

# Reaction of Oxygen with the Platinum Metals

## I—THE OXIDATION OF PLATINUM

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*This paper has been written to provide a framework for the observed facts relating to the reactions between platinum and oxygen at temperatures up to the melting point. A thin film of feebly-stable solid platinum oxide is believed to form on platinum surfaces in air or oxygen at room temperatures and to thicken as the temperature is raised to about 500°C, when it decomposes. The loss of weight of platinum at higher temperatures is attributed to the formation of gaseous PtO<sub>2</sub>, and deposition of platinum on cooler surfaces (above about 500°C) to its disproportionation. A succeeding paper will deal with the oxidation of the other platinum metals.*

Platinum, unlike Shadrach, Meshach or Abednego, does not emerge entirely unscathed after many hours in a burning fiery furnace, and although the loss of weight in air is small even at temperatures near the melting point, the full explanation of this effect has proved to be an involved and fascinating story which is only now beginning to show coherence.

Even the basic mechanism has been difficult to establish. It has long been known that when a platinum wire is heated in vacuum it loses weight only very slowly at a rate that can be accounted for in terms of the vapour pressure of the heated metal. In other words, a hot platinum wire evaporates slowly in a vacuum, just like any other metal, by the

escape of thermally activated ions from the surface.

When, however, a platinum wire is heated in an environment of air or oxygen it loses weight very much more rapidly. It is evident that in these conditions some oxide or oxides of platinum must be involved. The "apparent vapour pressure" of platinum in oxygen at 1400°C, for instance, is six million times as great as its vapour pressure in vacuum. This point is explicitly made, for perhaps the first time, in a recent paper entitled "Oxidation of the Platinum-Group Metals", by C. A. Krier and R. I. Jaffee of Battelle Memorial Institute (1).

The study of this reaction is accompanied by many difficulties. Most investigators, including indeed Krier and Jaffee, have based their conclusions on measurements of the loss of weight of specimens heated in simple, electrically-heated tube furnaces through which air is passed. Sometimes the rate of passage of the air or oxygen over the specimen has been recorded, but it is seldom that the volume of air in the furnace or the temperature distribution throughout the heated chamber has been observed or even considered significant.

In these conditions the problem bears a close resemblance to that of attempting to measure the solubility behaviour of a crystal of salt by noting the rate at which it changes weight when suspended in a stream of running water in which streaming and eddy formation is uncontrolled and no measurements are made on the resulting solution itself.

It is not surprising that there are still considerable divergencies between the results of different investigators. In the past those who have shown the clearest grasp of the problem almost certainly are Alcock and Hooper. In their work, which was reviewed by Alcock in this journal (2), efforts were made to ensure that the atmosphere above the platinum was saturated with the platinum oxide. In much other work evidence of incomplete saturation, supersaturation, or both, can often be detected.

One point on which there is general agreement is that the oxide that forms at high temperatures is  $\text{PtO}_2$ ; and although the platinum and oxygen atoms are very loosely held together, this compound is, in fact, just stable.

### **Solid $\text{PtO}_2$**

At room temperature, according to Professor Leo Brewer of the University of California (3),  $\text{PtO}_2$  is a solid having a heat of formation at  $25^\circ\text{C}$  ( $298^\circ\text{K}$ ),  $\Delta H_{298}$ , of  $-32$  kilocalories per mole (that is, the reaction between Pt and  $\text{O}_2$  is exothermic). This oxide, furthermore, is most probably invariably present on platinum surfaces at room temperature although PtO may also be formed. Krier and Jaffee interpret this in terms of chemisorption, but it would appear equally correct to consider that platinum is normally covered with a very thin film of oxide. Whatever the interpretation, it is well established that a strongly adherent layer of oxygen which is difficult to remove is formed on platinum during exposure to air. The presence of such a film has, in fact, been found to account very satisfactorily for the behaviour of platinum electrodes in many electrochemical reactions. In particular it accounts for the etching of platinum electrodes subject to an alternating potential in an aqueous electrolyte containing sodium chloride or hydrochloric acid. During one half of the cycle an oxide film is encouraged to grow by nascent oxygen; during the other half the oxide is dissolved in the electrolyte.

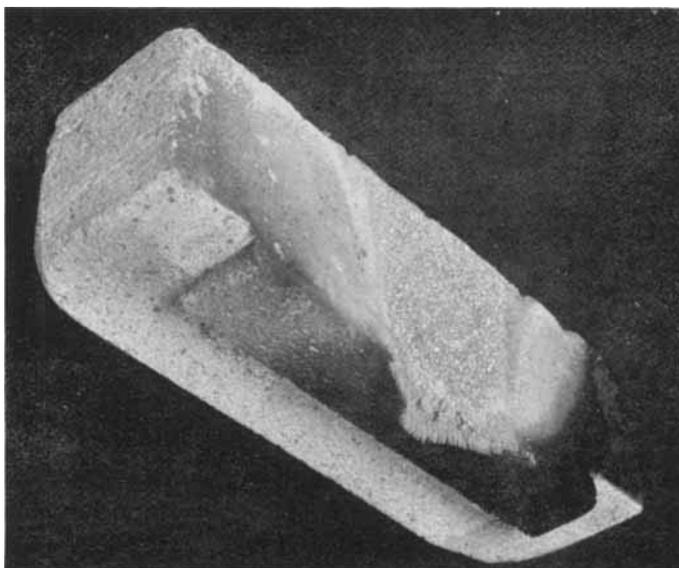
The fact that at room temperatures the film of oxide is so thin accords with its low heat of formation. After only a small amount of oxide forms, equilibrium is reached with the platinum surface and the surrounding oxygen, and further action thus must cease.

As the temperature is raised it seems likely that the oxide skin will first tend to thicken. One practical consequence of this is that platinum ware becomes increasingly susceptible to attack in the presence of air by such reagents as sodium carbonate as the temperature rises, since these molten salts, in addition to being oxygen carriers, dissolve platinum oxide as fast as it forms.

On further heating, however, a temperature is reached at which  $\text{PtO}_2$  cannot normally continue to exist as a solid. This is the temperature at which the dissociation pressure of  $\text{PtO}_2$  becomes equal to one atmosphere so that solid  $\text{PtO}_2$  decomposes into platinum and oxygen. The values quoted in the literature for the dissociation temperature of solid  $\text{PtO}_2$  vary and in a recent private communication Professor Brewer suggests that the limits cannot be more closely set than between  $550^\circ\text{K}$  and  $750^\circ\text{K}$ , or, say, between  $280$  and  $450^\circ\text{C}$  in 1 atmosphere of oxygen.

### **$\text{PtO}_2$ Gas**

In considering this reaction it is helpful to keep in mind that below the dissociation temperature the vapour pressure of platinum metal is higher than that of solid  $\text{PtO}_2$ . Above the dissociation temperature  $\text{PtO}_2$  (which under equilibrium conditions must always exist in small concentrations in the gaseous form) has the higher vapour pressure, rising with increasing temperature. It must also be appreciated that the solid oxide film on platinum is extremely thin at all temperatures. Above the dissociation temperature, evaporation of  $\text{PtO}_2$  will become more rapid owing to the increase in vapour pressure of  $\text{PtO}_2$  and the remains of the thin oxide film is probably swept away as vapour shortly after it decomposes.



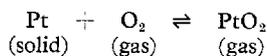
*Platinum deposits on a furnace brick removed after long service. Black oxide-containing deposits can be seen on the cooler edges and crystalline platinum deposits on the hotter surfaces*

The cleaning up of platinum from this thin film of solid oxide has been demonstrated recently very neatly.

Fryburg and Petrus (4), experimenting with "activated" oxygen (containing atomic oxygen) found that reactions of this with platinum were unpredictable below 750°C, as though the platinum was already protected with an oxide film, but above 750°C the platinum was always active as though clean.

Above the dissociation temperature the concentration of PtO<sub>2</sub> vapour in equilibrium with oxygen rises fairly rapidly and it becomes possible to measure it by direct loss of weight determinations on platinum specimens which preferably should have a high surface area. At 1227°C, for instance, Alcock has shown that the vapour pressure of PtO<sub>2</sub> in oxygen at a pressure of one atmosphere in equilibrium with platinum metal produces a concentration of  $3 \times 10^{-5}$  grams of platinum per litre and at 1737°C the concentration is  $7 \times 10^{-4}$  grams per litre.

If now the reaction



is considered from the point of view of mass action the rate of oxidation of platinum at a given pressure and temperature will

obviously depend on the concentration of PtO<sub>2</sub> in the atmosphere above the platinum.

Furthermore, if the temperature or the pressure is raised, the reaction will tend to go to the right—that is the platinum will lose weight through the formation of more volatile oxide; if the temperature or the pressure is lowered, the reaction will go to the left and some platinum oxide already formed will decompose, depositing platinum metal and liberating some oxygen.

### Formation of Platinum Spangles

It is of particular interest to consider the course of this reaction when there is a temperature gradient in the oxygen (or air) surrounding hot platinum. Such conditions are encountered in industry in platinum-wound electric resistance furnaces. In a typical furnace, the platinum element may be at around 1650°C and the refractory tube on which it is wound may be at an appreciably lower temperature, especially between the turns of the winding, on the inner surface, and at the ends.

It will thus be expected that the air directly in contact with the platinum winding will be appreciably hotter than the layers in contact with the cooler refractory. Thus, when PtO<sub>2</sub>

formed above the winding diffuses away it will quickly raise the concentration of  $\text{PtO}_2$  in the cooler areas to above the equilibrium value, and platinum will be deposited on the cooler surfaces. This, in fact, is what happens, and bright spangles of platinum crystals are a familiar sight around the wires of platinum wound furnaces which have been in service for long periods. Obviously the incidence of this redeposition is affected by the extent of convection currents around the furnace windings and the freedom of access of air, but all who handle electric furnaces will have observed the effect many times. Typical examples are shown here. It should be added that it is very probable that as the air from the neighbourhood of a heated platinum winding is cooled supersaturation may occur, and that surfaces will probably vary in their efficiency in providing nuclei for precipitation of platinum.

If, on the other hand, heated air carrying sublimed  $\text{PtO}_2$  comes in contact with a much cooler surface—below about  $500^\circ\text{C}$ —then the  $\text{PtO}_2$  will be shock-cooled and will deposit as the solid oxide.

This, again, can be observed near the exit of air-swept chambers heated by platinum resistors. In a recent paper Fryburg and Petrus (4) report that if platinum filaments are heated in a stream of oxygen at above  $900^\circ\text{C}$ , visible oxide deposits accumulate on the wall of the tube. One method of reducing these deposits to metal is to raise the temperature. These authors report that they leave a residue of metallic platinum if the tube, after evacuation, is heated to  $450^\circ\text{C}$ . They will equally decompose on heating in air.

The approach adopted in this brief outline has been chosen to emphasise particularly how metallic platinum deposits can form on hot surfaces near hotter platinum resistors. In considering the oxidation of platinum at lower temperatures at which solid oxide phases may exist, other approaches may sometimes be helpful. Vapour pressure considerations should not be neglected, and it is useful to keep in mind that the dissociation



*Large platinum crystals detached from a dismantled platinum heated furnace after long service at high temperatures. These formed adjacent to the heating elements ( $\times 12$ )*

temperature corresponds to the temperature at which the vapour pressure of the oxide becomes greater than the vapour pressure of the metal. In considering the decomposition of solid  $\text{PtO}_2$ , metallurgists in particular may need to be reminded that this cannot be regarded as a simple change from the solid to the gaseous phase, nor can it be interpreted in terms of the condensed phase rule as commonly accepted in preparing metallurgical phase diagrams in which pressure is neglected.

Pressure is an integral factor determining the behaviour of metallic oxides. At sufficiently high oxygen pressures, presumably, solid  $\text{PtO}_2$  will not dissociate but will transform directly to the gaseous phase when the appropriate temperature is reached. Finally, it is useful to bear in mind that even at high temperatures the concentration of  $\text{PtO}_2$  in air in equilibrium with platinum metal is very low and that significant loss of weight occurs only in moving air which can sweep away  $\text{PtO}_2$  as fast as it is formed. Even at temperatures near the melting point an oxygen atmosphere in equilibrium with platinum contains less than 1 milligram of platinum per litre.

This account has been confined to the reactions of platinum with oxygen. Similar considerations must apply to the oxidation of the other platinum metals, as well as of gold and silver, although there are, of course, differences in detail. Reliable figures for the heats of formation of the solid oxides of the platinum metals are not, in general, available, but it seems likely that they are higher than that of platinum. The films formed by solid oxides on palladium, rhodium and iridium, for instance, are thick enough to give tarnish colours at temperatures up to about 500°C, though they decompose or volatilise at higher temperatures. However, complications arise with palladium, silver, and probably rhodium and ruthenium, on account of the need for taking into account the solubility of oxygen in the solid metal. A detailed account of the reactions of the other noble metals is thus another story—as is the behaviour of alloys of the metals with each other and also the complications which follow the presence of certain impurities in the solid or the gas phases.

Finally, it is of interest to consider how these observations influence the concept of nobility as applied to the platinum metals. To the alchemist, silver and gold were noble because they resisted fire. (Not, it should be noted, because they were resistant to acids—silver is readily soluble in nitric acid.) In recent times, silver, gold and the platinum metals are widely classed as noble, but it has sometimes been difficult to reconcile the obvious affinity of osmium and ruthenium with oxygen with the concept of nobility. It would seem that these difficulties may be resolved if a noble metal is considered as one whose surface oxides sublime (with or without some prior partial decomposition) at a temperature below its melting point.

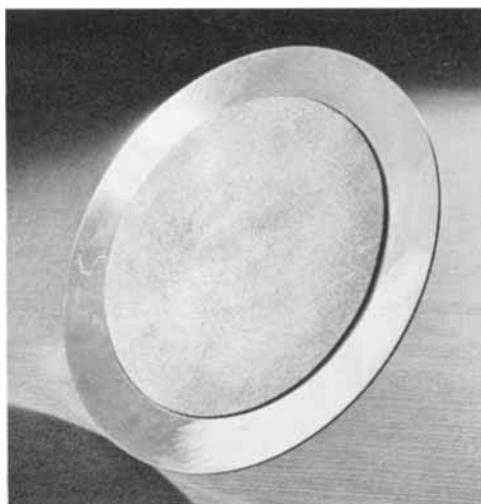
#### References

- 1 C. A. Krier and R. I. Jaffee, *J. Less-Common Metals*, 1963, **5**, 411-431
- 2 C. B. Alcock, *Platinum Metals Rev.*, 1961, **5**, 134-139
- 3 L. Brewer, *Chemical Reviews*, 1953, **52**, 1-75
- 4 G. C. Fryburg and H. M. Petrus, *J. Chem. Phys.*, 1960, **33**, 622-623

## Sintered Platinum Filters

The problems of filtering highly corrosive liquids such as hydrofluoric acid, or of filtration at very high temperatures, have been simplified by the introduction by Johnson Matthey of a range of sintered platinum filter discs of controlled pore size.

Made by hydraulic pressing a carefully graded mixture of platinum powder held in an organic carrier and sintering at high temperature, the filter discs are mechanically strong and present no difficulty in handling. Six standard discs constitute the range available, the mean pore size being from 5 to 100 microns, with an accuracy of  $\pm 15$  per cent. The largest disc available at present is 5 inches in diameter and the minimum thickness is 0.065 inch. They can be mounted, as shown in the illustration, into a solid platinum rim to facilitate installation. Cleaning the filters is naturally a simple operation as they are free from corrosive attack by almost all mineral acids and there is no tendency to form oxide films on heating.



*A platinum filter disc of 10 micron mean pore size, 5 inches in diameter, mounted in a solid platinum rim ready for installation in a filtration plant*