

## BEHAVIOUR OF PLATINISED ELECTRODES.

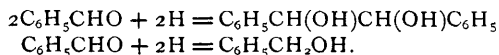
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*(A Paper read before the Faraday Society on Tuesday, May 15, 1906,  
DR. F. MOLLWO PERKIN, TREASURER, in the Chair.)*

As a result of some previous work on electrolytic oxidation, it became desirable to find some electrode on which the reduction of the aromatic aldehydes and similar easily reducible compounds could not be effected. In a Paper read before the members of the Society of Public Analysts it was shown that the reduction of arsenious oxide to arsenuretted hydrogen bears a very close relation to the potential of the cathode (Chapman and Law, *Analyst*, January, 1906), which may be expressed in the following formula :—

$$M_{AsH} = K_{As} \cdot P_H,$$

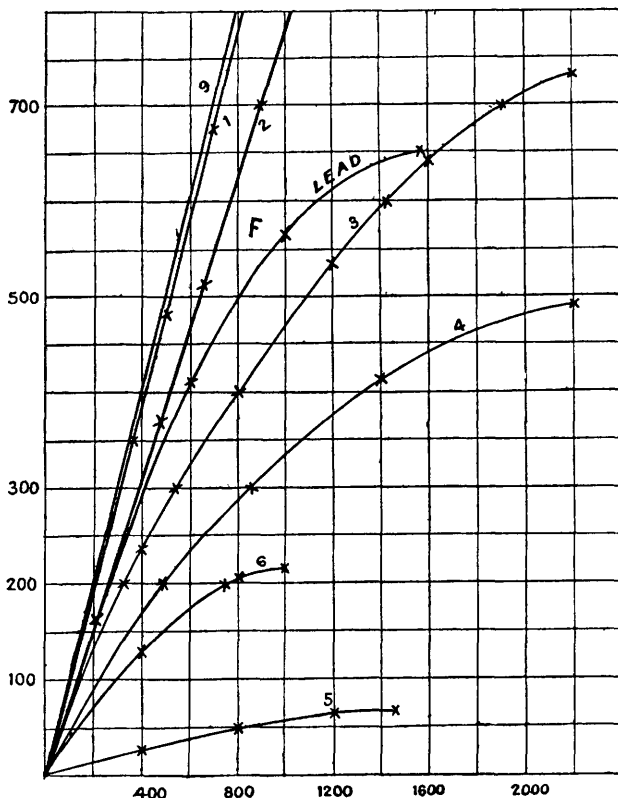
where  $M_{AsH}$  represents the small trace of arsenuretted hydrogen left in solution at the end of the experiment,  $K_{As}$  the amount of unchanged arsenious oxide, and  $P_H$  a factor depending on the potential of the hydrogen. From the above relation it is obvious that as the potential of the cathode is reduced the amount of reaction taking place becomes greatly diminished, for the factor  $M_{AsH}$  may be regarded as constant. The metal from which hydrogen is liberated at the lowest potential is platinised platinum, and as a consequence this substance was used in the reduction of benzaldehyde. The hydrogen absorbed, however, was almost complete, indicating that a very energetic reduction had taken place. This same cathode was used in three more consecutive experiments, but in each case the activity had become considerably less. These results are reproduced in the form of curves, 2, 3, 4, 6, being in the order in which they are mentioned in the text. Finally the same electrode was polarised for twelve hours at the cathode, and a fifth experiment was made, as is represented in curve 5. The activity had now become extremely small. In all this work alcoholic solutions of benzaldehyde were used, and 5 per cent. of sulphuric acid was added as electrolyte. A current of 1 ampere was used on a cathode whose superficial area on one side was 20 square centimetres. In the curves the abscissæ represents the hydrogen liberated in a hydrogen coulombmeter in the circuit, while the ordinates give the hydrogen absorbed during the experiment. Curve 9 represents the total absorption of hydrogen, which was never quite realised. It then became necessary to inquire into the cause of this reaction. Obviously it was not due to the high potential at which the reaction takes place, for when a lead cathode was used with a potential of 0.8 volts higher, considerably less reaction took place, as is seen in curve F; also the product of the reaction was totally different from what was expected. On all electrodes except platinum benzaldehyde gives hydrobenzoin, together with a little benzyl alcohol, according to the following equations :—



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With platinum black the products contained a small quantity of benzyl alcohol, but the bulk was some substance with a low boiling-point, and may be an aliphatic hydrocarbon. At present this reaction is still under consideration, but so far I have identified no further product.

The electrodes were prepared by depositing platinum from solutions of platinic chloride, and in this manner free chloride was always liberated. It seemed probable, therefore, that this substance had a considerable effect on the activity of the cathode. It was therefore determined to try other oxidising agents. The cathode of experiment 5 was then polarised at the anode for twelve hours, and a further experiment made. The reduction then proceeded,



as in curve 1, although this electrode liberated the normal amount of hydrogen in a hydrogen coulombmeter. Further, these electrodes reduce benzyl alcohol, and even toluene, giving the same product of low boiling-point, and, as far as I have been able to determine, this is the first recorded experiment of the electrolytic reduction of these latter compounds. The reaction must be catalytic in its origin, but the function of the oxidising agent is difficult to explain. It may be that this reaction takes place only when the deposited metal is in the state of very fine division. As the reaction proceeds the whole surface may become smoothed over, due to the action of the current, but becomes again roughened when used at the anode.