substance proves that *none* of this substance is present, and that any other correspondences between the two are mere chance.

The second sample is shown in Fig. 9, in comparison with sodium chloride and potassium fluoride, and it is evident that it consists of a mixture of these two salts (50.2% sodium chloride, 49.8% potassium fluoride) and *nothing else.*

These examples are very simple ones. It is possible to go much further. By narrowing the slits and using a smaller tube of test material very sharp, narrow lines can be obtained, and a mixture of several substances analyzed without ambiguity. Furthermore, by long exposures, so as to greatly overexpose the principal components of a mixture, substances present only in very small amounts can be made to show.

SCHENECTADY, N. Y.

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIV. OF CALIFORNIA.]

# THE APPLICABILITY OF THE PRECIPITATED SILVER-SILVER CHLORIDE ELECTRODE TO THE MEASUREMENT OF THE ACTIVITY OF HYDROCHLORIC ACID IN EXTREMELY DILUTE SOLUTIONS.

BY G. A. LINHART.

Received May 21, 1919.

A study of the hydrogen and silver-silver chloride electrodes in aqueous hydrochloric acid has received much attention in recent years and the subject has been reviewed in several articles of recent date.[1]

In all previous investigations, however, measurements in solutions as dilute as 0.01 *M* have been subject to slight uncertainty, and at higher dilutions they have proved unreliable. By using a cell of new design capable of holding a large amount of the electrolyte, by taking extraordinary care in the preparation of the materials, and by replacing the customary electrode of silver, covered with chloride through electrolysis, by a mass of finely divided silver in intimate contact with silver chloride, precipitated metathetically, it has proved possible to obtain results of high precision nearly to a concentration of 0.0001 *M*, as described below.

## The Preparation of Materials.

The *silver* was deposited by a current of 5 to 7 amperes in a cell consisting of an anode of silver and a cathode of fine platinum wire, dipping into a solution of silver nitrate. Under the influence of this large current the silver gathered about the platinum wire in loose, spongy clots, easily loosened by a light tapping of the wire. The silver so obtained was then washed (the water used throughout this investigation was prepared by

---

[1] Lewis, Brighton and Sebastian, THIS JOURNAL, 39, 2245 (1917); Noyes and Ellis, *Ibid.*, 39, 2539 (1917).

redistilling distilled water with alkaline permanganate) and kept under pure water until needed. The *silver chloride* was prepared from purified silver nitrate and hydrochloric acid and preserved in the dark under pure water, remaining white indefinitely.

## Description of the Apparatus.

In the cell represented by Fig. 1,[1] the hydrogen gas passes through the bubbler in the direction indicated by the arrows, enters the cell *via* the pin holes above the silver chloride, rises through the solution up to the iridized plate, and then passes out through the trap. The silver-silver chloride electrode is shown at the bottom of the apparatus and is connected to a lead wire by a sealed-in platinum wire and the column of mercury shown shaded in the diagram. The hydrogen electrode is connected with its terminal wire in similar manner.

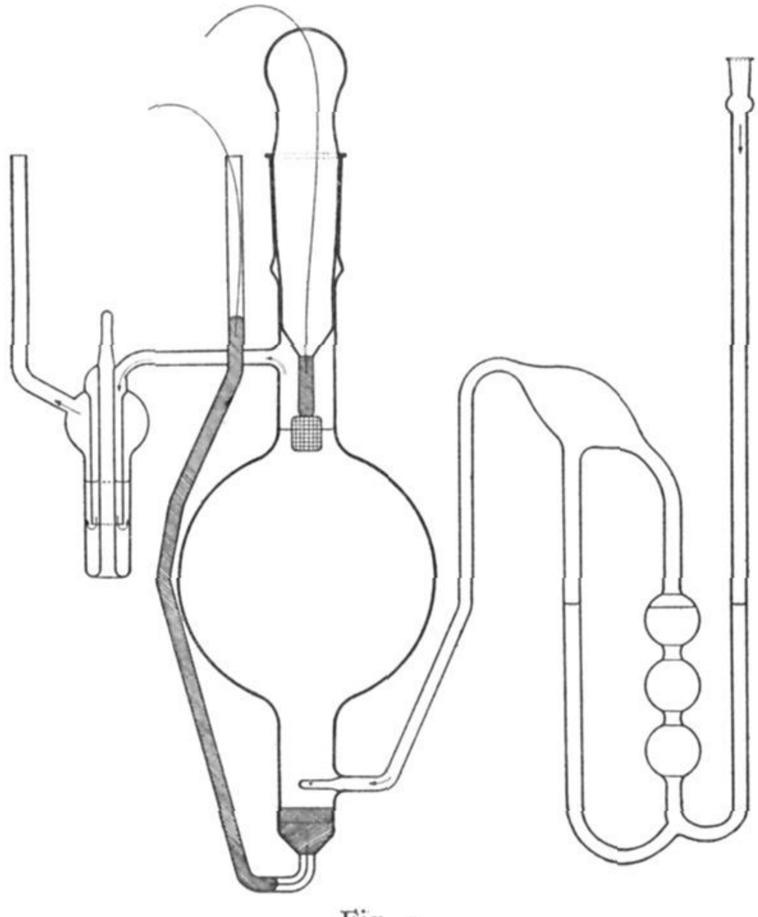

Fig. 1.

In order that the hydrogen shall not come in contact with grease, the seat of the glass stopper is so made that the upper portion of the finely ground surface may be covered with a film of stopcock grease without contaminating the lower portion of the ground surface. The connection between the hydrogen generator and the cell is made by a ground glass joint instead of the customary glass seal. This modification has been found more convenient and quite as efficient. The whole apparatus was affixed to a frame of asbestos board in order to eliminate the danger of breakage by handling of the glass parts.

The iridized electrode, the hydrogen generator, the electrical apparatus, and the thermostat were of the types described and figured in a recent article by Lewis, Brighton, and Sebastian.[2]

---

[1] This instrument was constructed by Mr. W. J. Cummings of this laboratory. For the drawing I am indebted to Mr. Thomas Fraser Young.

[2] *Loc. cit.*

## Experimental Procedure.

Requisite amounts of silver and silver chloride were separately washed many times by decantation with the same hydrochloric acid solution to be used in the cell for any particular experiment. The silver was then placed in the bottom of the cell to the depth indicated in the figure and covered with a layer of silver chloride. The whole cell was now filled with the hydrochloric acid to the levels indicated in the figure. The bulb of the cell measured about 1200 cc.

The whole apparatus was then connected, immersed in an oil thermostat, kept at 25° ± 0.01°, and allowed to come to equilibrium. This usually took from 3 to 4 days, depending upon the concentration of the acid, before the e. m. f. became reasonably constant. In Table I are given all the recorded readings and in Table II only those after the e. m. f. had become constant. The table headings are self-explanatory. All concentrations are expressed in mols per 1000 grams of water.

TABLE I.—RECORDED READINGS.

(*a*).

$\Sigma(\text{HCl}) = 0.04826$.

| E. m. f. | Time in hours. |
|---|---|
| 0.3799 | 12 |
| 0.3823 | 16 |
| 0.3842 | 21 |
| 0.3853 | 26 |
| 0.3864 | 36 |
| 0.3866 | 40 |
| 0.3868 | 46 |
| 0.3869 | 50 |
| 0.3870 | 61 |
| 0.3870 | 64 |
| 0.3870 | 68 |

(*c*).

$\Sigma(\text{HCl}) = 0.004826$.

| E. m. f. | Time in hours. |
|---|---|
| 0.4910 | 12 |
| 0.4954 | 16 |
| 0.4965 | 18 |
| 0.4978 | 21 |
| 0.4988 | 26 |
| 0.4996 | 35 |
| 0.4997 | 39 |
| 0.4998 | 43 |
| 0.4998 | 48 |
| 0.4998 | 61 |
| .. | ... |

(*b*).

$\Sigma(\text{HCl}) = 0.00965$.

| E. m. f. | Time in hours. |
|---|---|
| 0.4622 | 24 |
| 0.4625 | 25 |
| 0.4634 | 29 |
| 0.4642 | 33 |
| 0.4650 | 44 |
| 0.4651 | 48 |
| 0.4653 | 53 |
| 0.4653 | 58 |
| 0.4654 | 68 |
| 0.4654 | 72 |
| 0.4654 | 78 |
| .. | ... |
| .. | ... |
| .. | ... |
| .. | ... |
| .. | ... |

(*d*).

$\Sigma(\text{HCl}) = 0.001000$.

| E. m. f. | Time in hours |
|---|---|
| 0.5698 | 19 |
| 0.5716 | 22 |
| 0.5769 | 43 |
| 0.5775 | 51 |
| 0.5778 | 56 |
| 0.5781 | 66 |
| 0.5783 | 74 |
| 0.5784 | 79 |
| 0.5785 | 91 |
| 0.5786 | 103 |
| 0.5786 | 114 |
| 0.5786 | 127 |
| 0.5786 | 139 |
| 0.5787 | 149 |
| 0.5787 | 192 |
| 0.5787 | 200 |

(*e*).

$\Sigma(HCl)$ = 0.000483.

| E. m. f. | Time in hours. |
|---|---|
| 0.6106 | 12 |
| 0.6121 | 24 |
| 0.6139 | 38 |
| 0.6144 | 48 |
| 0.6149 | 60 |
| 0.6152 | 70 |
| 0.6157 | 80 |
| 0.6157 | 92 |
| 0.6157 | 104 |
| .. | ... |
| .. | ... |
| .. | ... |
| .. | ... |
| .. | ... |
| .. | ... |
| .. | ... |
| .. | ... |
| .. | ... |
| .. | ... |

(*f*).

$\Sigma(HCl)$ = 0.000242.

| E. m. f. | Time in hours. |
|---|---|
| 0.6556 | 19 |
| 0.6565 | 21 |
| 0.6563 | 28 |
| 0.6549 | 35 |
| 0.6534 | 43 |
| 0.6529 | 46 |
| 0.6519 | 52 |
| 0.6514 | 58 |
| 0.6512 | 68 |
| 0.6511 | 72 |
| 0.6511 | 77 |
| 0.6510 | 84 |
| 0.6509 | 92 |
| 0.6509 | 96 |
| 0.6509 | 101 |
| 0.6509 | 108 |
| 0.6509 | 116 |
| 0.6508 | 120 |
| 0.6509 | 124 |

(*g*).

$\Sigma(HCl)$ = 0.000136.

| E. m. f. | Time in hours. |
|---|---|
| 0.6899 | 20 |
| 0.6894 | 24 |
| 0.6889 | 28 |
| 0.6872 | 36 |
| 0.6860 | 45 |
| 0.6849 | 48 |
| 0.6833 | 59 |
| 0.6817 | 69 |
| 0.6814 | 76 |
| 0.6809 | 84 |
| 0.6803 | 96 |
| 0.6799 | 106 |
| 0.6797 | 116 |
| 0.6798 | 126 |

### TABLE II.

Readings after Electromotive Force had Become Constant.

| Expt. No. | $\Sigma(HCl)$. | E. m. f. | E. m. f. calc. to one atmos. $H_2$. | *E'*. | $\frac{\sqrt{(H^+)(Cl^-)}}{\Sigma(HCl)}$. | $\frac{(H^+)(Cl^-)}{(HCl)}$. |
|---|---|---|---|---|---|---|
| 1...... | 0.04826 | 0.3870 | 0.3874 | 0.2317 | 0.8513 | 0.2342 |
| 2...... | 0.00965 | 0.4654 | 0.4658 | 0.2274 | 0.9256 | 0.1111 |
| 3...... | 0.004826 | 0.4998 | 0.5002 | 0.2262 | 0.9475 | 0.0825 |
| 4...... | 0.001000 | 0.5787 | 0.5791 | 0.2242 | 0.9845 | 0.0626 |
| 5...... | 0.000483 | 0.6157 | 0.6161 | 0.2238 | 0.9920 | 0.0594 |
| 6...... | 0.000242 | 0.6509 | 0.6514 | 0.2236 | 0.9960 | 0.0600 |
| 7...... | 0.000136 | (0.6798) | (0.6805) | (0.2231) | ... | ... |

At extreme dilution, $E' = 0.2234 = E°$.

## Discussion of Results and Conclusion.

Concerning the solubility of silver chloride at 25° only 3 values are to be found in the literature,[1] all based on conductivity measurements, namely: $1.60(10)^{-5}$, $1.64(10)^{-5}$, $1.41(10)^{-5}$; average $1.55(10)^{-5}$, and the product $2.4(10)^{-10}$. Dividing this value by the concentration of Expt. 6 gives 0.0000010, or 0.4%, corresponding to 0.1 mv.; divided by the concentration of Expt. 7 gives 0.0000018, or 1.3%, corresponding to 0.3 mv. In the other experiments the correction becomes entirely negligible. In the third column of the above table the last two numbers have been so corrected for the solubility of silver chloride. The fourth column gives $E'$, the e. m. f. calculated to molal concentrations of the hydrogen ions and chloride ions on the assumption of 100% dissociation at each concentration. The extrapolation of this number to infinite dilution gives $E°$, the standard e. m. f. at hypothetical molal concentration of the ions. With this value the thermodynamic or "corrected" degree of dissociation at each concentration is obtained by familiar methods and given in the 5th column of the table above.

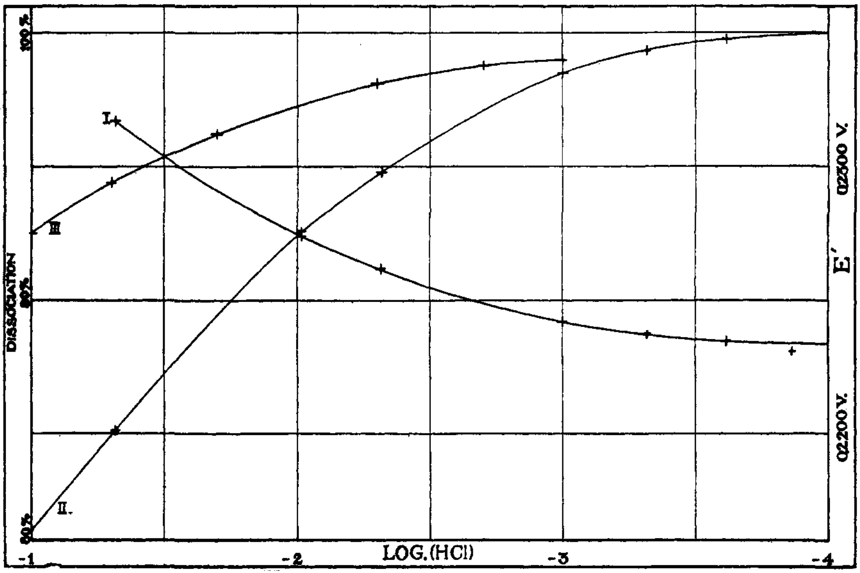

Fig. 2.

In Fig. 2, Curve I gives the values of $E'$. Judging from the trend of the curve the last value (Expt. 7) is probably 0.3 mv. too low, owing to the uncertainty of the concentration of the (HCl) to the extent of several tenths of a per cent., and also to the questionable solubility product of the silver chloride. Curve II gives the calculated degrees of dissocia-

---

[1] Thiel, *Z. anorg. Chem.*, **24**, 57 (1900).

tion, and, for comparison, Curve III gives the degrees of dissociation as measured by conductivity methods.[1]

NOTE.—In a private communication Professor Loomis informs me that a statement in regard to his work in one of my articles (THIS JOURNAL, 39, 2604 (1917)) is rather ambiguous: "The remark might be interpreted to intimate that I have claimed equal thermodynamic degrees of dissociation for KCl and HCl solutions at all concentrations. As a matter of fact my articles have dealt only with decinormal concentrations, and in my latest article I have suggested a possibility that my results may be accounted for by a slightly lower degree of dissociation for 0.1 *N* KCl than for 0.1 *N* HCl."

BERKELEY, CAL.

---

[CONTRIBUTION FROM CHEMICAL LABORATORY, EDGEWOOD ARSENAL.]

# A MODIFIED METHOD FOR THE ANALYSIS OF MIXTURES OF ETHYLENE AND ACETYLENE.[2]

BY WILLIAM H. ROSS AND HARLAN L. TRUMBULL.

Received May 23, 1919.

In the course of an investigation on the preparation of ethylene from acetylene, mixtures of these two gases were recovered in association with variable quantities of other gases as ethane and hydrogen. It thus became necessary in carrying on the work to make accurate analyses of gas samples containing ethylene in the presence of acetylene and other hydrocarbons in order to determine the effect on the production of ethylene of any special change in the conditions of the experiment.

In the preliminary work use was made of the Tucker and Moody[3] method for determining ethylene in the presence of acetylene. This method involves the use of an ammoniacal silver nitrate solution which is claimed to remove the acetylene completely but only a relatively small amount of ethylene. It was found, however, that the quantity of ethylene absorbed varied with the time that the mixture was shaken with the silver nitrate solution, and that the results obtained varied continuously with the time taken in making an analysis. This was demonstrated by shaking samples of 80% ethylene, known to be free from acetylene, with the silver nitrate solution for 5-minute periods, and reading the residual volume of gas after each period. The results are given in Table I.

In a number of tests made with known mixtures of ethylene and acetylene, note was made of the relative proportion of each absorbed when the mixture of gas was shaken with the silver nitrate solution for different lengths of time. It was thought that tolerably good results might possibly be obtained in the analysis of unknown mixtures if the gas were shaken in the silver nitrate pipet for the same length of time as that which gave best results with the known mixtures. This might possibly prove true

---

[1] Noyes and Falk, THIS JOURNAL, 34, 475 (1912).

[2] Published by permission of the Director of the Chemical Warfare Service.

[3] THIS JOURNAL, 23, 671 (1901); Dennis', *Gas Analysis*, p. 248.