One further point may be mentioned with regard to the ninth paragraph of Harding and Smith's comment on my criticism. They refer to "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."

I agree that such a hypothesis is very improbable and I had no idea of suggesting this. Though the application of the phase rule to such a system which is not in equilibrium is very unsafe, yet if we consider a very small volume in the interior of the metal where the changes are progressing slowly, the condition of equilibrium may approximately hold.

We have two components, metal and monatomic gas. Metal may be considered to have ceased to exist as pure metal and the phases present will be saturated solid solution, metallic hydride, free gas. If the pressure be increased, more gas will combine with the solid solution to form hydride. If it be decreased, hydride will decompose giving free gas and solid solution. The hydrides, therefore, form a distinct phase with a definite dissociation pressure for a given temperature, the whole process being exactly analogous to the decomposition of calcium carbonate by heat. The fact that hydrides are actually formed hardly admits of dispute, the evidence being almost overwhelming,[1] while the formation of the corresponding oxides is a well established fact. The question at issue is not whether these compounds exist, but whether they are responsible for the resistance changes observed by Harding and Smith.

In conclusion, I desire to express my appreciation of the courtesy and broad-mindedness with which Professor Smith and Dr. Harding have met my criticisms and also my admiration of the delicacy and ingenuity of their apparatus and the work under discussion.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY.]

COMMENT ON PROFESSOR NEWBERY'S REPLY.

BY EARLE A. HARDING AND DONALD P. SMITH.

Received October 7, 1919.

The first new explanation advanced in this reply assumes that the resistance of the palladium wire is reduced by an electrostrictive effect. Since, at 25°, the average pressure coefficient of the resistance of palladium[2] is only -0.1887×10^{-6}, the electrostriction necessary to cause a change of resistance of 25% would be of a magnitude far beyond any which could be produced by the small voltages applied (<6 volts). Moreover, this explanation assumes that the crosss section of the wire is reduced during

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[1] See *J. Chem. Soc.*, **109**, 1051, 1066, 1107, 1359 (1916); **111**, 470 (1917); also *Manchester Memoirs*, **61**, No. 9 (1917).

[2] Bridgman, *Proc. Am. Acad.*, **52**, 612 (1916).

the occlusion of hydrogen, whereas the reverse is the case. Occlusion is accompanied by expansion in all directions.[1]

Another explanation offered is that a shunt conduction through the electrolyte, by which the wire was surrounded, varied with the transfer resistance between wire and electrolyte, and that these variations were responsible for the changes of resistance observed. Such an explanation is clearly inapplicable to the experiments in which the supplementary gain of resistance was found to continue unaltered after the electrolyte had been withdrawn.[2] In the ordinary experiments, each wire was annealed to constant resistance in nitrogen, and its resistance was again taken after the introduction of the electrolyte, but before electrolysis was begun. In no instance could a change of resistance, due to the presence of the electrolyte, be detected with certainty. Hence the shunt conduction was itself negligible, and such second-order differences in this factor as may have resulted from changes of transfer resistance could hardly have exerted an appreciable effect. It should be borne in mind that our measurements of resistance were not made while the electrolytic current was flowing.

As regards Professor Newbery's further elucidation of his hydride explanation, it does not appear to us in any way to remove the necessity for attributing to these compounds the extraordinary conductivities discussed above.

We are, therefore, still of the opinion that the simplest explanation of the supplementary conductance is to be found in the assumption of a transient conducting form of hydrogen.

PRINCETON, N. J.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS.]

THE ELECTROLYTIC DETERMINATION OF THE HALOGENS: AN INDIRECT METHOD.

BY J. H. REEDY.

Received June 2, 1919.

The determination of the halogens by their electrolytic deposition on silver anodes has been regarded by most investigators as impracticable, since the silver anode begins to dissolve, either during the last stages of the electrolysis, or immediately upon completion of the halide ion deposition. Results are low, owing either to precipitation of silver halides in the solution or to the migration of silver to the cathode. Various expedients to overcome this difficulty have not proved satisfactory, and gravi-

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[1] Poggendorff, *Phil. Mag.*, [4] 37, 474–5 (1869); Thoma, *Z. physik. Chem.*, 3, 71 (1889).

[2] THIS JOURNAL, 40, 1516 (1918).