

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.

References

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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.