilized.

Discussion

The new method of dissolution is advantageous in several respects. In comparison with other methods, the rate of attack is very high. Although only the pure platinum metals and a platinum – 10% iridium alloy were examined, it is expected that no alloy will be resistant to attack. The products of the fusion are readily soluble in water. The principal disadvantage of the method is that large amounts of potassium are introduced into the sample. It is of interest to compare the mechanical aspects of the dissolution method of WICHERS *et al.*[2] with the one developed in this work. In the former, pressures as high as 4000 p.s.i. are developed in the reaction tubes at the operating temperature of 300°. Generation of chlorine during the reaction also causes pressure to build up and the tubes must be cooled in solid carbon dioxide before they are opened. In the present method, the pressures developed are probably no higher than 30–40 p.s.i. and have never been great enough to break the standard wall 13 mm Vycor tubes that were used. The room temperature pressure, even after 15 h of heating, was always slightly below atmospheric. The method has been used mainly for the dissolution of amounts of metals in the 1 to 20 mg range. However, scaling up to gram quantities should introduce no serious difficulty.

This work was supported, in part, by the United States Atomic Energy Commission under Contract AT(30-1)-905.

Department of Chemistry and Laboratory for Nuclear Science
Massachusetts Institute of Technology
Cambridge 39, Massachusetts (U.S.A.)

DAVID R. GABBE
DAVID N. HUME

[1] R. GILCHRIST, The Platinum Metals and Gold, in W. F. HILLEBRAND, G. E. F. LUNDELL, H. A. BRIGHT AND J. I. HOFFMAN, *Applied Inorganic Analysis*, 2nd Ed., Wiley, New York, 1963, p. 343.

[2] E. WICHERS, W. A. SCHLECHT AND C. L. GORDON, *J. Res. Natl. Bur. Std.*, 33 (1944) 363.

(Received September 5th, 1963)