represents all the best determinations, and is probably correct to within 1 in the third decimal place. For so small a value the change is insignificant.

Signed, F. W. Clarke,
T. E. Thorpe,
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[Contribution from the Electrochemical Laboratories of the University of Manchester.]

THE OCCLUSION OF HYDROGEN AND OXYGEN BY METAL ELECTRODES.

Criticism of the Paper by Harding and Smith.[1]

By Edgar Newbery.

Received May 26, 1919.

The very careful work and ingenious apparatus of Harding and Smith call for some remarks of appreciation; and at the same time the theory of conducting hydrogen as developed by them appears to be open to doubt. The following comments are not offered in any spirit of carping criticism, but rather with the thought of friendly collaboration and interchange of views, and the object of reaching the real truth underlying some very interesting phenomena.

When a current is first passed through an electrolytic cell containing a palladium cathode in dilute acid, hydrogen ions are discharged upon the cathode surface and the monatomic hydrogen thus formed is at once absorbed by the metal, being kept in the monatomic form by the dissociating action of the solvent metal. This hydrogen will gradually diffuse to the interior of the metal, and, since the solution has a lower conductivity than the pure metal, the electric resistance of the metal will rise.

After a comparatively short time the external layers of metal will become saturated with hydrogen and the single potential of the metal solid solution will be that of a hydrogen electrode. Hydrogen ions, on discharging, will now no longer disappear into the metal but will tend more and more to stick on the outer surface, being held there by electrostatic forces, thus insulating the outlying parts of the electrode. New ions must therefore penetrate farther and farther into the surface before they can discharge. These ions are again followed by others which arrive faster than the discharged ions can collect together to form molecules, and consequently "blocks" will occur in the large crevices (large compared with an ion) in the metal surface. Since these latest arrivals carry electric charges opposite in sign to the charge on the electrode and are separated from the electrode only by the diameters of two or three atoms or molecules, inconceivably great pressures are set up which may easily attain a

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[1] This Journal, 40, 1508 (1918).

magnitude of 10^{30} atmospheres close to the outer surface. These pressures are logarithmically proportional to the potential differences between the two attracting surfaces and will therefore be greatest near the solid-liquid boundary; but since the gas diffuses slowly to the interior of the metal increasing the resistance all the way, there will be a small fall of potential from the surface to the inner core of the palladium and consequently a gradually decreasing pressure extending an appreciable distance into the metal. The effects produced will therefore be more noticeable in fine wires or thin sheets than in thicker ones.

When very low current densities are employed, the above description will hold good. With higher current densities, however, a new set of phenomena appears. The pressures now become so great that the hydrogen is forced into actual combination with the metal, producing hydrides. These hydrides conduct like a metal and ionize like a metal, and their high solution pressures give rise to the excess back e. m. f. known as overvoltage.

When the current is interrupted, the external pressure is at once released. Immediately, therefore, the excess gas dissolved in the metal will tend to come out of solution, expanding the metal and making it spongy, thus increasing its resistance rapidly at first and more slowly afterwards. At the same time, the hydrides formed, which are only stable under high pressures, decompose and intensify the above effect. The consequence of this liberation of gas from within the metal will be that a series of small craters will be blown in the surface of the metal and these craters are easily visible under the microscope not only in the case of palladium, but with every metal so far experimented with.

Since there is good evidence, from overvoltage work, that the hydrides are good metallic conductors, it is probable that the disappearance of these will further increase the resistance of the metal, as the whole would conduct better when the pores are filled with conducting hydride under pressure than when filled with gas.

When a considerable quantity of gas has escaped, the internal strains in the metal will be released and the metal will gradually recover its original texture, the walls of the cavities filled with gas will fall together as the gas escapes, and the resistance of the metal will again fall. On heating and annealing, the metal will return completely to its original condition, provided the evolution of gas has not been so violent as to distort the surface permanently.

Changes of Length.

If the cathode is a palladium wire, changes of length occur (1) due to solution of hydrogen in the metal; (2) due to formation of hydride. Since the application and release of pressure occurs laterally and chiefly in the outer layers of the wire, the central core may be but slightly affected and will tend to hold the outer layers in position, thus masking the effect except with very fine wires. The change of length is therefore not a satisfactory guide to change of volume except in special circumstances. It might be expected that the formation of a solid hydride would have a greater expanding effect than the absorption of gas, and this is supported by the experimental evidence of Thoma and Fischer.[1] Since the quantity of hydride formed is dependent upon the current density, a definite length should correspond with each current density when equilibrium has been attained. Further, since the replacement of gaseous hydrogen by solid hydride diminishes the resistance of the metal, there should be an inverse relationship between resistance and length under these equilibrium conditions. This has been well established experimentally, as described in the paper under discussion.

Finally, the typical experiment curve,[2] Fig. 2, may be described as follows:

A to B.—Absorption of hydrogen with production of solid solution having higher resistance than pure metal. Metal becomes spongy.

B to C.—Formation of hydride which fills some of the cavities originally occupied by gas, thus reducing resistance.

C to D.—Release of external pressure resulting in spontaneous decomposition of hydride, and escape of gas internally, rendering metal still more spongy, and therefore of still higher resistance.

D to E.—Escape of gas externally, due to bursting of surface. Walls of cavities fall together and reduce resistance.

E to F.—First application of external pressure produces still closer conjunction of walls of cavities and rapid fall of resistance.

F to G.—Reabsorption of gas. Since passages have now been formed in the metal, this occurs much more rapidly and completely than in the first instance.

G to I.—Renewed formation of hydride. This will also occur more rapidly than before due to the existence of ready-made passages into the interior of the metal.

I to J.—Rapid expansion of cavities due to release of external pressure. More rapid than previously owing to weakening of external cohesive forces by the treatment undergone.

J to K.—Complete removal of gases and collapse of cavities.

The quantity of hydride produced appears to be dependent upon the current density though it is not proportional to the current density. Hence, for a given current density, the equilibrium stage attained will be approximately the same whatever the previous treatment.

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[1] M. Thoma, *Z. physik. Chem.*, 3, 69 (1889); F. Fischer, Drude's *Ann.*, 20, 503 (1906).

[2] *Loc. cit.*, p. 1513.

Briefly, my doubts of the "conducting hydrogen" theory are based upon a quantitative view of the effects produced. It appears certain that up to saturation point the hydrogen dissolved in palladium is very largely composed of atomic hydrogen, probably over 80%. This atomic hydrogen is responsible for the single potential of the hydrogen electrode, and if a metal is incapable of dissociating hydrogen in this way, it cannot be used in the construction of a hydrogen electrode. The addition of more hydrogen (supersaturation), one would expect would tend to diminish the total percentage of atomic hydrogen by bringing the atoms into closer proximity, just as a concentrated salt solution is less dissociated than a dilute.

The fact that up to saturation point the resistance of palladium is greatly increased by the inclusion of hydrogen (most of which is in the atomic state), renders it improbable that the addition of further hydrogen in the atomic state will decrease this resistance.

The action of the added hydrogen would not alter the single potential of the electrode. But experiment shows that under certain conditions the single potential of the palladium electrode takes a sudden leap to a much higher value, nearly 0.7 volt above the hydrogen electrode, and this same value is also shown under similar circumstances by nearly every metal capable of acting as a divalent metal in compound formation. This evidence, together with other which could be cited if necessary, is almost overwhelming in support of the view that a definite hydride is now formed in the metal. It must therefore be taken as proved that hydrides do exist in the metal under these conditions, although the question as to whether they are responsible for the changes of electrical resistance observed in palladium is still open.

The hydrides thus formed are stable only under the great electrical and mechanical stresses present at the time of their formation, and up to the present none of this special type of metallic hydride has been isolated. Nevertheless, it is possible to predict their properties with comparative certainty by analogy with many oxides produced under almost identical circumstances. Some of these oxides, lead dioxide, manganese dioxide, etc., are easily isolated and their properties well known. The property which specially concerns us here is their electrical conductivity, which is considerable, though far below that of the metal itself. Since the hydrides show so many properties in common with these oxides, it is only reasonable to consider that they have a quite appreciable electrical conductance. Further, if they form solid solutions in the metal, such a solution is likely to be a better electrical conductor than a solution of gaseous hydrogen in the same metal.

Whether, therefore, the hydrides form solid solution with the metal, or whether they merely fill cavities in the metal formerly occupied by gas, their appearance will be demonstrated simultaneously by a fall in the electrical resistance of the metal and by a rise in the (negative) single potential.

The accuracy with which the experimental wire recovers its original resistance when very carefully treated is at first sight puzzling, but on further examination becomes not only reasonable but gives us further interesting information as to the processes going on during formation of the hydrides.

It is well known that all metals in the massive state consist of crystals cemented together by amorphous material. This amorphous material is not, strictly speaking, a solid but a highly viscous liquid, and many of the mechanical and physical properties of the metals are due to this substance which forms an envelope for every crystal of the metal. Polishing the metal consists in pressing down the metallic crystals and smoothing over this liquid on the top. Since palladium is easily brought to a state of brilliant polish, it is probable that the amorphous material is fairly plentiful in this metal. It also appears probable that colloidal palladium and the amorphous metal have much in common even if they are not identically the same. The great so-called "catalytic" power of colloidal palladium is well known and appears to be due to its great dissolving and dissociating power for gases like hydrogen. It appears, therefore, that the solution of hydrogen in palladium is due mainly (possibly wholly) to the amorphous or liquid part of the metal, and further, that the hydrides are formed from the same substance. This substance, therefore, being a liquid, cannot have its shape destroyed, and if it is merely expanded and afterwards contracted again without any violent disturbances occurring sufficient to displace the crystals permanently, there is no reason why the final properties of the body as a whole should be different from the initial properties.

The greater solubility of hydrogen in the amorphous phase is observable in other metals than palladium, *e. g.*, the embrittling and hardening of iron after use as a cathode, is due to the weakening of the cohesive power and increase of viscosity of the amorphous binding material by solution of hydrogen and possibly, also, to the formation of minute crystals of solid hydride.

The observations under discussion, therefore, are of great interest in showing that both solution of hydrogen and hydride formation in palladium are almost entirely due to the action of amorphous or liquid palladium, the solid crystals taking little or no part in the process.

The application of the phase rule to this problem is very unsafe since we are dealing with a system highly heterogeneous and not in equilibrium. Even under the conditions represented by horizontal lines on the diagram in the paper under discussion, true equilibrium is not present since we have irregularly decreasing mechanical pressures and electrical stresses as we proceed from the surface of the wire to the internal core. If any attempt be made to apply the phase rule to this state, then these variable pressures must be considered in the character of new components, and since the pressures vary indefinitely, the number of phases possible is also indefinite.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY.]

THE OCCLUSION OF HYDROGEN AND OXYGEN BY METAL ELECTRODES.

Comment on Newbery's Criticism.

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The foregoing interpretation of our results, in terms of Professor Newbery's hypothesis of unstable hydrides, to which he has been led by extensive studies of overvoltage, involves several questions of wide bearing. We shall in the main confine ourselves, however, to pointing out difficulties which attend the explanation of our own observations in the manner suggested, and commenting on the objections raised with regard to "conducting hydrogen."

Since the conduction of a platinum wire cathode has been shown to rise above that of the unaffected metal,[1] it would, in this instance at least, be necessary to attribute to the supposed hydride a volume conductivity greater than that of its metallic component, and hence of a higher order than any hitherto observed for compound or solid solution. The same applies to the oxide which must logically be assumed to account for the analogous effect found with a palladium anode.[2] If compounds, whether formed in fixed or in variable proportions, afford the explanation, they must therfore belong to a new category having extraordinary electrical characteristics.

The changes of resistance exhibited by the cathodes when electrolysis is renewed after temporary interruption, consist in three parts: a very rapid initial drop (seen in Curves 1, 2 and 3 of Fig. 6, of the original article, in the enlarged reproduction of No. 1 given at the lower left side of the same figure, and at E–F in Fig. 2); a subsequent rise to the maximum; and a final decline to the steady value determined by the current density. It is not readily apparent why the formation of the supposed hydrides, stable only at very high pressures, should be most in evidence in the first stage of this occlusion, when electrolysis has just begun and the pressure of hydrogen within the electrode must be relatively low. Nor does it seem

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[1] THIS JOURNAL, 40, 1530 (1918).

[2] *Loc. cit.*, Fig. 8, p. 1524, *et seq.*