

**I. A STUDY OF THE HYDROGEN ELECTRODE, OF
THE CALOMEL ELECTRODE, AND OF CONTACT
POTENTIAL; II. THE APPLICATION OF THE
HYDROGEN ELECTRODE TO THE
MEASUREMENT OF THE HYDROCHLORIDE,
AND THE IONIZATION OF ACETIC ACID IN THE
PRESENCE OF NEUTRAL SALTS**

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NATHANIEL EDWARD LOOMIS

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- I. A Study of the Hydrogen Electrode, of the Calomel Electrode, and of Contact Potential.
- II. The Application of the Hydrogen Electrode to the Measurement of the Hydrolysis of Aniline Hydrochloride, and the Ionization of Acetic Acid in the Presence of Neutral Salts.

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A Study of the Hydrogen Electrode, of the Calomel Electrode and of Contact Potential

I. INTRODUCTION.

For several years we organic chemists have felt the need of some direct, very rapid, and accurate method for determining the hydrogen (also hydroxyl) ion concentration of dilute solutions. Such a method would be of special value in the study of many organic reactions involving, for example, the hydrolysis of salts or the saponification of esters, the reactions of addition products in cases of catalysis by hydrogen ions, and many others in which the system is gradually changing.

The methods commonly in use heretofore have presented serious difficulties in their general application. The conductivity method, for example, which has had the widest range

of application, rapidly diminishes in accuracy with increase in dilution of the solution, and furthermore, the measurement of small concentrations of acids in the presence of other electrolytes, especially the salts of these acids with weak bases, is almost impossible. Special methods, such as the use of diazoacetic ester, as suggested by Bredig and Fraenkel,¹ have been used brilliantly in some cases, but are too limited in their range of application. Methods involving titration are of course useless in systems in which a state of equilibrium is established comparatively quickly, for the equilibrium is disturbed as soon as any one of the components is removed.

Although colorimetric methods in the hands of Veley, Salm, Tizard, Szyszkowski and others yield beautiful results in many cases, it has been found that neutral salts affect the colors so greatly in other cases that the method is useless or at least uncertain.

The hydrogen electrode has been recognized by Acree as a possible instrument for the solution of this problem.² Particularly suggestive is the work of H. G. Denham,³ who measured the degree of hydrolysis of several inorganic salts and of aniline hydrochloride. He obtained results agreeing extremely well with those determined by Bredig by the conductivity method. Efforts to duplicate his results and other work on similar lines in this laboratory at first met with serious difficulties, but these are being gradually overcome.

In view of the extreme importance of any favorable results in this field, it seemed worth while to make a careful study of the hydrogen electrode, with special reference to its constancy, the value of its potential in different acids, the ease of reproduction, etc.; in other words, to attempt to make it a standard electrode for use in the same way that calomel and mercurous sulphate electrodes are used. To make the hydrogen electrode an accurate instrument for measuring

¹ Z. Elektrochem., 11, 525 (1905); Z. physik. Chem., 60, 202 (1907).

² Desha: Diss., Johns Hopkins Univ., 1909. This work was begun in 1907-8, and reported at the Christmas meeting of the American Association for the Advancement of Science, in 1908. See Science, 30, 624. Lapworth has also for some time advocated an attempt in this direction.

³ J. Chem. Soc., 98, 41 (1908).

hydrogen ion concentrations, the measurements must be made with a much higher degree of accuracy than has ordinarily been done.

Early in the investigation it was realized that much of the accuracy of the work would be dependent upon the constancy and ease of reproduction of the calomel electrodes which were used with the hydrogen electrode. For this reason the study of the calomel electrode was gone into very thoroughly.

The method of approaching the problem under consideration resolved itself into five lines of investigation:

1. The study of the relative efficiency of the apparatus used by others and of newer forms devised by me to eliminate various sources of error. The literature and our own experience in this laboratory have shown that there is still much to be done in this line. In this connection I cannot refrain from expressing my deep obligation to Professor H. N. Morse for his kindness in giving me many valuable suggestions when I needed the benefit of the rare knowledge and mechanical skill that have enabled him to overcome such great difficulties in his own researches.

2. The study of the calomel electrodes. A large number of calomel electrodes were prepared and measured against each other so that the value adopted for the potential of the calomel electrode was the average of a number and not dependent upon a single electrode.

3. The preparation of a large number of platinum electrodes which were intercompared by the method used for the calomel electrodes.

4. The direct comparison of the hydrogen electrode with the calomel electrode, involving experiments to determine the efficiency of various solutions in eliminating contact potential.

5. The application of the hydrogen electrode to the determination of the hydrogen ion concentration of various solutions. The hydrolysis of aniline hydrochloride and the effect of neutral salts upon the dissociation of acetic acid were especially studied (see the next part of this dissertation).