A STUDY OF THE ETHYLENE ELECTRODE¹

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The constancy and reproducibility of the hydrogen electrode and calomel battery having been shown to be sufficiently accurate, it has seemed advisable to extend its application to other series of measurements even though it has been necessary to study these cases somewhat qualitatively. These studies have been termed qualitative for the reason that many improvements in methods and apparatus will be necessary before accurate results can be obtained. The hydrolysis of aniline hydrochloride, as carried out by Denham,² by Desha,³ and by Loomis,⁴ gave values quite satisfactory as compared with the calculated values. In a case of this kind we have a solution of varying composition and increasing complexity. The hydrogen electrode has proved to be very accurate, direct, and rapid in such cases.

Let us examine the hydrolysis of an amide in the presence of hydrochloric acid:

After a moment's consideration it is seen that there is no method (*e. g.*, conductivity method) of determining the concentrations of all the constituents of such a system for the reason that too many unknown factors are present. The application to this case of the hydrogen electrode, which furnishes a measure of the hydrogen (hydroxide) ion concentrations would be of great help; the method is best seen in simple organic substances like aniline hydrochloride. This substance is selected for the reason that considerable data

¹ Contribution from Chemical Laboratory of Johns Hopkins University.

² Jour. Chem. Soc., **93**, 41 (1908).

³ Diss. Johns Hopkins Univ., 1909.

⁴ *Ibid.*, 1911.

obtained by other methods are at hand and agree sufficiently well when the formula

$$\frac{K_w}{K_b} \left[\frac{[C_H^+]^2 \times \text{volume}}{1 - \frac{\text{Percent hydrolysis}}{100}} \right] \times \text{ionization}$$

is used for calculating this relationship. The reader's attention is called to the work of Loomis, Denham, Desha and Bredig in this connection.

Other cases of applicability are: the hydrolysis of cane sugar,

ester and amide catalysis,

breaking down of diazoacetic ester into glycolic acid ester and nitrogen,

the change of diacetone alcohol into acetone,

and especially cases in which the compounds are weakly dissociated. In cases of this last type the conductivity method presents extreme difficulties.

Ethylene Electrode

The most important investigation carried out under this topic of qualitative experiment consisted in the use of a new electrode which we have termed the ethylene electrode. This consists in the use of ethylene gas on one side and chlorine, hydrogen, oxygen, etc., gas on the other side of the system. Ethylene gas was prepared by the method of Gladstone and Tribe, in which ethylene bromide and copper-zinc couple were used. The copper-zinc couple was prepared by pouring a solution of copper sulphate over granulated zinc several times until a good coating of copper was obtained. Alcohol and ethylene bromide in the proportions 12 : 1 were

used and to this mixture water was added to slight turbidity. The mixture was placed in a small balloon flask with a tight stopper and then the copper-zinc couple was added. The gas soon began to be evolved and it was passed through another flask completely surrounded by a freezing mixture in order to condense any ethylene bromide that might be carried along mechanically. The gas is then conducted through a solution of sodium hydroxide, potassium dichromate and water into a third cylinder containing dilute sulphuric acid. From this cylinder the gas is received in a gasometer by the displacement of water. Several liters of the gas were collected in this way and reserved for use in the electrode work. As far as it has been possible to gain any information from the literature nothing has been attempted with an electrode of this kind.

The apparatus necessary for experiments of this kind consists of two platinum electrodes of the same type as described in connection with the hydrogen electrode. In order to make a complete system it is necessary to use some known element whose electromotive force has carefully been worked out. In connection with this phase of the work, the chlorine element has been chosen and reference to the very important work of Lewis and his co-workers is made at this time. The electrolyte chosen for the system was 0.1 *N* hydrochloric acid, which was carefully standardized in this laboratory. This acid was first prepared by the method of Hulett, and then pycnometric measurements were made on the stock solution and these were supplemented by a great many quantitative determinations. A more complete description of this phase of the work will appear in a monograph on this subject. The container used for this study was essentially a U tube with a stopcock between the two halves of the apparatus. A diagram of this apparatus will likewise appear in the above-mentioned monograph.

Method of Experimentation

Emphasis is again laid upon clean apparatus and good chemicals even though the work is only qualitative in this particular case. About three hundred cubic centimeters of tenth

normal hydrochloric acid was placed in the U tube. The stopcock between the two halves was closed and the apparatus was ready for the insertion of the electrodes. A three-hole gum stopper was used for each half of the apparatus. One hole was used for holding the electrode in place, the second for the inlet of gas, and the third for the exit of gas. The inlet tube extended below the level of the lower edge of the electrode and thus allowed the gas to bubble against the surfaces of the electrode. The exit tube was drawn to a capillary so that outside air was excluded. The entire apparatus was placed in a constant temperature bath and the gases allowed to flow into each side of the apparatus for fifteen or twenty minutes until saturation was nearly complete. The gas in each case was run through a wash solution of tenth normal hydrochloric acid. The wires leading to the potentiometer were adjusted and the system was in condition to make the ordinary electromotive force measurements. The following tables show the results of three different samples of ethylene:

TABLE I
C₂H₄-Pt-0.1 N HCl — 0.1 N HCl-Pt-Cl₂

Time	E. M. F.	Time	E. M. F.
12.15	0.850925	3.05 ¹	0.741360
12.25	0.856430	3.10	0.723500
12.28	0.857228	3.20	0.714000
12.40	0.874720	3.30	0.708250
12.45	0.873475	3.40	0.704350
12.55	0.864720	3.45	0.696300
1.00	0.864750	3.55	0.693400
2.00	0.821220	4.00	0.691300
2.30	0.816920	4.05	0.688950 ²
2.35	0.817140	4.10	0.487500 ³
2.40	0.817650	4.20	0.874000
2.45	0.819940	4.30	0.747320 ⁴
2.50	0.824170	4.35	0.647300
2.55	0.823810	4.45	0.420000 ⁵
3.00	0.822880	5.00	0.448100

¹ At this stage of the experiment oxygen and ethylene in equal volumes were allowed to flow in against the electrode.

² Ethylene stopped for five minutes.

³ Oxygen stopped for ten minutes.

⁴ Oxygen in equal proportions started.

⁵ Oxygen in large excess.

TABLE II
 $\text{C}_2\text{H}_4\text{-Pt-0.1 N HCl} - \text{0.1 N HCl-Pt-Cl}_2$

Time	E. M. F.	Time	E. M. F.
2.35	0.901200	4.00	0.081000
2.40	0.902610	4.05	0.109200
2.45	0.914500	4.15	0.200000
2.47	0.917300	4.20	0.377000 ²
2.50	0.931400	4.25	0.457000
2.55	0.927500	4.30	0.459200
3.20	0.927600	4.40	0.571000
3.25	0.929500	4.45	0.749500
3.30	0.936000	4.50	0.929000
3.35	0.945600	4.55	0.931500
3.40	0.928000	5.00	0.928500
3.50	0.053700 ¹	5.05	0.927500
3.55	0.044200		

TABLE III
 $\text{C}_2\text{H}_4\text{-Pt-0.1 N HCl} - \text{0.1 N HCl-Pt-Cl}_2$

Time	E. M. F.	Time	E. M. F.
10.35	0.887000	12.01	0.967450
10.55	0.923250	12.10	0.964600
11.00	0.951050	12.20	0.962700
11.10	0.961200	12.40	0.963600
11.30	0.943900	1.00	0.962500
11.55	0.964200	1.02	0.961500

The choice of chlorine as a part of this system was brought about by the fact that ethylene and chlorine combine readily and form ethylene chloride. It will be noticed that the initial electromotive force in all three experiments is approximately nine-tenths of a volt. The system remained fairly constant under uniform conditions. In order to find out if this observed E. M. F. was due to the presence of oxygen or hydrogen in the C_2H_4 , oxygen was allowed to flow into the system in a volume equal to that of the ethylene and we noticed a dropping off of the potential, as we should expect. This

¹ The ethylene gas was entirely shut off and only oxygen allowed to flow in.

² Oxygen stopped entirely and only ethylene entering.

case is observed in Table I, Note 1. The same table shows the rise and fall of the potential as the amounts of oxygen and ethylene are varied (Notes 2, 3, 4, 5).

The same fact is more distinctly noted in the case of Table II, Note 1, where the E. M. F. becomes very small. It is noticed in this table that the E. M. F. increased as soon as the flow of oxygen was stopped and "pure" ethylene was allowed to bubble in, and that the system returned quite rapidly to its normal value. Table III shows an experiment in which ethylene is used against chlorine, and the E. M. F. remaining fairly constant at approximately 0.9625 volt. These experiments show apparently that ethylene gas when used in a gas electrode sets up an electromotive force of considerable amount and probably proceeds in a manner described below. As analysis of the ethylene showed that it is not absolutely pure, the next phase of our work will be to prepare the pure gas free from hydrogen, oxygen, ethane, etc., in order to prove beyond any question that pure ethylene gives the electrode described above.

The object of these studies is to learn whether ethylene combines with chlorine, bromine, hydrogen, etc., through an electronic transfer which can be used to develop an E. M. F.; as the preliminary study is certainly in harmony with this idea we may interpret the reaction as follows for the present:

Summary

The work which has already been carried out on the study of the ethylene electrode indicates that it is an entirely new system; that it is a system possessing a very high electromotive force; that it is easily reproducible and constant as illustrated by the three separate tables submitted. Furthermore, it is apparent that chemically pure ethylene is difficult to prepare. Finally, the theory of its action as a gas electrode involves the idea that the ethylene loses two electrons to the electrode and then combines with the chloride ions.

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