CXCI.—*The Effect of Temperature on Platinum Black and other Finely-Divided Metals.*

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WHEN a freshly-coated platinum plate has been heated to a temperature somewhat above red heat and allowed to cool, the original velvet-black surface becomes grey, the extent of the colour lightening depending on the temperature and the duration of the heating.

This change in platinum black is not attended by any alteration in weight, and cannot therefore be due to oxidation or to the removal of the deposited surface. Moreover, the change does not take place at any definite temperature, as a plate heated in a resistance furnace and examined at every 50° began to show the change at 300°, the effect increasing with rise of temperature until, at 900°, the deposit had become almost white.

In order to determine whether the heating produced any other change in the platinum black beyond the alteration of colour, several properties of the metal were examined, measurements being made immediately after the deposition of a fresh coat and also after heating the coated plate to a series of definite temperatures. The properties which gave most satisfactory results were the decomposition of hydrogen peroxide by the finely-divided metal and the absorptive capacity of the plates for hydrogen and oxygen when the plates were used as electrodes in a storage cell charged with dilute sulphuric acid. The alteration of the overvoltage shown by the plates in dilute acid was also examined, but no definite results were obtained, although both the anodic and the cathodic decomposition potentials with polished platinum differ considerably from those shown by platinised electrodes.

The results of the hydrogen peroxide decompositions and the storage capacities of the plates as electrodes are shown in the set of curves. The first two sets were obtained with platinum, the third with silver, and the last with palladium. In all cases the abscissæ represent the temperatures to which the plates were

heated, and the ordinates correspond either with cubic centimetres of oxygen evolved per minute, or with the time in minutes taken for the storage cell, constructed of the given plates in dilute sulphuric acid, to fall to a potential of 0.4 volt when discharged through a fixed external resistance. The full-line curves represent the results of the peroxide decompositions, and the dotted curves the

I. *Platinum.*
III. *Silver.*

II. *Platinum free from chlorine.*
IV. *Palladium.*

results for cell capacity. The capacity measurements were satisfactory only in the case of platinum, as palladium absorbs an excessive quantity of hydrogen, whilst silver unites with the radicle of the acid used.

The first set of curves for platinum was obtained by using plates platinised in the ordinary way, that is, by reversing the current every half minute during the deposition of the platinum black. It was thought that such plates might contain considerable quantities of chlorine, so a second set of measurements was carried

out in which the current was not reversed during the plating and the cathode was kept in a separate vessel from the anode, the two being connected by means of a syphon. By this method, not only is no chlorine evolved at the cathode, but also the possible diffusion of chlorine from the anode is practically prevented. It will be seen from the curves that the catalytic action of the chlorine-free plate is not augmented to the same extent by low temperature as is the case with the plate which possibly contained occluded chlorine. Further evidence of the presence of chlorine in the plate was obtained by plating with reversal of current and then—after washing—by heating the plate in a closed vessel through which a current of air was drawn, the air being afterwards passed through a starch-iodide solution. Under these conditions the starch gave a blue colour, due to the liberation of iodine by the chlorine, but when the platinum was deposited free from chlorine in the manner indicated, no blue colour was obtained.

Considering the catalytic action of the metals as shown by the full-line curves, two points should be noted; first, the temporary increase in activity which occurs after heating to certain temperatures, and secondly, the gradual falling off in activity as high temperatures are reached. The first effect may be explained by the evolution of occluded gas, the escape of which would not only increase the roughness of the plates, but also, in some cases, help the catalysis by the removal of a catalytic poison. The falling off in catalytic power which takes place when high temperatures are reached is probably due to a decrease in the specific surface of the deposited metal, accompanied by an alteration in the size and number of points at which the liberated oxygen can escape in the form of bubbles. The storage capacity of the plates when used as electrodes in a storage cell also falls off, after heating, in the manner shown by the dotted curves in the first two figures. In this case also the same explanation will hold good, that is, the decrease in specific surface produced by heating will be accompanied by a falling off in the occlusive power of the plates for gases, and therefore also in their storage capacity when used as electrodes in a storage cell.

If the view of the decrease of specific surface be accepted, then it should be possible to detect such an alteration by application of the microscope. Photomicrographs of the plates, made before and after heating, were unsatisfactory owing to the lack of contrast between the different parts of the plated surface. The plan was therefore adopted of photographing a plated wire against a bright background, so that in effect a silhouette of the plated wire was obtained; the wire was then heated, usually by an electric current, and then rephotographed. Wires of platinum, silver, iron, and

copper were examined in this manner; with the exception of platinum, the wires were heated in an atmosphere of hydrogen to avoid oxidation. Substances of low melting point were not investigated owing to the difficulty of judging the temperature when heating by the current, that is, in all cases the melting point of the wire was considerably above red heat. The results obtained are shown in the table. The figures given are proportional to the diameters of the plated wires before and after heating, the diameter of the unplated wire being taken as unity in each case. In all cases a portion of the plating was removed from the freshly-coated wire, so that the original diameter was always shown in the photographs, thus providing a standard and avoiding errors of focus. The results clearly indicate that heating is in all cases followed by a decrease of specific surface.

	Diameter before heating.	Diameter after heating to dull redness.
Platinum	1.31	1.15
Silver	1.21	1.11
Iron	2.00	1.41
Copper	1.66	1.36

Faraday (*Phil. Trans.*, 1857, **147**, 145) observed that a gold leaf mounted on glass and heated to about 500° lost its green colour when viewed by transmitted light and became transparent, the green colour being restored on burnishing. Turner (*Proc. Roy. Soc.*, 1908, [A], **81**, 301) repeated the experiment and took photomicrographs of the transparent gold. By this means he showed that the film had ceased to be continuous and had gathered itself up into a network of gold strands, the effect of burnishing being to flatten out the strands again so as to reproduce the original surface. Beilby (*Proc. Roy. Soc.*, 1904, **72**, 226), and Chapman and Porter (*ibid.*, 1910, [A], **83**, 65) investigated the same phenomenon and advanced the view that the effect was produced by the surface tension of the metal, which was able to operate owing to the lower rigidity produced by heating. Chapman and Porter also showed that a freely-suspended leaf merely contracts in area but remains continuous on heating, the network effect only being produced when the leaf was mounted on glass. With the thickness of leaf they employed, the contraction started at the definite temperature of 340° .

A different explanation of the observed effects also seems possible. A very finely-divided metal may have a considerably lower melting point than the same substance in bulk, and as a result of this incipient melting the smaller particles would attach themselves to the larger, which would not only grow, but would also become cemented together by the liquid smaller particles, the whole effect corresponding with a low-temperature sintering of the finely-

divided metal. The increased vapour pressure of a finely-divided liquid in the state of mist, where the large drops grow at the expense of the smaller, and the increased solubility obtained by using a substance in a fine state of division, are corresponding phenomena. Therefore it may be assumed that fine division alters the melting point as well as the vapour pressure and the solubility. Whatever the cause may be, there seems little doubt that finely-divided metals show a very considerable decrease of specific surface when heated to temperatures much below their usual melting points.

Further evidence in support of the theory can be deduced from the fact that finely-divided metals, when used as catalysts, are always more active when produced by reduction at low temperatures, the same being true in connexion with the activity of the metallic pyrophori made from nickel or iron. In both cases the metal produced at a low temperature has a high specific surface, which is considerably reduced by the particles melting together at higher temperatures. It should be noted that the sintering effect may be to some extent prevented if the catalytic metal is mounted on a carrier such as asbestos, for under such conditions the metallic particles are to a certain extent kept separate from each other. It is also interesting to note that, as a rule, surface catalysts are substances of very high melting point, and that the optimum temperature for any given catalyst is always considerably below its melting point.

EXPERIMENTAL.

The plates used measured 25 by 35 mm. and were fitted with wires of the same metal welded on to them. The electrolysing solutions were chlorides in the case of palladium and platinum, cyanide in that of silver, and sulphates in the cases of copper and iron. After deposition of the metal, the surface was cleaned by using the plates as electrodes in a solution of dilute sulphuric acid; the plates were then washed in distilled water and dried. The heating of the plates was carried out in a small resistance furnace, the temperature being noted by means of a thermo-couple.

The storage cell was filled with *N*-sulphuric acid, and the plates were charged by connecting them with a 2-volt accumulator for fifteen seconds; the current was then broken and the cell allowed to discharge itself through a voltmeter of 390 ohms resistance and graduated to 1/100th of a volt. The time required for the cell voltage to fall to 0.4 volt was taken as an indication of the storage capacity of the plates.

Before the plates were used for the decomposition of hydrogen peroxide, the platinum and palladium plates were saturated with

oxygen, and the silver with hydrogen, by using them as electrodes in a cell filled with dilute sulphuric acid. The peroxide used was of approximately two-volume strength, and the same solution was always employed for any series of measurements, the strength being checked from time to time by titration with potassium permanganate. Twenty-five c.c. of the solution were placed in a wide test-tube, and allowed to stand in a bath until it attained a temperature of 18° ; the electrode was then introduced and the tube was closed by a rubber stopper connected with a three-way tap open to the air. Fifteen seconds after the introduction of the electrode, the tap was turned so as to make connexion between the test-tube and a Hempel gas-burette. The quantity of oxygen evolved per minute was noted, the figure plotted being the mean value obtained during the first three minutes.

The wires used in obtaining the photomicrographs were plated in the same way as the plates; the diameter varied between 0.15 and 0.3 mm. The platinum wire was merely held between terminals fitted into the edge of a slip of wood mounted on the microscope stage. A slip of paper was placed beneath the wire and illuminated from below so as to form a bright background, against which the wire was silhouetted. The heating was carried out by means of the electric current, no attempt being made to measure the temperature, but, judging by the colour of the glow, it always lay between 650° and 850° . The copper, silver, and iron wires were all mounted—after plating—between two steel wires passed through a rubber stopper. During heating, the stopper carrying the wires was used to close an inverted bottle, through which a stream of purified dry hydrogen was passed, the heated wire being in all cases allowed to cool in the atmosphere of hydrogen. After heating, the rubber stopper was removed from the bottle, mounted on the stage, and the wire photographed.

Conclusion.

The metals, silver, copper, iron, platinum, and palladium, when deposited electrolytically in a fine state of division, show the phenomenon of sintering at temperatures considerably below their ordinary melting points. It is thought that this effect may be parallel to the abnormal vapour pressure and solubility of finely-divided material. The effect probably has considerable influence on the optimum temperature of a finely-divided metal when used as a catalyst.

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