

The Disappearance of Hydrogen in the Presence of Potassium and Lithium Ion Sources

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Citation: [The Journal of Chemical Physics](#) **2**, 752 (1934); doi: 10.1063/1.1749390

View online: <http://dx.doi.org/10.1063/1.1749390>

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there are consequently good grounds, though the evidence is not direct, for supposing that X_O is an oxygen atom. Furthermore, it is possible that the collision which gives rise to branching is that between X_P and O_2 , yielding two oxygen atoms.

The existence of an upper limit can be attributed to two causes (a) removal of the chain carriers by a reaction of higher order than that of branching, e.g., phosphine, (b) a deactivating influence of the reactants on a collision complex which would otherwise give rise to two chains, e.g. hydrogen, (c) other causes not at present included in the theory. It will be a matter for further experiment to decide, by closely examining the relationship between the kinetics of the stable and explosive reactions, which mode of

deactivation causes the upper limit in other chain reactions. Such experiments may reveal whether, as in the case of phosphine, explosion occurs at the upper limit more readily than theory predicts.

The authors are greatly indebted to Dr. E. B. Ludlam and Professor E. K. Rideal for their advice and encouragement during the course of this research. One of them thanks the Royal Commissioners of the Exhibition of 1851 for a Senior Studentship and the other (H. L. R.) is indebted to the Trustees of the Moray Fund of Edinburgh University for a grant for apparatus. They are also grateful to Dr. C. Ouellet for carrying out the experiment with the quantum counter.

NOVEMBER, 1934

JOURNAL OF CHEMICAL PHYSICS

VOLUME 2

The Disappearance of Hydrogen in the Presence of Potassium and Lithium Ion Sources

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(Received August 30, 1934)

The disappearance of hydrogen in the presence of iron-alkali catalysts, sources of K^+ ions and a synthetic spodumene mixture, a source of Li^+ ions, was investigated. In these experiments, like those previously reported by the authors, no gas phase reaction was detected which could be attributed to the bombardment of hydrogen by positive ions with speeds up to 565 volts. It was concluded that all cleanup effects could be accounted for by reactions on or within the materials used as ion sources.

FURTHER results on the cleanup of hydrogen in the presence of materials and mixtures used as ion sources clear up a number of points upon which apparent disagreement in results was reported and conflicting opinions expressed.^{1, 2}

In the previous paper by the authors it was found that with the platinum-coated glass anode source of positive ions,³ an effect was observed, which was found to be due, not to the positive ions but to a surface reaction intimately associ-

ated with the electrolysis of potassium through the glass anode.

The present paper deals with further results from similar tests with an iron alkali catalyst, a source of potassium ions, and with an artificial spodumene, a source of lithium ions.

The apparatus, Fig. 1, was essentially the same as in previous work,² except that in some of the experiments a grid was used to accelerate the ions to their full velocity as soon after leaving the filament as possible. Pressures were measured with a Pirani gauge.

The results from an Fe-K catalyst (No. 920, containing 0.2 percent K_2O) source are shown in Fig. 2. These results were obtained after the catalyst had been reduced at about 650°C for a total time of 24 hours. No definite cleanup due to the positive ions was observed. On the

¹Leipunsky and Schechter, *Zeits. f. Physik* **59**, 857 (1930). A. Schechter, *Zeits. f. Physik* **75**, 671 (1932). A. C. G. Mitchell, *J. Frank. Inst.* **210**, 269 (1930). *Zeits. f. Physik* **78**, 138 (1932).

²C. H. Kunsman and R. A. Nelson, *Phys. Rev.* **40**, 936 (1932).

³F. G. Cottrell, C. H. Kunsman and R. A. Nelson, *Rev. Sci. Inst.* **1**, 654 (1930).

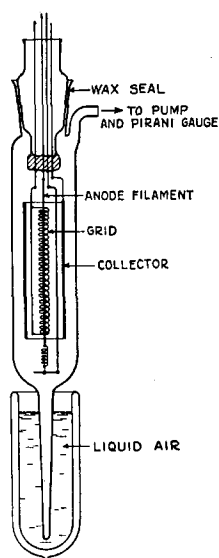


FIG. 1. Experimental tube.

contrary a marked slowing up of the cleanup rate occurred at about the time the potential was turned on. The added cleanup to be expected, at the rate of one molecule per ion, is shown by the broken line. From this it is apparent that the changes in the primary cleanup rate itself would entirely mask any added phenomena of this order of magnitude due to the positive ions. The positive ion current is plotted in the same figure, the average value being about 5×10^{-7} amp.

Typical results from reduced Fe-Al-K catalyst (No. 922 containing 1 percent Al_2O_3 and 0.26 percent K_2O) are given in Figs. 3 and 4. Curve (1), Fig. 3, in effect is a continuous curve up to 83 minutes when a break is observed which is definitely associated with the striking and continuation of a glow discharge. The superimposed straight lines, as in the previous curve, are drawn for the purpose of analysis and discussion only. In the case of the glow discharge, when the current increased from 6×10^{-6} to 9×10^{-5} amp., the cleanup rate increased by an amount corresponding to about 0.3 of a molecule per ion. It was found in separate tests with this tube that at these hydrogen pressures a glow discharge could occur and be maintained at potentials as low as 200 to 250 volts, while in other tubes and under different conditions higher potentials were required. Curve (2) was taken with a tube con-

taining a grid and again there was no evidence of a cleanup due to positive ions; any changes occurring in the slope of the curve were independent of the positive ion currents. Before this test was made the catalyst had been reduced for a period of about 70 hours at temperatures of about 650–700°C.

Fig. 4 gives the results of two tests on catalyst No. 922. The tube contained no grid but a plate potential of 300 volts was used to speed up the K^+ ions in the presence of hydrogen.

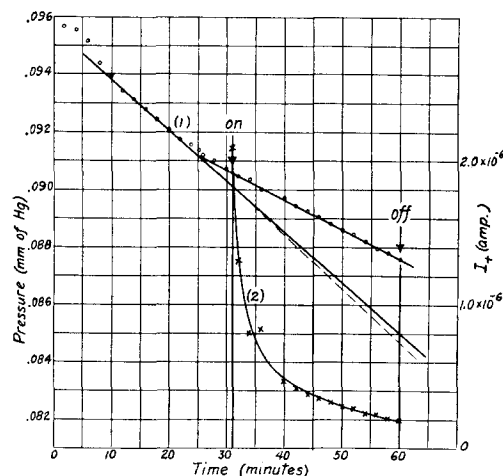


FIG. 2. K^+ ions and hydrogen in tube without grid. Fe-K oxide catalyst No. 920 as ion source. Temperature about 750°C. Curve (1), hydrogen pressure; curve (2), positive ion current with a plate potential $V_p = -310$ volts. Broken line indicates calculated decrease at one molecule per ion.

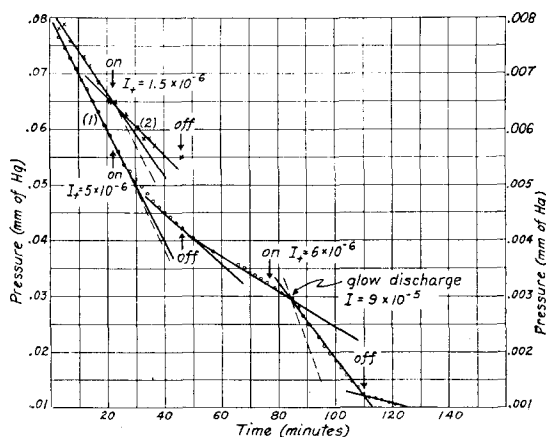


FIG. 3. K^+ ions and hydrogen. Fe-Al-K oxide catalyst No. 922 as ion source. Plate potential $V_p = -310$ volts. Temperature about 750°C. Curve (1), ordinates at left—tube without grid; curve (2), ordinates at right—tube with grid. Broken line indicates calculated decrease at one molecule per ion.

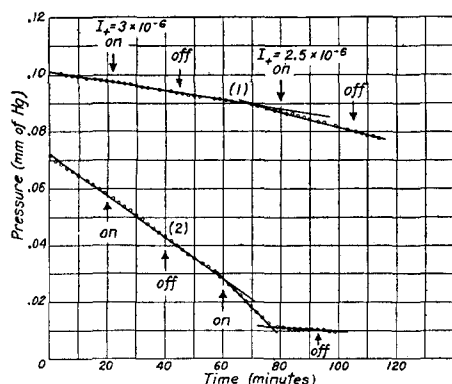


FIG. 4. K^+ ions and hydrogen in tube without grid. Fe-Al-K oxide catalyst No. 922 as ion source. Plate potential $V_p = -300$ volts. Temperature about 750°C .

After curve (1) was obtained a small amount of hydrogen was pumped from the tube, the test continued and curve (2) obtained. No change in rate or breaks in the curve can be associated with the 300 volts potential or speed of the positive ions. In curve (1), at 80 minutes or when the potential was turned on, an increase in rate was observed which started about 10 minutes before this time. Other tests were made using potentials up to 565 volts with results similar to those observed at the lower potentials.

Investigations of the reduction of the catalyst coated filament have shown several things. First, complete reduction is not necessary for good ion emission, in fact the emission seemed to reach a maximum when the catalyst was from 5 to 10 percent reduced. Secondly, in order to make the reduction process as complete as possible it should be carried out in either a flow system, or with an absorption bulb at reduced temperature, that is, under conditions which remove the products of the reduction as rapidly as they are formed. Thirdly, the catalyst material was ineffective as an ion source by the time the material was completely reduced. There is thus considerable weight of evidence in favor of concluding that in the case of the iron catalyst, the residual cleanup observed without ions is due to reduction of the catalyst by hydrogen and not thermal dissociation of the hydrogen as assumed by Leipunsky and Schechter.

The results from a spodumene source of Li^+ ions are given in Fig. 5. The hydrogen cleanup was extremely rapid at the start and no effect

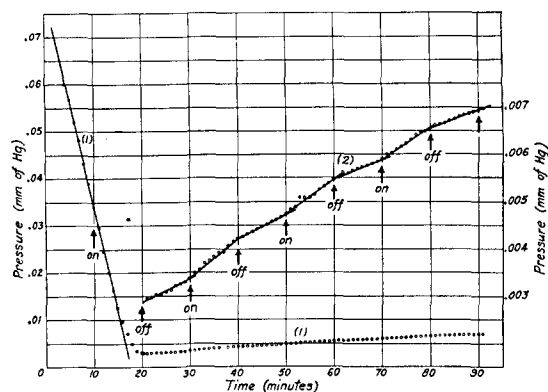


FIG. 5. Li^+ ions and hydrogen in tube with grid. Synthetic spodumene as ion source. Grid potential $V_g = -183$ volts, $V_p = -(183+26)$ volts; temperature about 800 to 850°C . Curve (1), ordinates at left; curve (2), ordinates at right.

could be observed due to the accelerated positive ions. After 20 minutes, there was an increase in pressure, as shown in curve (1). This was of considerable interest and gave further information on the cleanup reaction. Curve (2) shows this part of the curve plotted to a scale of ordinates magnified by a factor of ten. The accelerating potential was turned on and off at the times shown on curve (2). The grid and plate were -183 and -209 volts, respectively, with reference to the filament. The effect of applying the accelerating potential is quite evident. Apparently this curve consists of a cleanup of the hydrogen in the tube, accompanied by a slow gassing which can only be detected after the hydrogen has disappeared. The rate of gassing appears to be markedly increased by the application of an accelerating potential for the positive ions.

This interpretation was confirmed by further tests on gassing alone. Typical results are shown in Fig. 6. For these tests the tube was pumped to a good vacuum (less than 10^{-6} mm Hg), trapped off, and the filament glowed as for a hydrogen run. The pressure change was then observed as the accelerating potential was turned on and off at ten minute intervals. Curve (1) shows the results obtained when a run was made without liquid air on the condensation trap. This curve displayed the same characteristics as Fig. 5, showing an increased rate of gassing when the potential was on. Curve (2) was taken with liquid air on the trap, and is similar to (1), but

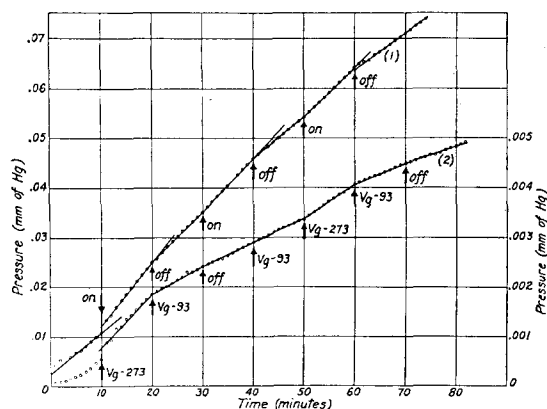


FIG. 6. Li^+ ions in evacuated tube with grid. Synthetic spodumene as ion source. Curve (1), gassing at room temperature (no liquid air on trap); ordinates at left; $V_p = -93$ volts, $V_g = -(93+13)$ volts. Curve (2), gassing with liquid air on trap; ordinates at right; $V_p = V_g - 18$ volts. Temperature 800 to 850°C.

in addition shows a variation in rate which was a function of the potential. As in the case of the catalyst source, tests up to 565 volts gave no additional information on the hydrogen cleanup.

As seen from these two curves there was about 15 times the gas present at room temperature as at liquid air temperature. From a number of similar comparison tests one may conclude that from 5 to 10 percent of the gas given off was noncondensable in liquid air, and was probably nitrogen and oxygen. A rough analysis of the condensable gases was made as follows. After pumping off the noncondensable gases, the liquid air bath was replaced by a mixture of carbon dioxide snow (dry ice) and acetone. After some time the gases evolved from the trap at -78°C were collected with a Toepler pump. The collected gas was then tested for CO_2 by absorption in an alkali solution. This test showed that about 90 percent of this gas was CO_2 .

The remainder of the gas which was still condensed at -78°C was water vapor as shown by its behavior in the McLeod gauge, vapor pressure, and condensation.⁴ The average gaseous products from the spodumene materials used in these experiments were therefore about 5 to 10

percent N_2 and O_2 , 15 to 22 percent CO_2 and 63 to 80 percent water vapor.

The interpretation of these results is similar to that given in the previous paper.² In the case of the catalyst filaments a continuous slow reduction of the catalyst material accounts for the observed cleanup. The spodumene is more complicated since as herein shown it breaks down spontaneously when heated, this decomposition being further hastened by applying a potential which draws out positive ions. The spodumene⁵ was an artificial product made up by fusing a mixture of Li_2CO_3 , $\text{Al}(\text{NO}_3)_3$ and SiO_2 , so that there was probably at least all of the following compounds present; Li_2SiO_3 , Li_2CO_3 and LiNO_3 . These compounds probably break up as follows: $2\text{Li}_2\text{SiO}_3 \rightarrow 4\text{Li} + 2\text{SiO}_2 + \text{O}_2$; $2\text{Li}_2\text{CO}_3 \rightarrow 4\text{Li} + 2\text{CO}_2 + \text{O}_2$; $2\text{LiNO}_3 \rightarrow 2\text{Li} + 2\text{NO}_2 + \text{O}_2$.

Thus if the filament is run in a vacuum, CO_2 , O_2 , N_2 or oxides of nitrogen will be evolved and drawing positive ion current should accelerate the gassing as was found experimentally. When hydrogen is present its cleanup is accounted for by combination with the oxygen evolved.

CONCLUSIONS

The additional information obtained from these tests gave no indications whatever of a gas phase reaction due to the bombardment of hydrogen by positive ions with speeds up to 565 volts. All effects may be accounted for by the reactions on or within the material used as ion sources. These effects are accelerated by electrolysis. The additional cleanup of hydrogen due to K^+ and Li^+ ions in the gas phase if it exists at all is certainly less than 0.1 molecule per ion at speeds of from 250 to 565 volts. The gaseous product from the synthetic spodumene material used as ion sources consisted of about 5 to 10 percent N_2 and O_2 , 15 to 22 percent CO_2 and 63 to 80 percent water vapor.

The writers wish to thank Dr. R. T. Milner of this laboratory for suggestions in collecting the gases and also for their chemical analysis.

⁴ N. R. Campbell, Proc. Phys. Soc. (London) **33**, 287 (1921).

⁵ E. J. Jones, Phys. Rev. **44**, 707 (1933).