2. The results of J. M. Cabell and F. L. Hahn have been fully confirmed: the presence of both oxygen and moisture is required for the reaction between hydrogen sulfide and silver to take place at ordinary temperatures and pressures.
3. A theory has been advanced which takes into consideration the need for both oxygen and moisture.

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HYDROGENATION OVER METALLIC CESIUM

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If hydrogenations can be induced by alkali metals as catalysts, one would look to the intermediate compound theory for explanation, as the hydrides of these metals are readily formed and decomposed at moderate temperatures. Experiments on one such reaction over metallic cesium seem to indicate, however, that although hydrogenation occurs the hydride is not the catalyst and even hinders the reaction.

Experiment showed that ethylene and hydrogen reacted when admitted to distilled cesium even at room temperature. The rate as measured by pressure drop gave evidence of poisoning of the catalyst, for the decrease upward of ten millimeters per hour at the start, diminished steadily, and the total pressure only approached that consistent with ethane formation after a long period of time. At 200° the process was much more rapid, but a similar diminution in rate was observed.

Reaction was also found between carbon monoxide and hydrogen, commencing very rapidly at room temperature, and as rapidly diminishing, becoming zero at a pressure not susceptible of ready interpretation. Thus poisoning was again evident, though the experimental difficulties in analyzing the gases were such that the quantitative measurements were performed on the more easily handled ethylene and hydrogen.

Analysis showed that the reaction produced ethane, and also that (unaccounted for) hydrogen had disappeared from the gas phase. This is ascribed to the formation of cesium hydride, for the once silvery metal was covered with a white layer. Confirmation of this hypothesis was sought by heating the pure metal in an atmosphere of hydrogen, in which case the pressure decreased, and a similar white coating was obtained. When ethylene was admitted to this supposed hydride at room temperature no pressure change was observed, but analysis of the gas after some hours showed the presence of small quantities of ethane. Moissan[1] failed to find any reaction between ethylene and cesium hydride, a discrepancy

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[1] Moissan, *Bull. soc. chim.*, **31**, 556 (1904), *et al.*

to be explained by the slowness of the reaction, rendering his flow method too insensitive. At 200° the reaction was quite rapid, and a slight pressure decrease was observed. The hydrogen was almost completely removed from the hydride, for the white substance disappeared and the surface, although dull, was once more metallic in appearance. Ethane and some hydrogen were found in the gas, the latter arising from the thermal decomposition of the hydride, which is appreciable at that temperature[1] though extremely small at 25°. The pressure decrease may be due to adsorption of ethylene on the metal surface, or to a polymerization catalyzed by the metal. Both processes are believed to occur.

The catalytic activity depended on the treatment of the metal. When the surface had been heavily coated with hydride by prolonged heating in hydrogen, its effect on an ethylene hydrogen mixture at room temperature was very slight.

When the hydride was removed as above by heating with ethylene, the activity was much enhanced. Analysis of an ethylene-hydrogen mixture after a considerable pressure drop had occurred showed the presence of large amounts of ethane, more indeed than corresponded to the ethylene introduced. This phenomenon, which appears to be real, must be due to ethylene adsorbed during the dehydrogenation process. Excess hydrogen disappeared in the reaction, and the white coat attributed to hydride was again formed.

If, after removal of the hydride as above, the bulb was heated in vacuum so that a fresh surface of pure cesium was distilled to the cooler parts of the bulb, the reaction rate was the greatest of all. The reaction products were ethane and hydride as before.

An attempt was made to cause nitrogen and hydrogen to react in the same way. There was a pressure decrease, but analysis showed that it was due to the formation of hydride, with perhaps a small amount of nitride. Ammonia was not found, nor was the amide which Moissan obtained from nitrogen and cesium hydride, this latter presumably because the total quantity of hydride was so small in these experiments.

An attempt to repeat the ethylene-hydrogen reaction over sodium gave nothing but hydride formation until a temperature close to 300° was reached, when the ethylene began to polymerize rapidly and to cover the surface with tar. A small amount of ethane was formed at this temperature, however, before the tar had rendered the surface completely inactive.

These results would seem to show that even over an alkali metal only adsorbed hydrogen is available for hydrogenation, and that hydride formation serves merely to diminish the free surface. Even over a surface as completely covered with hydride as possible, however, some reaction is observed, for the equilibrium pressure of hydrogen over so unstable a compound must be high enough at all temperatures so that some free surface is present. When part of the surface is covered with adsorbed ethylene, reaction is hindered, as the hypothesis would demand.

That these reaction conditions have some generality is shown by the work of Pease and Stewart,[2] who investigated the same reaction over calcium hydride and metallic calcium. The hydrogenation of ethylene over calcium does not go through the hydride stage, although this substance is an effective catalyst for the reaction.

One may not venture, however, to extend these principles, for Weichselfelder and Kossodo[3] have shown that in some cases of hydrogenation over nickel, and over nickel hydride, formation and decomposition of the hydride undoubtedly took place. It thus is impossible to predict the mechanism of such catalyzed reactions until further experimentation has furnished a clue.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 233]

THE USE OF THE IODINE MONOCHLORIDE END-POINT IN VOLUMETRIC ANALYSIS. I. THE TITRATION OF IODIDE

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Introduction

In the so-called "iodate methods"[1,2] of volumetric analysis there is usually added to a hydrochloric acid solution of the reducing substance to be analyzed a standard solution of an iodate until the iodine at first liberated is oxidized to iodine monochloride by the reaction $I_2 + 2HCl + O$ (from iodate) $= 2ICl + H_2O$. The end-point is determined by the disappearance of the iodine color in an immiscible organic solvent, usually carbon tetrachloride or chloroform, which is shaken in a closed flask with the aqueous solution. This end-point is sharp and permanent, and permits of back titration. According to Kolthoff[3] the sensitivity of the detection of free iodine by this method exceeds that by the conventional starch indicator, and a correction factor for the end-point is unnecessary. Results given below of tests which have been made under various conditions confirm this and show the extreme sensitivity of the end-points obtained.

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[2] Pease and Stewart, THIS JOURNAL, **47**, 2763 (1925).

[3] Weichselfelder and Kossodo, *Ber.*, **62B**, 769 (1929).

[1] Andrews, *Z. anorg. Chem.*, **36**, 83 (1903); THIS JOURNAL, **25**, 756 (1903).

[2] Jamieson, "Volumetric Iodate Methods," The Chemical Catalog Co., New York, 1926.

[3] Kolthoff and Furman, "Volumetric Analysis," John Wiley and Sons, New York, 1929, Vol. II, p. 352.