

Reactions of Oxygen with the Platinum Metals

II—OXIDATION OF RUTHENIUM, RHODIUM, IRIIDIUM AND OSMIUM

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In the second part of this survey of the oxidation of the platinum metals attention is given to the formation of solid oxide films on the more reactive metals ruthenium, rhodium, iridium and osmium. The films formed in air on these metals are thick enough to give tarnish colours at temperatures of 400 to 500°C, and they may be in equilibrium with an appreciable partial pressure of gaseous oxides at temperatures below that at which they decompose. Diagrams showing the solid (oxide and metal) phases and the vapour pressures of the gaseous oxide phases in equilibrium with one atmosphere of oxygen at temperatures up to about 1800°C are given for four of the platinum metals. A third part of this paper will deal with the oxidation of palladium.

The first part of this review (1) dealt particularly with the oxidation of platinum at temperatures above about 600°C, when (at atmospheric pressures) no solid platinum oxides can exist and the products of the reaction are volatile. The volatile oxides, it was emphasised, do not remain attached to the platinum surface and their rate of formation must necessarily be related to the geometry of the container in which they are confined, the temperature distribution throughout the system, and in addition the

pressure, the composition, and the rate and pattern of circulation of the diluent gases.

The same general considerations must also apply to the rates at which the volatile oxides of ruthenium, iridium, rhodium and osmium are formed.

In the particular case of palladium, complications result from the need to consider the solubility of oxygen in the solid metal, so its reactions with oxygen will be considered separately.

The table summarises the presently known data on the dissociation temperatures of the solid oxides and the nature of the gaseous oxides which can exist.

It should be added that the compositions quoted for the solid oxide phases are those of ideal crystals. In general, solid oxides nearly always have a range of compositions, but the possible range has not yet been established for the platinum metal oxides.

It should further be noted that although RuO_4 and OsO_4 can be prepared as solid oxides in a metastable condition at room temperature, they are not believed to form solid films on surfaces of their parent metals in an oxidising atmosphere.

No figures have been included in this table for the rates by which these metals lose weight when heated at high temperatures in oxidising conditions since, in spite of a great deal of recent experimental work, it is becoming increasingly evident that the factors controlling transport of the volatile oxides have not been sufficiently controlled to make the pub-

Solid Oxide Phase in equilibrium with metal and one atmosphere of oxygen at room temperature	Dissociation Temperature at 1 atm of oxygen	Gaseous Phases
PtO ₂ RhO ₂ IrO ₃ RuO ₂	280-450°C (3) 1400°C (4) 1120°C (5) 1540°C (2)	PtO ₂ RhO ₂ IrO ₃ (6) RuO ₄ (2) (predominates slightly at lower temperatures) RuO ₃ (2) (predominates at higher temperatures)
OsO ₂	650°C (4)	OsO ₄ (4) OsO ₃ (4)

lished results meaningful. For these reasons it is not proposed to discuss further at this stage the formation of the volatile oxides of these metals.

Solid Oxides

It is proposed, instead, to review a little more closely the growth of films of solid oxides on these metals. As is apparent from the table, the solid oxides of rhodium, iridium, ruthenium and osmium are much more stable than the solid oxide of platinum, and are thus more readily studied.

In the first part of this review, the characteristics of solid PtO₂ were only very briefly touched upon. It was pointed out, however, that at temperatures below about 350°C (the precise temperature is uncertain, but is probably in the range 280 to 450°C) platinum surfaces are, when under a pressure of one atmosphere of oxygen, covered with a film of PtO₂. It was suggested this film may thicken as the temperature is increased. It was not, however, made clear that the behaviour of the film cannot be predicted from the thermodynamical data quoted (any more than the loss of weight by formation of volatile oxides can be predicted thermodynamically), but will depend largely on the physical characteristics of the oxide film.

The film of solid PtO₂ is so very thin that its characteristics are not readily determined. At room temperatures there is some electrochemical evidence to suggest that it can be

thickened by anodic treatment in an electrolyte, but that in these circumstances the thickness reaches a maximum value in a matter of minutes. It has been calculated that a completely oxidised surface is covered with about 0.3 millionths of a gram of PtO₂ per square centimetre.

These observations would imply that at room temperatures the solid film of PtO₂ is dense and completely protective, like the film on stainless steel. How completely the protective properties are maintained as the temperature rises is at present a matter for speculation, but it would seem that the most likely clues to the possible characteristics of the solid oxide film at higher temperatures, but still below its decomposition temperature, may be derived from a study of the rather more reactive platinum metals.

Rhodium, iridium, ruthenium and osmium all, like platinum, remain bright and visibly free from more than very thin films of oxide at room temperature. As with platinum, a freshly-formed surface of any of these metals becomes covered with a film of oxide in a matter of seconds, but, as with platinum, the film first formed presumably acts as a barrier to smother further growth in some way. No visible tarnish ever develops in any normal environment.

When any one of these four metals is heated in air or oxygen to a temperature above about 400°C (and below the decomposition temperature of its solid oxide), thickening

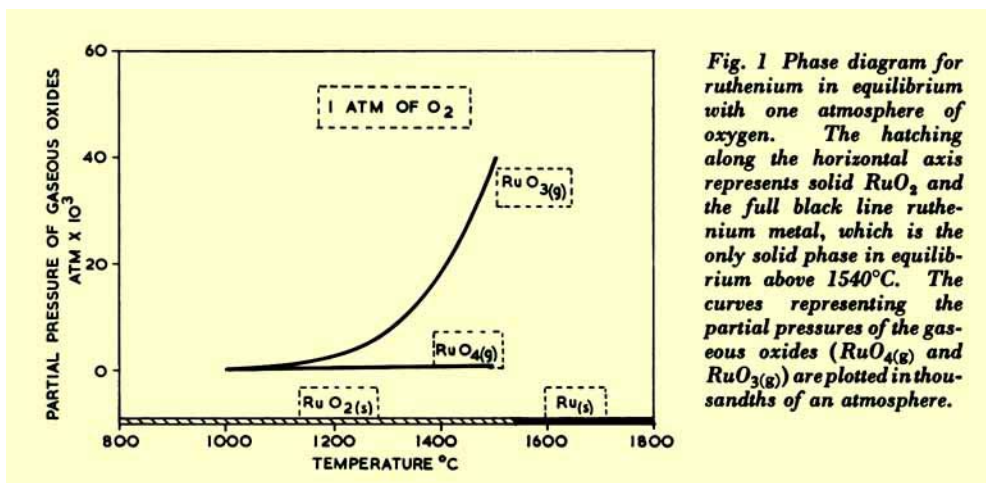


Fig. 1 Phase diagram for ruthenium in equilibrium with one atmosphere of oxygen. The hatching along the horizontal axis represents solid RuO₂ and the full black line ruthenium metal, which is the only solid phase in equilibrium above 1540°C. The curves representing the partial pressures of the gaseous oxides (RuO₄(g) and RuO₃(g)) are plotted in thousands of an atmosphere.

of the oxide skin is clearly to be seen. There is not the slightest doubt that there is a change in the physical nature of the oxide layers. Whether the growth is due to enhanced diffusion of either metal or oxygen ions through the layer or whether it is due to cracking or the development of porosity has not been established, but the fact that the film is thick enough to have a colour of its own is clear enough.

The films, although thicker than those which form at room temperatures, are still by no means unprotective. They show not the slightest signs of growing unrestrainably. They, too, very quickly reach a maximum thickness, and thereafter apparently remain appreciably constant in weight and thickness for as long as the temperature is not further raised – at least in the temperature range up to, say, 900°C.

In passing, it is of interest to recall that these tarnish films are extremely refractory chemically. The film formed on ruthenium (or on ruthenium-platinum alloys), for example, resists pickling by boiling aqua regia. The films are most simply removed by heating to above their decomposition temperature, the metal being then quenched in water to prevent the films from reforming during cooling. Alternatively, of course, they can be reduced by heating in hydrogen and then either quenching the work rapidly in water

or cooling it in a reducing atmosphere.

It should be emphasised also that at temperatures up to about 900°C the rates of tarnishing of even these more reactive platinum metals are very small – too small to be easily detected by any method dependent on measuring the changes in weight of a specimen.

Vapour Pressure of Solid Oxides

The picture so far presented seems clear enough. At relatively low temperatures – say up to 500°C for platinum and up to 900°C for rhodium, iridium and ruthenium – the platinum metals are at the most susceptible to slight tarnishing by a very thin and more or less protective film of solid oxide; and at a specific temperature, depending on the oxygen pressure and on which particular platinum metal is concerned, the solid oxide film can no longer exist, so that when the metal is quenched from above this temperature it is bright and free from tarnish.

It remains to consider how far the solid films themselves can contribute, by their own vapour pressure or by reaction with oxygen, to the losses of weight which are observed when the platinum metals are heated in air – particularly at temperatures just below the decomposition temperature of the solid oxide.

This mechanism needs particularly to be examined when dealing with the more reactive

of the platinum metals, and it is fortunate that reliable vapour pressure data for the oxides in the ruthenium-oxygen system (the most complex, apparently, of the platinum metal-oxygen systems) are now available. A very careful study(2) of this system has recently been made by Wayne E. Bell and M. Tagami of the General Atomic Division of General Dynamics Corporation, working in the John Jay Laboratory for Pure and Applied Science, San Diego, California, so it can be said that the oxidation pattern for ruthenium heated in oxygen under equilibrium conditions is well established.

In Fig. 1 an attempt is made to show diagrammatically the solid and gaseous phases which would be expected to be in equilibrium when ruthenium is exposed in a confined volume of oxygen at a pressure of one atmosphere at various temperatures over the range from 800 to 1600°C. At temperatures up to 1540°C the ruthenium is considered as being covered completely by a layer of solid RuO_2 . It is, unfortunately, impossible to say how thick the layer is or how protective and continuous it is at various temperatures in this range, but the assumption here made is simply that it is sufficiently protective as to be regarded as the only solid phase in contact with the oxygen. At tem-

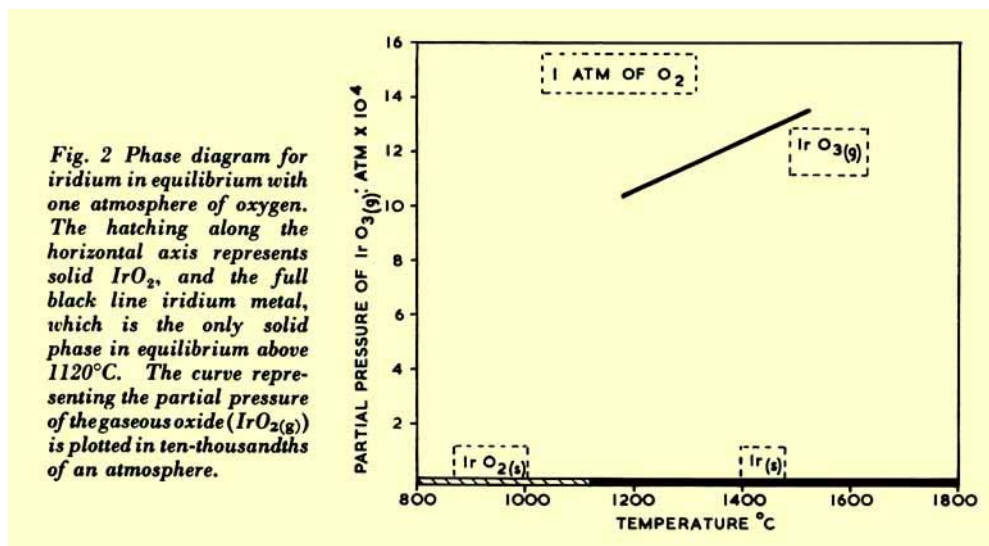
peratures above 1540°C, of course, the solid ruthenium oxide can no longer exist and clean ruthenium metal is in contact with oxygen.

It will be seen that at temperatures above about 1000°C small amounts of RuO_3 and RuO_4 will form and if the temperature is raised to 1500°C the vapour pressure of the RuO_3 starts to increase rapidly. The vapour pressure of RuO_4 also rises, but much more slowly.

The total of the vapour pressures of these oxides in equilibrium with one atmosphere of oxygen reaches an order of one-thousandth of an atmosphere at a little over 1100°C, and this vapour pressure (being about one thousand times greater than that of PtO_2 at the same temperature) is quite sufficient to account for appreciable losses of ruthenium when a specimen is heated in a current of oxygen.

This accounts for the well-known observations that ruthenium specimens when heated to around this temperature lose weight much more rapidly than platinum when heated at the same temperature, and on removal from the furnace are seen to be heavily discoloured and tarnished.

It is unfortunate that very little experimental evidence is available on the oxidation of osmium, although it seems probable that it follows the same general pattern as that of



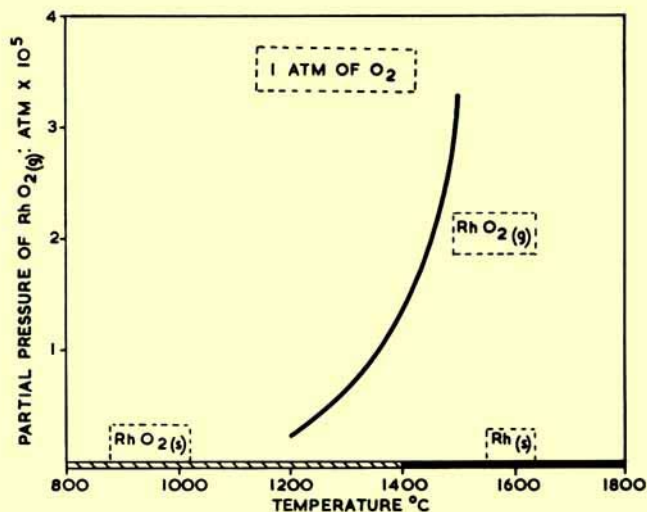


Fig. 3 Phase diagram for rhodium in equilibrium with one atmosphere of oxygen. The hatching along the horizontal axis represents solid RhO_2 , and the full black line rhodium metal, which is the only solid phase in equilibrium above 1400°C . The curve representing the partial pressure of the gaseous oxide ($\text{RhO}_{2(g)}$) is plotted in hundred thousandths of an atmosphere.

ruthenium as described above. The position is a little better with regard to the oxidation behaviour of iridium and rhodium, and such results as are available are set out diagrammatically in Figs. 2 and 3, and for convenience a similar phase diagram for platinum is given in Fig. 4.

Comparison of Phase Diagrams

In making the comparison between the curves for these three metals, particular note should be made of the variations in the scales for vapour pressure. The vapour pressure

curves are based on the results of Alcock and Hooper (7) and the decomposition temperatures of the solid oxides are from the sources quoted in the table on page 52.

Brief comments only seem necessary and the curves illustrate very well the paucity of the vapour pressure data available. With rhodium it is interesting that the solid oxide skin appears to exert an appreciable partial vapour pressure of $\text{RhO}_{2(g)}$ at temperatures several hundred degrees below its temperature of decomposition. With iridium, the outstanding features of the vapour pressure

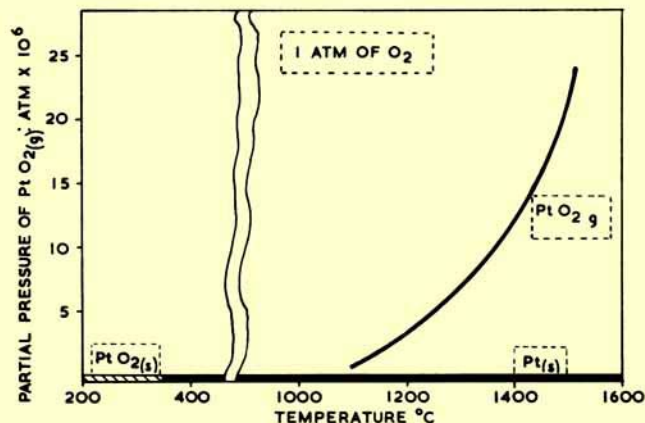


Fig. 4 Phase diagram for platinum in equilibrium with one atmosphere of oxygen. The hatching along the horizontal axis represents solid PtO_2 , and the full black line platinum metal, which is the only solid phase in equilibrium above about 350°C . The curve representing the partial pressure of the gaseous oxide ($\text{PtO}_{2(g)}$) is plotted in millionths of an atmosphere.

curve are that there is such a relatively small change in partial pressure between 1200 and 1500°C, as well as that the value of the partial pressure over the whole of this range is so high. It would be of particular interest to know the course of the vapour pressure curve when extended to lower temperatures below about 1100°C when the surface of the metal is covered by a film of solid oxide. One question that inevitably arises concerns the possibility of an inflection in the vapour pressure curve at the temperature corresponding to the decomposition temperature of the solid oxide.

It will be appreciated that this discussion is necessarily based on the results of studies made under equilibrium conditions. So long as this is borne in mind these results can be of the greatest help in assessing the importance of the factors that are likely to influence the loss of weight of the platinum metals when heated at high temperatures in service, although it must always be emphasised that they cannot in themselves enable a quantitative determination to be made of the losses that occur in kinetic systems.

Many questions still call for an answer. It would be of the greatest interest, for example, to know much more of the structure of the solid oxide films on ruthenium and the other platinum metals. It would further be of

great interest to know the steps by which RuO₃ and RuO₄ are formed. Is the reaction one between oxygen and solid RuO₂, and when this happens on the surface of an oxide-coated piece of ruthenium, how is the porosity and thickness of the oxide film affected?

The possible influence of traces of moisture in oxygen on the rate and progress of the formation of oxide films on platinum metals has hitherto been entirely overlooked. When the mechanism of oxidation is considered in the light of all that has been said above, however, it is obvious that the structure and characteristics of the thin oxide films involved may very well be influenced by quite small amounts of water vapour, as well perhaps as of carbon dioxide, which would be present in industrial conditions. It is evident that here there is an immense field for further enquiry.

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Galvanic Couples with Platinum Metals

SURFACE POISONING BY INTERMETALLIC COMPOUNDS

There is a fascination in observing how a skilled experimenter learns to exploit little known phenomena. For instance, the seasoned analytical chemist knows instinctively that if a sample of tin is slow to dissolve in acid the reaction can be made to proceed simply by placing a clean platinum wire through the liquid into contact with the tin. Some years ago, Buck and Leidheiser (*Nature*, 1958, **181**, 1681) observed that some platinum metals were more effective than others in catalysing reactions of this type, the relative effect of each platinum metal depending on the particular base metal with which it was coupled.

They now report (*Nature*, 1964, **204**, 177) some further observations on platinum metal and base metal couples, both in direct contact and (connected externally) separated by a porous diaphragm. The results indicate that the behaviour of the platinum metals is influenced by films of intermetallic compounds which form on the surface. When used to catalyse the dissolution of tin, for instance, platinum and iridium are not seriously poisoned, but palladium rapidly loses its catalytic powers, and X-ray diffraction analyses show the formation on its surface of PdSn₄ and also of an unidentified compound.