

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

**HYDROGEN AS A HALOGEN IN METALLIC HYDRIDES**

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The compounds of hydrogen with electropositive metals, the metallic hydrides, appeared to be substances of quite anomalous character until Lewis<sup>1</sup> advanced his theory of valence. According to this theory, hydrogen is not only the first member of the alkali group, but also the first member of the halogen group. In the second row of the periodic table, which begins with lithium and ends with neon, lithium readily gives up its single valence electron and forms lithium ion, while fluorine readily adds another to its 7 valence electrons forming the stable group of 8, the arrangement of electrons being identical with that of neon.

In the first row of the periodic table, which contains only hydrogen and helium, the hydrogen atom should be able not only to give up its electron to form hydrogen ion, but to take up an additional electron forming hydride ion, having a structure identical with that of helium.

According to his interpretation, the hydride of an electropositive metal is a true salt. Indeed, in their physical properties, the hydrides closely resemble the halides. Some of the preparations of earlier investigators were gray substances of indefinite composition which were doubtless mixtures of metal and hydride. The pure hydrides of potassium and sodium prepared by the method described below form in brilliant white crystals which appear to be small pointed prisms. Potassium hydride decomposes with explosive violence in moist air. Contrary to the view of Moissan,<sup>2</sup> they do not dissolve in molten metals. This is shown by the constancy of dissociation pressures observed by Keyes<sup>3</sup> and by experiments of my own. Liquid sodium in contact with hydride was filtered through glass wool and analyzed. No hydride was found in the filtrate. With respect to melting points, the hydrides resemble the fluorides. Lithium hydride melts at 680°, lithium fluoride at 800°; calcium hydride remains solid up to the decomposition temperature which is about 1100°, while calcium fluoride melts at 1350°.

If hydrides are true salts, they should, in the fused state or in solution, conduct an electric current; such current should deposit the metal at the cathode and hydrogen at the anode. In order to test this view, Lewis and Stafford<sup>4</sup> fused pure lithium hydride and found it to be an excellent conductor of electricity. The experiment, however, was not entirely conclusive since lithium hydride at its melting point is somewhat dis-

<sup>1</sup> G. N. Lewis, *THIS JOURNAL*, **38**, 762 (1916).

<sup>2</sup> Moissan, *Compt. rend.*, **134**, 71 (1902).

<sup>3</sup> Keyes, *THIS JOURNAL*, **34**, 779 (1912).

<sup>4</sup> Ref. 1, p. 774 (footnote).

sociated, and the melt therefore contains some metallic lithium, which might be responsible for the conduction, and which indeed was found to make the mixture a conductor even after it had solidified and cooled to room temperature. This experiment has more recently been repeated by Moers,<sup>5</sup> who obtained similar results and also showed that in electrolysis metal was deposited at the cathode and some hydrogen was set free, although he could not prove that this was liberated at the anode.

It is the purpose of the present investigation to show that in the electrolysis of a solution of a hydride, hydride ion passes to the anode, where it is liberated in the amount required by Faraday's law. The test might be made with a pure molten hydride or with a solution. Since no pure hydride can be melted without forming a certain amount of free metal through dissociation, it was decided to work with solutions, especially since the high tendency of hydrides to dissociate permits us to predict that the potential required for deposition of hydride ion at the anode would be far less than that required for any other anion.

#### Preparation of Hydrides

In many respects lithium hydride would have been the easiest to prepare and use, but at the time this investigation was made metallic lithium was not available. The experiments were, therefore, confined to the hydrides of sodium, potassium and calcium. The preparation in quantity of sodium and potassium hydrides is a matter of some difficulty. The method of Keyes<sup>3</sup> could not be used to produce more than thin surfaces of hydride. Moissan's<sup>2</sup> method gave hydrides badly contaminated with unchanged metal. The following method was developed and found to give small quantities but of good purity. Electrolytic hydrogen was passed through a platinized asbestos column heated to 400°, then through two drying tubes containing phosphorus pentoxide, the second of which was always kept full by replacing with new tubes when necessary, and finally bubbled through sodium-potassium eutectic alloy.

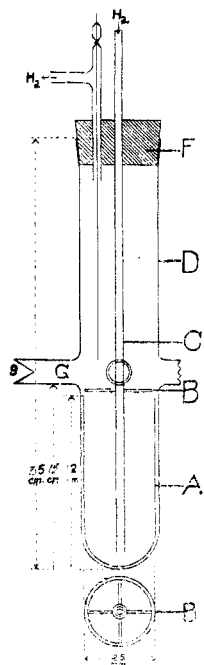


Fig. 1.

The apparatus in Fig. 1 consists of a steel test-tube A placed in the bottom of a long Pyrex glass tube D. A steel tube C, 3 mm. in diameter, extends from a rubber stopper at F into the steel test-tube. B is an iron wheel trap fastened to C at a point just above the top of the steel test-tube. Four glass tubes G were sealed into the side of the long tube, 14 cm. from the bottom. The ends of these tubes G were made very thin, and conical inward. This made it easy to break them later by dropping them on a similarly pointed projection.

Hydride was prepared and recovered by the following manipulation. A piece of

<sup>5</sup> Moers, *Z. anorg. Chem.*, **113**, 179 (1920).

metal, about the size of a marble, was dried from kerosene and dropped into the steel tube. After the apparatus had been thoroughly washed out with hydrogen, the lower end of the apparatus was immersed in a eutectic bath of potassium and sodium nitrates to a depth of 12 cm., and the temperature of the bath maintained at approximately 400°. Hydrogen was allowed to pass through the steel tube and bubble through the metal. Under these conditions, crystals of the hydride formed at B. To fill the tube in the vicinity of the trap with sodium hydride required 7 hours.

After the hydride was prepared, the trap was raised by pulling the rod through the rubber stopper and the crop of crystals was knocked from the trap into one of the side tubes. This was sealed off by means of a torch and the trap was lowered into position for another crop of hydride. Four tubes were filled and sealed in this way.

Calcium hydride was prepared by heating calcium turnings in an iron test-tube to 500° and admitting small quantities of hydrogen until no more absorption took place. The product, a compact white crystalline material, was sealed in glass tubes in presence of dry hydrogen. Upon leaching with liquid ammonia, it was found to be free from unchanged metal, since the ammonia developed no blue color.

### Choice and Preparation of Solvent

Moissan<sup>5</sup> reported qualitative insolubility of potassium and sodium hydrides in liquid ammonia. From conductivity measurements of liquid ammonia in contact with sodium hydride, the writer found that it hardly increases the conductivity. Potassium hydride increases the conductivity of ammonia, but this is due to amide formation, noted by Ruff and Geisel.<sup>6</sup>

If these hydrides are salts, fused halides might be expected to be solvents. The eutectic mixture of potassium and lithium chloride containing 40 mol % of the former and melting at 352°, was chosen because of its low melting point. Due to the difficulty in drying lithium chloride, the following procedure was found necessary. The eutectic mixture was heated to about 365° and a current of dry hydrogen chloride bubbled through it for an hour. The temperature of the salt was then raised to approximately 700° and the stream of gas continued for half an hour. Dry hydrogen was then bubbled through for half an hour to wash out the hydrogen chloride. Salt dried in this way was sealed in tubes similar to those used for the hydrides.

TABLE I

Voltage Volts	Current Milliamperes	Voltage Volts	Current Milliamperes
0.75	1.5	2.00	22.6
1.50	2.4	2.15	97.1
1.75	5.5	..	..

A glass cell containing iron electrodes was used to study the variation of direct current with voltage applied at electrodes, electrolyzing the dry fused eutectic mixture. Table I gives the results and shows that there is little electrolysis with a potential of less than 2 volts.

<sup>6</sup> Ruff and Geisel, *Ber.*, **39**, 828 (1906).

### Properties of the Hydride Mixed with Solvent

A tube of eutectic mixture (Fig. 2) was placed in B, a tube of potassium hydride in A, and the vessel closed and attached to the vacuum line. The walls of the vessel were heated with a smoky flame while the vessel was being evacuated, to remove films of moisture. The apparatus was then sealed off from the line, and the capsules were broken by shaking them against the points at the bottom of each tube. The temperature of the eutectic mixture was then raised to 350–360°, where it melted, and was poured into A, where it came into contact with the hydride. The solution formed reacted vigorously with the glass, showing that a metallic container would be essential.

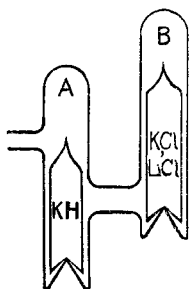


Fig. 2.

By a method similar to that just described, a eutectic mixture of potassium and lithium chlorides was mixed with calcium hydride in an iron test-tube, in a closed tube. The melt was shaken and allowed to stand for half an hour, after which the upper portion of melt was decanted into a side tube and cooled quickly. The side tube was broken off, dropped into gas-free water, and the hydrogen evolved measured. The gas collected N.T.P. was 13.4 cc. The alkalinity produced was 0.000636 mol of hydroxide ion. This would account for 14.5 cc. of gas if the hydride were pure. This result shows that the hydride was not decomposed by the salt, and indicates that a true solution was formed, since the upper portion of melt contained hydride.

### Electrolysis of a Solution of Calcium Hydride in Eutectic Mixture

Porcelain was found to be only slightly attacked by the hydride solution and was used in the cell pictured in Fig. 3. To study the electrolysis of hydride solution this cell was designed and used.

**Description of Cell.**—ABCD is a tube for drying salt, E is an iron test-tube 3.6 cm. x 10 cm., and serves as the anode; F is the anode chamber leading to O; G is a porcelain tube used to separate anode and cathode chambers; H is the cathode chamber; I is a heavy iron rod, the cathode, supported from the porcelain tube by means of glass spokes. It terminated 0.5 cm. above the end of the porcelain; J is a water condenser for keeping the de Khotinsky joint at K cool; L is the cathode lead wire; M is the anode lead wire; N is a stopcock leading from the cathode chamber to the line;

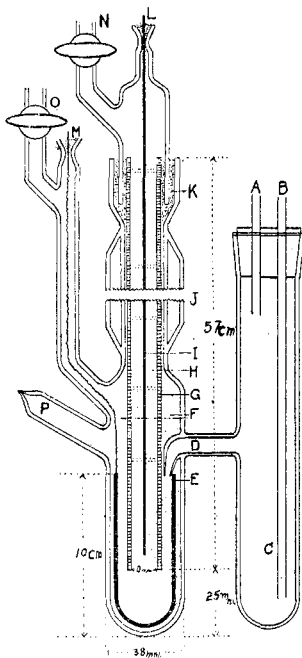


Fig. 3.

O is a stopcock leading from the anode chamber to the line; P is the tube through which calcium hydride was added.

**Procedure.**—The apparatus was tested and found to be vacuum tight. It was filled with hydrogen, and while the hydrogen was passing through, about 25 cc. of solid eutectic was added to ABCD at C. C was surrounded with a small electric furnace and the eutectic was dried as described previously. Finally, the complete apparatus was washed with hydrogen, and 8 g. of calcium hydride was added through Tube P. This tube was sealed off. The eutectic mixture was poured into the iron tube E, and then ABCD was sealed off at D. The solution of calcium hydride in the eutectic mixture filled the bottom of the iron tube. The porcelain tube dipped approximately 2 cm. into the liquid, separating the anode and cathode chambers. Tubes O and N in Fig. 3 were sealed to the vacuum line, O connecting with a bulb in which the gas evolved could be collected at low pressure. The lower part of the cell was immersed to a depth of 15 cm. in the nitrate bath (the latter at temperatures between 360° and 370°). L was attached to the negative and M to the positive pole of a source of direct electric current. The switch was left open. Stopcocks O and N were opened; the complete apparatus was evacuated to 0.01 mm. pressure and the pump closed off. Half an hour was allowed to determine whether any hydrogen was evolved through thermal dissociation of the hydride. None was found. Current was then passed through the cell. The gas collected in the anode side was drawn off and analyzed for hydrogen by the method of sparking with air. No gases were found in the cathode side after any of the three electrolyses. The results are shown in Table II.

TABLE II  
THREE ELECTROLYSES OF CALCIUM HYDRIDE SOLUTION

Voltage across cell	Current Milliamp.	Time Min.	Theoretical	Gas found Cc.	H <sub>2</sub> found Cc.
			H <sub>2</sub> Cc.		
1. + 2.	..	..	..	3.45	3.15
0.8-0.9	20	30	4.18	4.62	3.55
0.4-0.5	10	47	3.28	3.57	3.54

In the first run of Table II, the current fluctuated and no account of the coulomb input was made. The hydrogen found was 91% pure. In the second run, 85% of the hydrogen required by Faraday's law for negative hydride ion was found. The gas was 77% hydrogen, the impurity of which can be attributed to electrolyzing at too high voltage. In the third run, 107% of the hydrogen required by Faraday's law was found, the purity being nearly 99%.

Owing to necessary correction for hydrogen left in the cell, the error in these experiments might amount to 10%. The apparatus and its manipulation were already so complicated that it seemed undesirable to seek higher accuracy. The result of the last experiment is, therefore, accepted as final.

Thus it may be regarded as demonstrated that when a solution of calcium hydride in the fused mixture of potassium and lithium chlorides is electrolyzed at low voltage, hydrogen is evolved at the anode to the amount calculated by Faraday's law for hydride (H<sup>-</sup>) ion. These experiments do not show whether the hydride in this solution behaves as a strong

or as a weak electrolyte. It seems probable, however, that even the pure hydride if it could be obtained in the molten state would prove to be an excellent conductor of electricity.

### Summary

A new method was worked out for the preparation of pure sodium and potassium hydrides. They were obtained in the form of beautiful white, needle-like crystals. Potassium hydride decomposes with explosive violence in moist air.

Calcium hydride was prepared free from metallic calcium.

The eutectic mixture of potassium and lithium chlorides was found to be a solvent for hydrides.

A solution of calcium hydride in this eutectic mixture was electrolyzed, and hydrogen was given off at the anode in the quantity required by Faraday's law. No gas was liberated at the cathode.

The writer wishes to acknowledge his appreciation of the many helpful suggestions of members of the Faculty at the University of California where this investigation was made, and to thank Professor G. N. Lewis especially, at whose suggestion and under whose direction this research was prosecuted.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

## BIMETALLIC ELECTRODE SYSTEMS IN ELECTROMETRIC ANALYSIS. I. SYSTEMS COMPRISING TWO DISSIMILAR METALS

BY H. H. WILLARD AND FLORENCE FENWICK

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### Introduction

A large amount of investigation has been made during the past 10 years on the extension of the use of the electrometric indicator in volumetric analysis and the simplification of the apparatus required for potentiometric work. In connection with the latter, various changes have been suggested both for the measuring instruments employed<sup>1</sup> and the electrode arrangement used. Kolthoff<sup>2</sup> has classified the electrode systems used in electrometric analysis under the following three heads. (1) The system ordinarily used, consisting of an unattackable metal electrode and a constant half-cell, usually a calomel reference electrode. (2) The Pinkhof system, in which the calomel electrode is replaced by a compensation electrode

<sup>1</sup> Hildebrand, *THIS JOURNAL*, **35**, 869 (1913). Forbes and Bartlett, *ibid.*, **35**, 1527 (1913). Kelley and Conant, *ibid.*, **38**, 341 (1916). Kelley, Adams and Wiley, *J. Ind. Eng. Chem.*, **9**, 780 (1917). Roberts, *THIS JOURNAL*, **41**, 1358 (1919). Treadwell and Weiss, *Helv. Chim. Acta*, **2**, 680 (1919). Goode, *THIS JOURNAL*, **44**, 26 (1922).

<sup>2</sup> Kolthoff, *Chem. Weekblad*, **50**, 659 (1920).