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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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.*

to follow from the hydride hypothesis, without the addition of special assumptions, that the production of hydrides should predominate during the first and last stages, while formation of solid solution prevails in the intermediate part of the process.

The initial drop of resistance, just mentioned, is attributed by Professor Newbery to "closer junction of the walls of cavities," implying a contraction of the wire. It was perhaps not made plain that the falling first portions of the curves of Fig. 4*a* represent the ends of the evolution curves, and that the length of the wire, in these and in all our experiments, *increased* instantly upon renewal of electrolysis. During the drop of resistance from E to F the wire is therefore expanding; and for this the hydrides do not seem to offer a ready explanation.

The assignment of the supplementary conductance to hydrides seems also unadapted to account for the initial drop of resistance observed when a wire previously subjected to oxidation is made to serve as cathode (*loc. cit.*, middle of p. 1525), and the absence of this drop when unoxidized wires are employed. Any effect left by oxidizing influences must be of a kind to delay, rather than to hasten, the attainment of high hydrogen pressures, and hence must operate in the earlier stages of electrolysis to diminish the quantity of hydrides, if these are stable only at high pressures. The consequence of oxidation should, therefore, be the opposite to that found.

Turning to Professor Newbery's objections to the supposition of a conducting form of hydrogen, we may point out that his statement that "the addition of more hydrogen (supersaturation), * * * 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," overlooks the fact that an electrode, during the persistence of the supplementary conductance, is not yet in a state of equilibrium; and that the analogy is not to an electrolyte to which more ionogen is added, but rather to a slowly reacting mixture, into which is rapidly introduced an excess of one of the reactants It is evident that in such a case the added factor (and any intermediate product), would be present in more than equilibrium proportion until the end state had been reached.

We are unable to see the force of the objection that "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." This appears to us to be fully met by the consideration set forth in the paper under discussion (p. 1518, *et seq.*).

Nor can we agree that "the action of the added hydrogen would not alter the single potential of the electrode." It appears to us almost inevitable that the accumulation of a transient intermediate form within the metal should raise the electrolytic solution pressure of hydrogen.

While we would not deny the possibility that Professor Newbery's explanation may be the correct one, we must therefore still regard our own as involving a less sweeping and more definite assumption. A metallic compound, existing within an alloy side by side with a solid solution from which it differs diametrically in properties, but from which it does not form a distinct phase, constitutes something new to metallography; and the novelty of the conception is not diminished by supposing both solid solution and compound to form part of an amorphous cement, the existence of which is itself by no means universally admitted. The unique electrical properties with which the compound must further be endowed, add to the scope of the assumption.

On the other hand, to suppose that the hydrogen (or oxygen) which has yielded its charge to the electrode and penetrated the latter, not improbably in a monatomic condition, is capable of again receiving charges from the metal and transporting these charges under the influence of the potential gradient associated with the measuring current, appears to imply nothing new save, perhaps, the conception that the hydrogen retains its mobility after entering the metal until it enters into the close chemical relationship of the solid solution, or as otherwise transformed; and for this conception the behavior of the palladium wires appears to us to afford strong support not only in the changes of length, but in the disruptive effect produced when hydrogen-filled wires are quickly raised to a temperature above the critical point at which a rapid fall of resistance occurs (bottom of p. 1510, *et seq.*). This seems to indicate very clearly that at this temperature the solid solution releases hydrogen into a mobile form which exerts great internal pressures.

The conception makes at present no pretense of being more than a working hypothesis. As such it has the advantage of being quite definite, and hence suggesting many questions of fact. Since some of these are at present the subject of experiment, further elaboration of our point of view may appropriately be deferred.

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