

Loss of Platinum Oxide from Heated Platinum

A BOUNDARY LAYER DIFFUSION MECHANISM

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The loss of weight of platinum heated in air is fortunately low, owing to the very low vapour pressure of the PtO₂ that volatilises. This article reviews recent studies of heated platinum filaments which suggest that a viscous boundary layer of gas hinders escape of the PtO₂ molecules that are formed. At atmospheric pressure 99.85 per cent of the molecules of PtO₂ formed may be trapped in this layer.

When platinum is heated in air or oxygen to above about 800°C a volatile oxide, PtO₂, is formed and the subsequent course of the reaction—that is, the rate of oxidation of the platinum—is dependent on the speed at which the volatile oxides are removed from the vicinity of the solid heated surface. So much is now very generally understood and accepted, and some of the consequences of this mode of oxidation, shared by all the platinum metals, have been surveyed broadly in a recent series of papers (1) in *Platinum Metals Review*.

The characteristic that mainly governs the rate at which platinum loses weight in these conditions is the partial vapour pressure of PtO₂, and it is in many ways fortunate that at the temperatures at which platinum is used in air at atmospheric pressure in industry this pressure is extremely low. At 1250°C, for instance, about 0.03 milligrammes of platinum provide sufficient PtO₂ to saturate a litre of oxygen at the same temperature (at

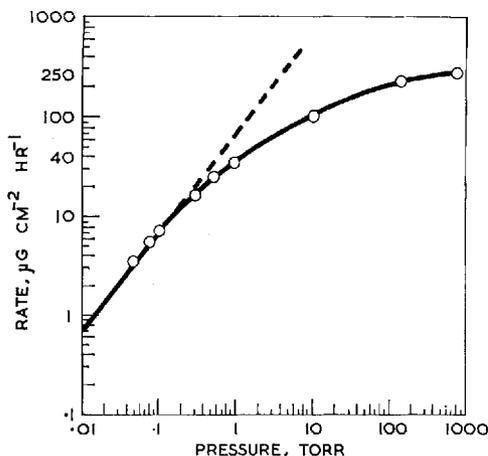
normal pressure) so that very large quantities of hot moving oxygen (and even larger volumes of air) are needed to cause a significant loss of weight of a heated platinum vessel or thermocouple.

The partial vapour pressure of PtO₂ in oxygen at atmospheric pressure above a clean heated platinum surface is, in fact, very much less than might be imagined from some theoretical considerations, and the reasons for this have been discussed by Dr George C. Fryburg of the Lewis Research Center of the National Aeronautics and Space Administration, Cleveland, Ohio, in a most interesting review (2).

For some years Dr Fryburg has been engaged in a detailed study of the reactions that take place on the surface of thin platinum ribbons heated by the passage of an electric current when surrounded with an atmosphere of oxygen, usually at a reduced pressure.

Fryburg suspended his ribbons, a little over half a thousandth of an inch thick and 0.01 to 0.05 of an inch wide, as U-shaped loops about six inches long in a water-cooled Pyrex bulb 1.25 inch in diameter and ten inches long, supplied with oxygen at pressures up to 100 torr. At higher pressures, convection currents caused temperature variations along the ribbon, and it was then necessary to use a single shorter horizontal specimen.

The ribbon was heated by direct current, maintained constant by a servo-mechanism, from a bank of lead storage cells. The



Rate of oxidation of platinum ribbon at 1060°C under various pressures of oxygen (Fryburg)

temperature was measured by a disappearing filament optical pyrometer and, checked by resistance measurements of the ribbon, was believed to be established with an accuracy of $\pm 5^\circ\text{C}$. The loss of weight of the ribbons was too small to be determined directly, but after each run the oxide which condensed on the cooled walls of the container was dissolved in boiling 12N hydrochloric acid and the platinum in solution determined colorimetrically.

The results of a typical run are shown in the diagram above, reproduced from Fryburg's paper.

Effect of Pressure

The significant—and at first sight very curious—feature of the results is the effect of pressure. It is only at very low pressures of oxygen, below about 0.25 torr, that the expected direct proportionality is found between the oxygen pressure and the rate of oxide formation. It is in this low pressure region only that the factor controlling the loss of platinum is the rate of collision of oxygen molecules with the platinum surface, and in these conditions only do the molecules of PtO_2 gas move away as fast as they are formed.

As the oxygen pressure is increased above 0.5 torr the rate of oxidation falls more and

more below the straight line relationship, so much so that the rate at 1000 torr is only about six times that at 1 torr. The higher the pressure of oxygen, and thus the more oxygen molecules that collide with the hot surface every second, the more difficult it appears to be for the PtO_2 gas molecules that are formed to escape from the vicinity of the hot filament.

Two other observations are worth noting. With this size of bulb, at pressures from 0.15 to 10 torr and with this experimental arrangement, the rate of loss was unaffected by quite wide variations in the flow rate of the gas through the apparatus—from zero up to 220 cm per second. And the rate of oxidation at the higher pressures depended on the width of the ribbon—the wider the ribbon the lower the rate.

Fryburg suggests that all these results can be explained on a "back reflection" theory. "At low pressures", he writes, "the mean free path of the volatilising oxide molecules in the surrounding gas is large compared [with] the width of the ribbon, and all the oxide escapes and is condensed on the cooled bulb. . . . As the pressure increases, the mean free path decreases and the oxide molecules suffer collisions at distances closer and closer to the ribbon. The chance of being back-reflected to the ribbon increases, and any oxide molecule that is back-reflected is decomposed on the hot ribbon; the platinum is redeposited on the platinum surface."

Viscous Film of Gas

This all adds up to the view that the filament may be considered as being surrounded by a viscous, stationary film of gas which is not easily dislodged. The partial pressure of PtO_2 in the viscous film obviously cannot exceed the equilibrium value at that temperature; when more molecules are formed they must diffuse through the film. Only when a molecule reaches the outer boundary of the film will it escape from the filament and then be carried away in the convection current.

If more molecules are formed than can escape from the film, they will be back-reflected to the filament. The partial pressure of PtO₂ in the oxygen-rich atmosphere at the filament surface will then exceed the equilibrium value and platinum must be re-deposited.

Dr Fryburg suggests in his paper that any back-reflected molecule of PtO₂ on striking the hot filament from which it was earlier formed will automatically be decomposed by reason of its instability at the high temperature. It seems important to appreciate that PtO₂ will only be unstable if the partial vapour pressure of PtO₂ in the surrounding gas is equal to or exceeds the equilibrium value.

Many matters for speculation admittedly still remain. Does the viscous gas film hinder the access of oxygen molecules to the filament, as well as trapping PtO₂ molecules already

formed? If so, is such shielding or is back-reflection the more important factor in reducing evaporation? It is interesting that there seems little visible evidence of re-deposition of platinum in photographs of the surfaces of heated specimens (3).

But it would seem that an excellent case has been made out for the existence on a platinum filament heated in air of a viscous tightly-bound layer of gas which, at atmospheric pressures, prevents 99.85 per cent of the molecules of PtO₂ that should be formed from ever escaping into the surrounding atmosphere.

References

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Platinum as a Propane Fuel Cell Electrocatalyst

COMPARISON WITH OTHER PLATINUM GROUP METALS

The exceptional activity of the platinum metals as electrocatalysts in low-temperature fuel cells has been noted for some years. Numerous studies have been carried out to examine their behaviour in a variety of systems, and among recent published work in this field have been papers describing platinum black anodes operating in phosphoric acid at 110 to 200°C with hydrocarbon fuels (1, 2).

A more recent comparison of four platinum metals under similar conditions was carried out by W. T. Grubb of the General Electric Company, Schenectady, and confirmed the marked superiority of platinum over palladium, rhodium and iridium (3). The metals were Teflon-bonded to the anode structures in the form of their blacks, and their electrocatalytic performances compared at 150°C in an 85 per cent phosphoric acid electrolyte using propane as fuel. During test runs when hydrogen was employed as the fuel, both platinum and iridium gave very high current densities, exceeding 800 mA/cm². Using propane, however, platinum proved very much more active than iridium, sup-

porting more than 1000 times the current density although its surface area was substantially lower than that of iridium. Palladium and rhodium gave only marginally better results with propane than iridium.

The fact that the difference in catalytic activities between platinum and iridium is so large in hydrocarbon oxidation, whereas it is much less in the oxidation of hydrogen and other catalytic reactions, is remarkable, particularly in view of the close similarities in electronic and crystal structures of the two metals.

It is assumed that very specific catalytic properties are required for hydrocarbon electro-oxidation in the moderate temperature region.

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