184. *The Reaction of Atomic Hydrogen with Metallic Copper.*

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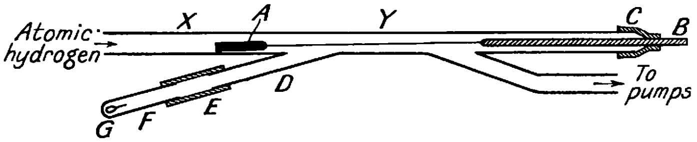
Pietsch and Josephy (*Naturwiss.*, 1931, **19**, 737) found that a surface of metallic copper, roughened with emery-paper, became coated with a bluish-white deposit when exposed to atomic hydrogen. There was a critical concentration for the success of the reaction which they obtained by passing hydrogen through their apparatus at a velocity of about 1 l. per hour. Higher concentrations led to the disappearance of the deposit, presumably by the heat evolved by the combination of atoms on the surface. (We have actually melted the metal thus.) Micro-tests with ammonium hydroxide, sodium hydroxide, and potassium thiocyanate indicated that the coated copper gave rise to cupric ions which were absent in control experiments on similarly roughened copper foil untreated with atomic hydrogen.

Work on the reduction of aqueous copper sulphate with hypophosphorous acid has given materials which have been variously described as CuH by Sieverts (*Z. anorg. Chem.*, 1909, **64**, 29), and as CuH_2 by Bartlett and Merrill (*Amer. J. Sci.*, 1895, **17**, 185), but stated by Berthelot (*Ann. Chim. Phys.*, 1898, **14**, 203) to contain water, phosphorus, and oxygen. On the other hand, Hüttig and Brodkorb's preparations (*Z. anorg. Chem.*, 1926, **153**, 235) proved to be cuprous, and contained water which could only be diminished below that corresponding to $CuH,2H_2O$ with some dissociation of the hydride, so that, after drying in a vacuum, the preparations had less hydrogen than is required for CuH. Material dried in this way loses hydrogen slowly when heated to about 110°, at which temperature the remainder is evolved explosively. In view of the nature of atomic hydrogen, the formation of a cupric compound by its action is hardly to be expected, and it is unfortunate that the precautions taken to avoid oxidation during the testing operations are not stated.

We have examined the reaction, and find that the hydride is quite black, and that it dissolves in 70% hydrochloric acid to give cuprous ions. Certain incidental observations on the action of aqueous ammonia on metallic copper were made.

The atomic hydrogen was prepared in a discharge tube similar to that used in earlier work in this laboratory (*Proc. Roy. Soc.*, 1933, *A*, **142**, 275; this vol., p. 7), but modified so that the electrodes can be removed through ground joints, and the tube cleaned and treated with phosphoric acid when necessary. After preliminary trials, the apparatus illustrated below was incorporated between the discharge tube and the pumping system. A piece of copper foil, *A*, was attached by thin copper wire to the glass rod, *B*, which was free to move through the gland *C*, constructed with pressure tubing and lubricated with vacuum oil. After being subjected to atomic hydrogen at *X*, the foil was drawn back to *Y*, and thence it was pushed down the side tube *D*, through the rubber joint *E*, into *F*. The tube *F* contained hydrochloric acid, freed from dissolved air, and a sealed bulb containing ammonium hydroxide in excess of the acid present. Before each run, *F* was evacuated and filled with hydrogen, two or three times, to ensure the complete removal of oxygen, after which it was isolated from the system by a screw-clip at *E*.



It was found that a hydride could be formed on foil roughened with emery-paper, but a more reactive surface was obtained by superficially oxidising the copper in air and subsequently reducing the oxide film by means of molecular hydrogen. The hydride is preparable only at low temperatures, such as were maintained with a hydrogen stream below 0·5 l. per hour. Faster streams not only destroyed the hydride, or prevented its formation, but rendered the prepared surface resistant to normal attack. The hydride, when formed in sufficient quantity to overcome interference effects, was black.

After the copper had been coated with hydride, the discharge was stopped, the apparatus was filled with hydrogen to atmospheric pressure, the passage into *F* was opened and the foil was submerged in the acid in *F*. We found 10% hydrochloric acid to be without apparent effect on the hydride, and concentrated acid to destroy it with the liberation of bubbles of (presumably) hydrogen without, however, dissolving any copper. The hydride proved to be soluble in 70% aqueous hydrochloric acid and with this the coated copper was treated for about one minute and then withdrawn. The tube *F* was immediately closed with the screw-clip and removed from the apparatus, and the contents were made alkaline with ammonia by breaking the bulb *G*. The solution remained colourless for some time, but developed a blue colour as soon as air was admitted. Evidentally the copper was originally present in the cuprous condition, and gave rise to cuprous ions which became oxidised on exposure to air. Several repetitions of this experiment were attended with identical results, and controls, differing only in the absence from them of atomic hydrogen, showed that the ions did not arise from solution of the metallic copper. We therefore conclude that the hydride formed is cuprous.

We found that copper is insoluble in air-free aqueous ammonia, but rapidly soluble in presence of air. Moreover, the blue solution of the tetrammine is slowly reduced by the metal in absence of air: These reactions are being investigated further.

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