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Some Factors Involved in the Disappearance of Hydrogen in the Presence of Potassium or Lithium Ion Sources

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The rate of clean up of hydrogen was observed on potassium and spodumene glass surfaces, sources of K and Li ions respectively. Although there has been considerable difference of opinion as to the nature of this disappearance of hydrogen, i.e., whether it is a surface or gas phase reaction, our results show that the entire effect can be accounted for by a reaction on or within the hot glass, very likely the formation of water vapor.

CONSIDERABLE interest has recently been shown in the relative activity of positive ions and electrons in activation and chemical reaction. The experiments to be reported are concerned with the disappearance or clean up of gases in connection with hot surfaces used as positive ion sources and were conducted in the same manner as the recent experiments of Leipunsky and Schechter[1] and Mitchell.[2]

In the various experiments positive thermions of lithium, potassium or caesium were accelerated toward a collector with speeds up to 400 volts in a chamber containing hydrogen and immersed in liquid air. The disappearance of hydrogen was measured as a function of the positive ion current and speed of the positive ions. Leipunsky and Schechter used a platinum strip coated with an iron-aluminum-potassium oxide mixture and reported a clean up corresponding to 10 molecules of hydrogen per lithium ion at 125 volts to 1000 molecules of hydrogen per potassium ion at 270 volts, and observed some critical potentials.

Mitchell found an initial rate of decrease in the pressure of hydrogen due to the hot filament alone and an increased rate of decrease in pressure when lithium and caseium ions from spodumene and pollucite, respectively, left the surface and bombarded the hydrogen gas with from 15 to 320 volts speed. In this case the number of hydrogen molecules disappearing per positive ion varied from 0.01 to 0.5. The hydrogen clean up was independent of the voltage and no critical potentials were observed.

Although some of our preliminary experiments were carried out on supported iron-aluminum-potassium oxide surfaces, effective catalysts for ammonia synthesis, most of the work was done on glass coated filaments illustrated in Fig. 1. This source of positive ions has been previously described.[3] Either potassium glass or spodumene was drawn in the form of a tube and

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[1] Leipunsky and Schechter, Zeits. f. Physik **59**, 857 (1930).

[2] Mitchell, J. Frank. Inst. **210**, 269 (1930).

[3] Cottrell, Kunsman and Nelson, Rev. Sci. Instr. **1**, 654 (1930).

sealed onto a platinum or tungsten core and mounted as the anode in a vacuum tube. The outer surface of the anode was coated by sputtering with a thin coating of platinum. This platinum coating was earthed or kept at zero potential and a source of potential that could be varied applied to one end of the filament. With a current flowing through the core sufficient to heat the anode to a dull red temperature, an electrolytic potential will drive the potassium or lithium ions either to the core or to the platinum coated surface depending on the direction of the applied potential. The hot anode surface was about 2½ cm². The positive ions were drawn from the surface through the hydrogen to the platinum gauze collector by placing a suitable potential on the latter. This source of ions has the advantage that at a given

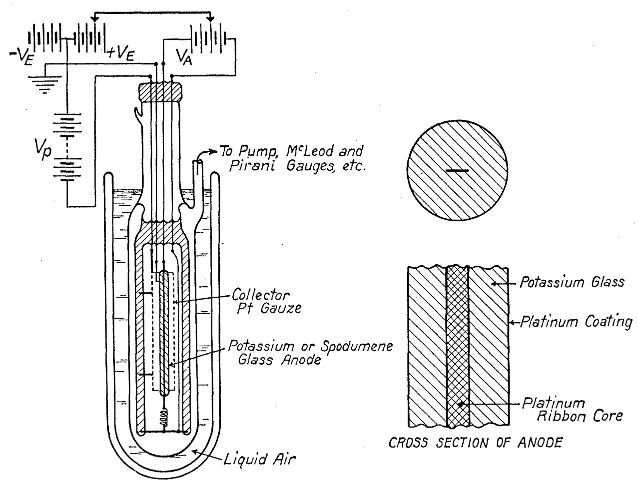

Fig. 1. Apparatus for the study of the disappearance of gases on glass coated filaments.

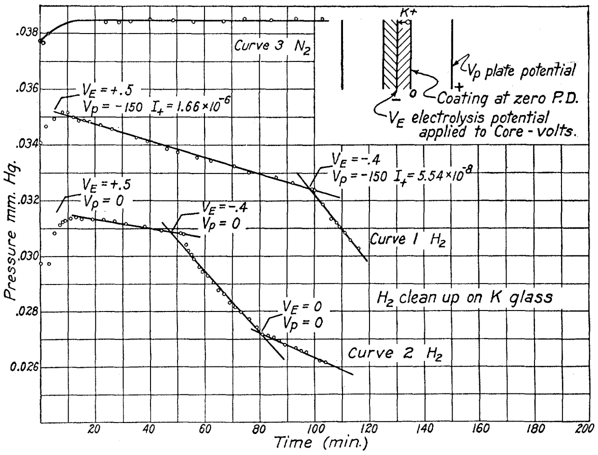

Fig. 2. H_2 clean up and arrangement of potentials with a potassium glass filament.

temperature the positive ion current can be varied through wide limits. The volumes of the bulbs immersed in liquid air varied from about 200 cc to 250 cc. By means of the Pirani gauge 0.07 percent change in pressure could be detected between 0.01 mm and 0.1 mm, the pressure range studied. This was 30 to 100 times as sensitive as the McLeod gauge.

Fig. 2 gives the results for a potassium glass filament, a source of K^+ ions. In the upper right hand corner of the figure the arrangement of potentials to the elements of the tube is shown. As V_E is varied from positive to negative the K^+ ion current is decreased, so that the electrolytic decomposition of the glass and direction of mobility of the K^+ ions can be varied at will. The results of these curves show that for nitrogen (curve 3) there is no decrease in pressure or disappearance of gas whatsoever. Curve 1 for hydrogen shows an increase in the rate of decrease of the hydrogen pressure as the positive ion current is decreased or as K^+ is kept from going to the surface and entering the gas phase at 150 volts speed. In curve 2, $V_p=0$, that is, no ions enter the gas phase and therefore no gas phase reaction takes place, the reaction of hydrogen clean up taking place on or within the hot surface. Curves 1 and 2 are practically identical and there is no indication in this or any similar test that the K^+ ions entering the hydrogen gas contributed a measurable amount to the decrease in the pressure of hydrogen. Our explanation of these results is that K^+ from K_2SiO_3 is electrolyzed through the glass, away from the surface and toward the core, leaving the SiO_3 ion temporarily free. Hydrogen soon replaces potassium giving H_2SiO_3, which decomposes to SiO_2 and H_2O. Thus what actually takes place is the formation of water vapor on the hot surface. Fig. 3 shows similar results for a spodumene filament, a Li^+ source. This curve is typical of a complete run starting with a new filament at room temperature. A period of approximately 25 minutes was required to reach a stable condition of temperature and surface in equilibrium with hydrogen. The factors concerned during this initial period are not too

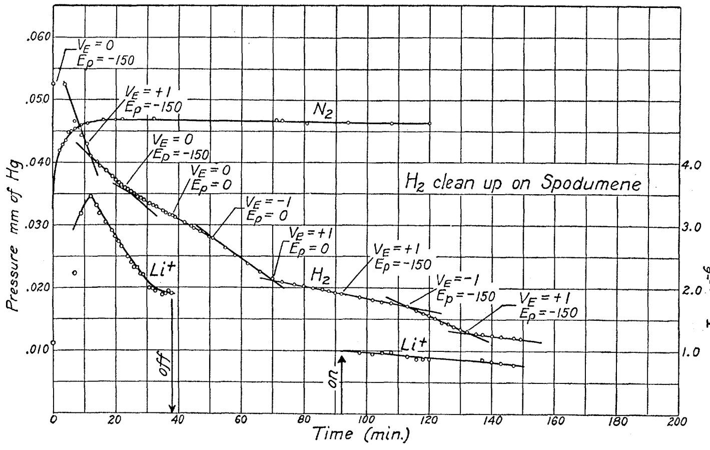

Fig. 3. H_2 clean up, lithium ion currents and potentials with a spodumene glass filament.

well known. After this initial period the clean up of hydrogen is independent of the lithium ions entering the gas phase, and depends on the rate of electrolysis of lithium away from the surface toward the core. A similar reaction resulting in the formation of water vapor accounts for these results. Taylor[4] has advanced this explanation in connection with experiments on the clean up of hydrogen at glass surfaces under the influence of an electric discharge. Some study was made of the condensible products of the reaction. Of the hydrogen cleaned up about one half disappeared completely, the other half behaved like water vapor in that it was condensed at −65° to −75°C at these pressures.[5] The part that disappeared completely could be accounted for by its adsorption as water vapor on the walls of the glass vessel. No effort was made to recover this by a heating of the glass bulb.

In none of our experiments was there an indication of a gas phase reaction between the alkali ions and hydrogen. By varying the electrolysis potential through the hot glass, rates were obtained comparable to those of Leipunsky and Schechter or Mitchell, calculated on the basis of hydrogen disappearing per alkali ion. The proportionality between positive ion currents and clean up observed by Mitchell was probably due to the fact that every alkali ion leaving the surface was replaced by hydrogen. Preliminary results on the iron-aluminum-potassium oxide catalysts indicate a decrease in hydrogen pressure, depending on the extent to which the catalyst oxide mixture was reduced, and on complete reduction there was no further clean up. It therefore appears that a calculation of the hydrogen disappearance on the basis of positive ions entering the gas phase is not tenable, but that a surface reaction, very likely the formation of water, was the controlling factor in these experiments.

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[4] J. Taylor, Proc. Roy. Soc. **A123**, 252 (1929).

[5] N. R. Campbell, Proc. Phys. Soc. London **33**, 287 (1921)