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The Determination of Hydrogen Ion Concentration by the Electrometric Method

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"THE DETERMINATION OF HYDROGEN ION CONCENTRATION

by the

ELECTROMETRIC METHOD"

Submitted In Partial Fulfillment

of the

Requirements for Department Honors.

BY

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"THE DETERMINATION OF HYDROGEN ION CONCENTRATION

by the

ELECTROMETRIC METHOD"

The principle underlying all determination of ion concentration is that of electrolytic dissociation. This theory states that acids, bases and salts in solution dissociate into the radicals which form them, and each radical assumes a definite charge: hydrogen and the metals being positively charged and the hydroxide radical and acid groups negatively charged. It has been demonstrated by various means that these substances, acids, bases and salts, do dissociate in solution. One of the chief methods of proof is the ability of such solutions to conduct an electric current. The class of compounds which do not dissociate in solution of water do not affect the passage of a current through water. On the other hand, the dissociating compounds show a marked conductivity when in solution. With increased dilution of the electrolyte the conductivity is decreased to a lesser extent than the lowering of concentration which is consequent to the dilution. These compounds carrying charges and conducting a current are thus called electrolytes.

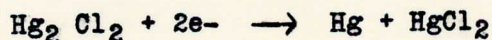
Electrometric titration is a measurement of the concentration of the ions present in a solution. Titration is a neutralization process--adding an acid to a base or vice-versa until the stoichiometrical amount of the one, which will exactly react with the other, has been added.

Since flow of a current depends upon the establishment of a difference of potential between two connected points, the measurement of the ion concentration of the solution depends upon this fact. "A metal in contact with a solution of its ions, as well as an 'unattackable' metal like platinum in contact with a solution of metal ions capable of either giving up

electrons to--or taking up electrons from, the platinum, develops a potential which is a function of the concentration of the ions in solution, other conditions remaining constant.

Since, at the end point in every titration, there is a marked change of concentration of one of the reacting substances, the potential, which depends upon the concentration of the ions present, either increases or decreases suddenly." ¹

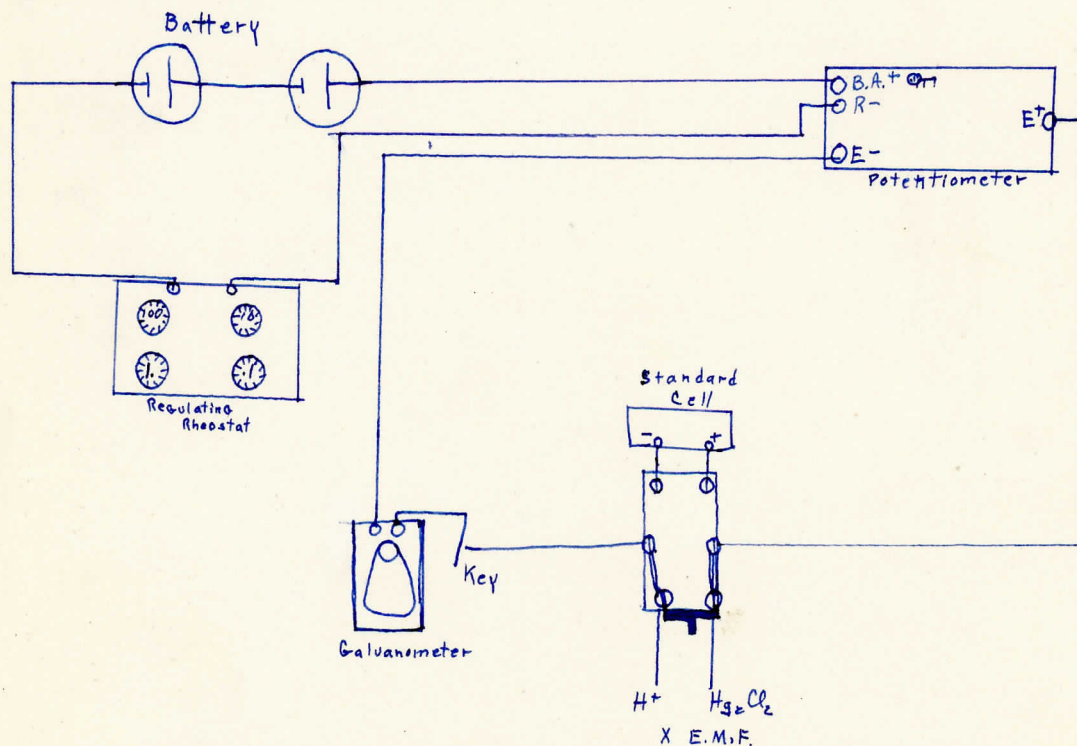
However, the strength of the current which passes through the solution cannot be measured directly, but must be calculated in reference to some known standard. The most ordinary method for this type of work is to use a Weston, Eppley, or other standard cell as the known potential and compare with it the potential difference measured across the solution of unknown strength. For this purpose two reference electrodes must be used. Those used in these experiments were a normal calomel electrode, or half cell, and a hydrogen electrode. The procedure is as follows: molecular hydrogen (H₂) is passed into the electrode vessel, passing over the Pt electrode. When the electrode is functioning, the platinum black activates the molecular H₂ passing over it and changes the gas from the molecular state H₂⁰ to the ionic condition 2H⁺. In so doing the hydrogen loses an electron from each atom. At the same time there is a reaction occurring in the calomel electrode where there is a difference of solution pressure between Hg, Hg₂ Cl₂ in 1N.KCl, and as the electrons are set free at the Hydrogen electrode they travel to the calomel electrode where they are taken up by the mercurous chloride which reacts as follows:



1. Popoff, S. "Quantitative Analysis". 2nd Ed. p. 437.

The hydrogen electrode is directly in contact with the solution whose potential is to be measured, and the calomel half-cell is in contact by means of a column of 1N.KCl solution in a tube with a capillary end, immersed in the solution of unknown strength.

In these titrations the unknown potential was compared with a standard cadmium sulphate-mercury cell of the Eppley laboratories, having an E. M. F. of 1.0893.



A. Electrometric Titration Apparatus.

As in the diagram A, the standard and unknown cell were brought in the circuit by means of a double throw switch. The potentiometer was set to correspond to the voltage of the standard cell, 1.0893, then the

resistance was adjusted so that there was no deflection of the galvanometer when the circuit was closed. To determine the E. M. F. of the solution to be titrated the switch was reversed to bring the solution into circuit, and the potentiometer dials set so that the galvanometer registered zero when contact was made with the tapping key. Then by combining the readings of the two dials of the potentiometer, the E. M. F. may be read off directly for the following reason: when the resistance was so adjusted to the standard cell that no current deflected the galvanometer, the total resistance including that of the protective rheostat and the resistance box was 1089 ohms, since the E. M. F. of the standard cell was also 1.089 volts, each ohm corresponds to an E. M. F. of 1 millivolt. Consequently, not changing the resistance box setting, and adjusting only the potentiometer resistance, the variable E. M. F. may be directly read.

The apparatus used in the experiments was thoroughly cleaned in chromic acid solution, and washed and then rinsed with distilled water.

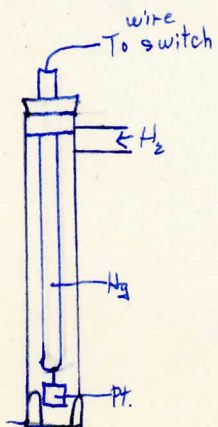
The mercury used in the calomel electrode was prepared by purifying it as follows. The mercury was slowly passed through a solution of dilute nitric acid, emerging from a pin-hole in a filter cone in the form of a fine spray. This metal slowly settled through the acid and collected in the bottom of the tube where it passed over an attached S shaped siphon into distilled water. The purified mercury was thus freed from traces of other metals. After being washed with distilled water to remove acid, the Hg. was washed with KCl solution of the strength to be used in the calomel electrode.

The calomel paste was prepared by adding HCl conc. to a concentrated

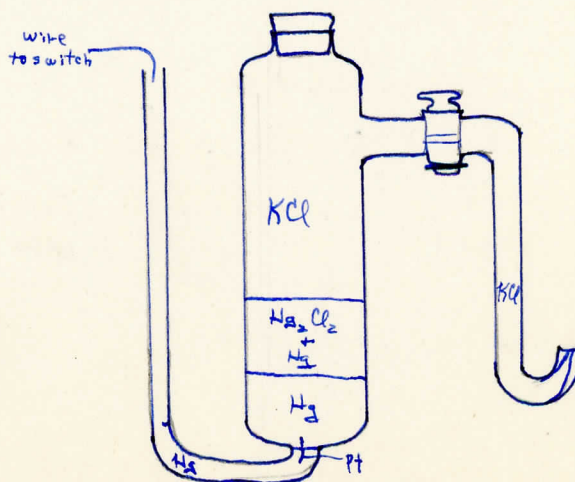
solution of mercurous nitrate. The mercurous chloride slowly settled out in fine needle-like crystals, however in the presence of excess of acid, when the beaker of solution was put under the automatic stirrer to break up lumps, the mercurous chloride was slowly converted to mercuric chloride and slowly dissolved. This was reconverted to mercurous chloride by adding about twenty grams of metallic mercury and heating on the steam bath with frequent stirring. With the excess metal present the final precipitate formed a fine mixture of metallic mercury and calomel. This was washed with distilled water and filtered by suction in a Büchner funnel. It was then transferred to a beaker and enough distilled water added to cover it.

The potassium chloride was purified by recrystallization from distilled water. Since 74.55 g. are needed for one liter of 1 Normal KCl, 350 grams of KCl were used to begin the purification, and recrystallizing the material three times, a yield of approximately 170 grams was obtained.

To prepare the calomel electrode for use: a layer of purified mercury was placed in the bottom about three-fourths of an inch in depth, over this was placed an inch layer of calomel-mercury paste, then the cell was filled with 1 Normal KCl solution saturated with calomel. To make contact with the circuit the side arm of the electrode was filled with mercury.



Hydrogen Electrode



Calomel Electrode

The hydrogen electrode was prepared for use by depositing finely divided platinum with electrolytic apparatus from a 2% solution of platinum chloride. The tube of the electrode was filled with mercury and attached to the cathode by means of a copper wire, and the solution was connected with the anode. The attachment was reversed frequently until a coat of Pt. black sufficiently heavy to cover the sheen of the sheet platinum was obtained. The electrode was washed with distilled water and kept immersed in a KCl solution until used. The hydrogen electrode must not be allowed to become dry.

The first experiment performed was the titration of hydrochloric acid with sodium hydroxide, both solutions being one-tenth normal. Phenolphthalein was added to check the end point of the indicator against the true neutralization point as indicated by the change in E. M. F.

The second group of experiments was the titration of a weighed amount of standard sodium carbonate of a factor purity of 99.828%.

The third group of experiments with the hydrogen electrode was concerned with the titration of Mohr's salt, ferrous ammonium sulphate $6 \text{ H}_2\text{O}$, with standardized potassium permanganate solution, in acid medium (H_2SO_4).

Further work involved the quinhydrone ($\text{C}_6\text{H}_4 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_4 \cdot (\text{OH})_2$) electrode. This is used in solutions where the pH is less than 7, that is, in acid solutions. Quinhydrone in solution reversibly dissociates to quinone and hydroquinone. In such an acid solution of quinhydrone a platinum electrode will show a potential difference, which may be calculated by the equation

$$E_h = E_k - 0.000,198 T \text{ pH.}$$

E_h is the potential difference exhibited by the quinhydrone electrode when

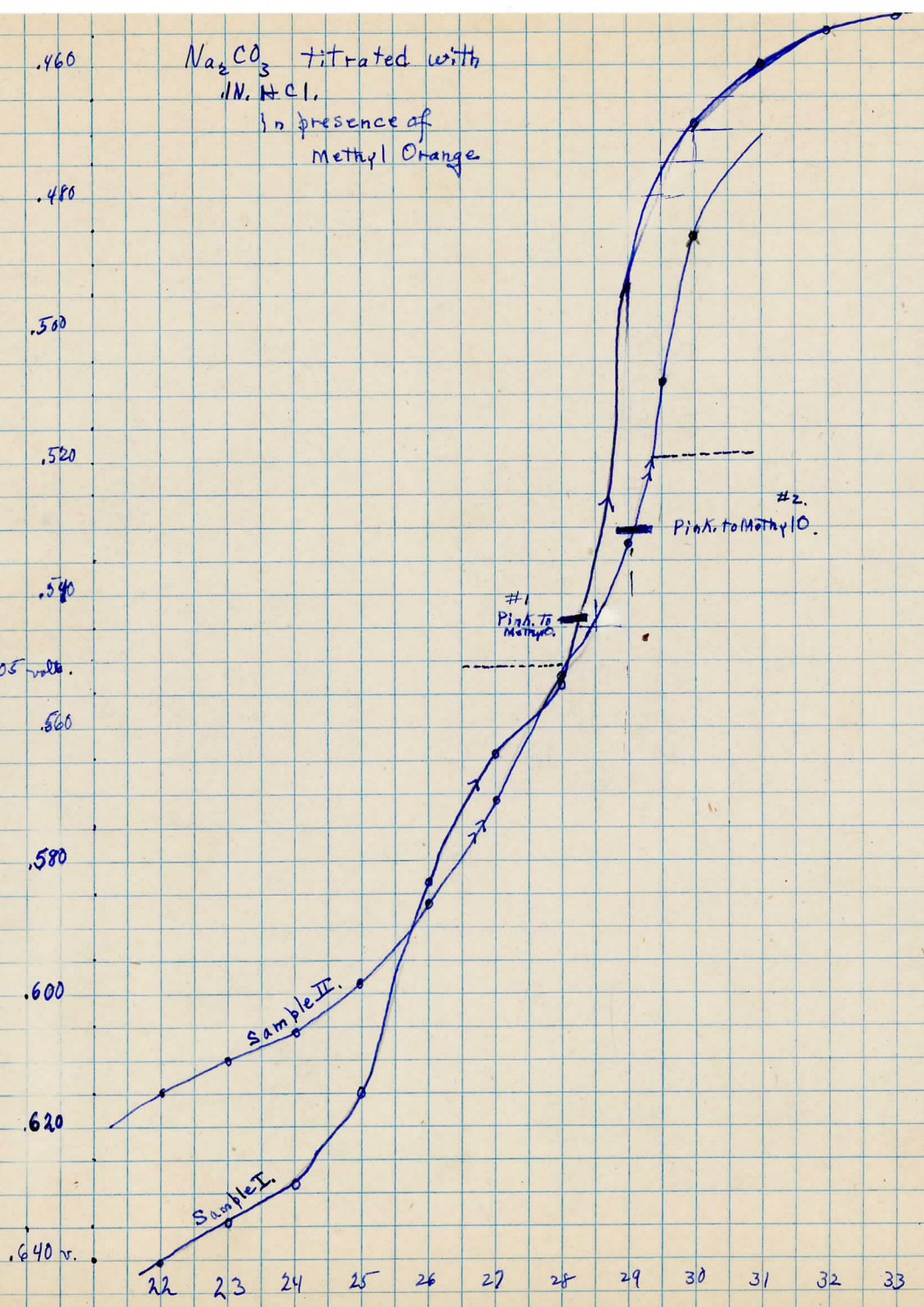
referred to the normal hydrogen electrode as a standard.

E_k is a constant for the quinhydrone electrode, established by using a solution of known pH and measuring the potential difference between a quinhydrone electrode in the solution, and a hydrogen electrode in the same solution, in the absence of quinhydrone. For a temperature of 25°C $E_k = .699$.

T in the equation is expressed as absolute, 273+°C. The quinhydrone was prepared by dissolving 100 g. of ferric ammonium alum in 300 cc. of water at 65°C, and slowly, with stirring, adding it to a solution of hydroquinone, 25 grams in 300 cc. of water. The solution is cooled in ice, and the fine green crystals are filtered with suction, washed three times with cold distilled water and recrystallized once from alcohol.

The quinhydrone electrode is formed by adding a little quinhydrone to the acid solution under examination and a platinum (blank) electrode inserted. The ordinary calomel electrode is then connected with the solution.

The graphs shown for the experiments are self-explanatory, showing cc. plotted against E. M. F. values, or against pH values.



Na₂CO₃ .99828% pure

→ Sample I. = .1599g.

→ Sample II. = .1603g.

Calomel + hydrogen electrodes, @ 25°C.

$$\frac{E.M.F. \text{ obs.} - E.M.F. (\text{of cal. el.})}{.05910} = \text{pH.}$$

↓
(.00, 198, 37 x 273 + 0CT)

Sample I.			Sample II.		
cc.	E.M.F.	pH.	cc.	E.M.F.	pH.
22.	.6415	6.03	22.	.615	5.59
23	.6345	5.92	23	.6105	5.51
24	.628	5.81	24	.6055	5.43
25	.615	5.59	25	.588	5.29
26	.583	5.05	26	.587	5.11
28	.554	4.55	27	.572	4.86
29	.494	3.54	28	.536	4.59
30	.468	3.10	29	.5325	4.19
31	.46	2.96	29½	.507	3.76
32	.455	2.88	30	.486	3.24
33	.45	2.81			

Calomel factor = .2848 @ 25°C

Dashlines ----- indicate position of theoretical endpoint

cc

E.M.F.
in
Volts.

20 cc. of .1N. HCl titrated with .1N. NaOH.
Calomel + Hydrogen electrodes.

cc.	E.M.F.	pH.
10	.4472	2.577
12	.4525	2.837
14	.465	3.049
16	.475	3.218
17	.4885	3.447
18	.515	3.895
19	.6257	6.629
20	.9375	11.05
21	.959	11.41
22	.975	11.62
23	.9785	11.74
24	.985	11.85

1.0300
 .9300
 .8300
 .7300
 .6300
 .5300
 .4472

1 space =
.02 volts.

PH?
theoretical
end point.

Pink to
Phenolphthalein

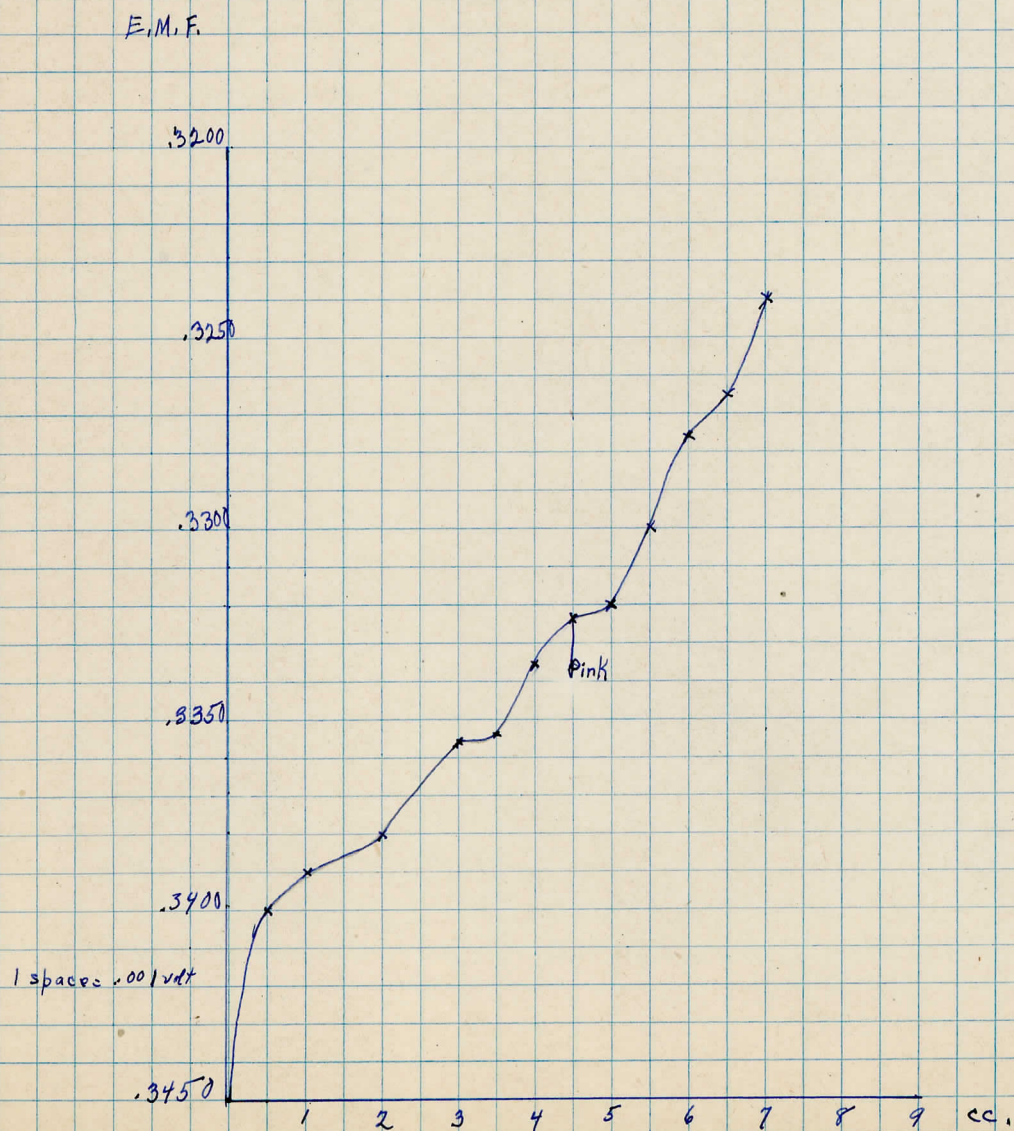
$$pH = \frac{E.M.F. \text{ observed} - E.M.F. \text{ of Calomel cell}}{.000,19837 (273 + tC)}$$

.000,19837 = .0541
at 25°C.

E.M.F. of Calomel electrode at 25°C.
= .2848

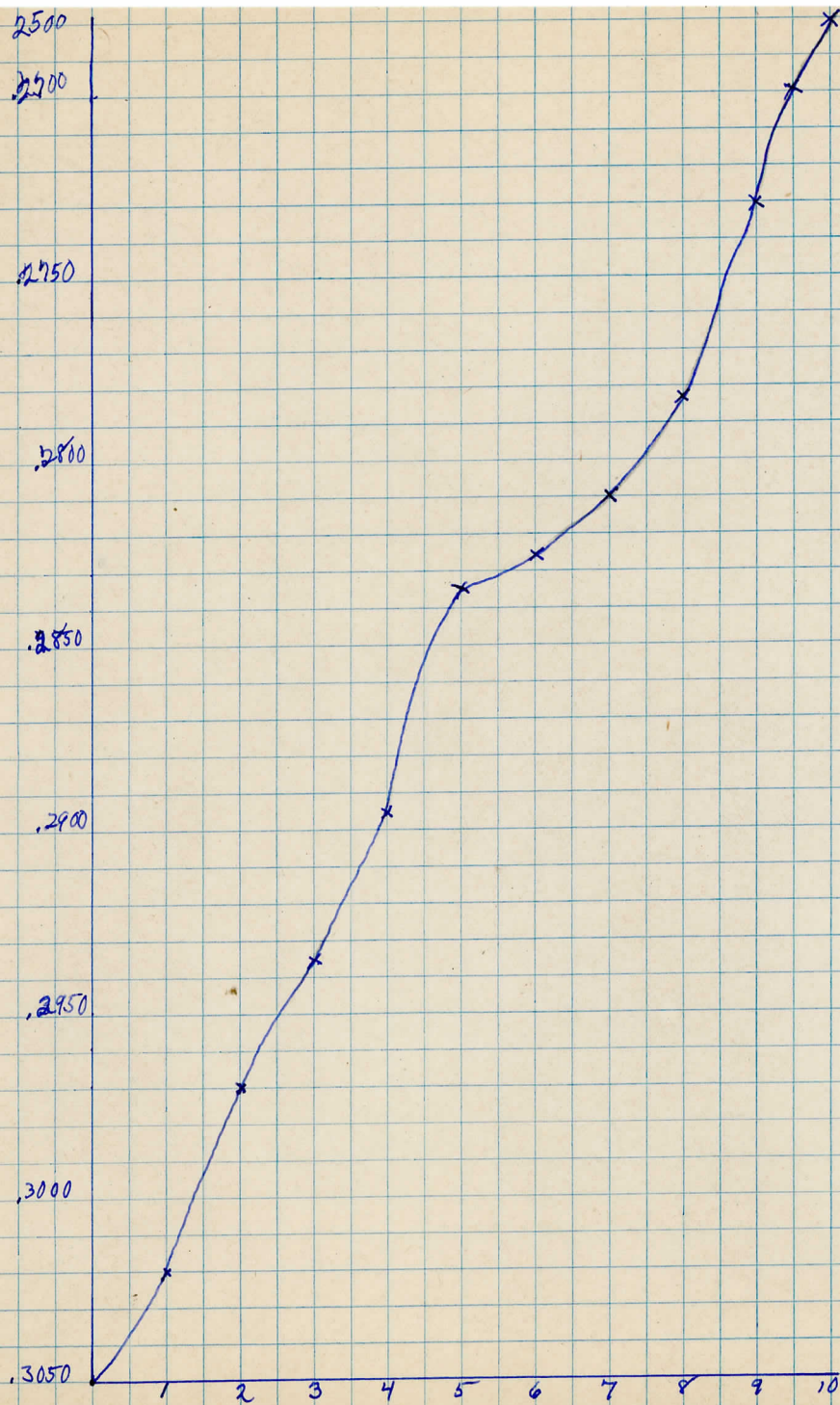
10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 CC.

20 cc .1N. Mohr's salts titrated with KMnO_4 in presence of $6\frac{2}{3}$ cc. of 9M. H_2SO_4 .
 1 cc. $\text{KMnO}_4 = .006254 \text{ g. Fe}$



cc.	E.M.F.
0	.3450
$\frac{1}{2}$.3400
1	.3390
2	.3380
3	.33565
$3\frac{1}{2}$.3356
4	.3335
$4\frac{1}{2}$.3325
5	.3320
$5\frac{1}{2}$.3300
6	.3275
$6\frac{1}{2}$.3265
7	.3240
8	.3

Pink — 5



10cc $\frac{.1N}{10}$ HCl. titrated with $\frac{.1N}{10}$ NaOH

CC.	E.M.F.
0	.305
1	.302
2	.297
3	.2935
4	.2895
5	.2835
6	.2825
7	.2810
8	.2782
9	.2730
9½	.2700 - Endpoint.
10	.2500

quinhydrone electrode

BIBLIOGRAPHY

- Brockman, C. J. "Electro-Organic Chemistry"
John Wiley and Sons, New York, 1926.
- Clark, W. Mansfield "The Determination of Hydrogen Ions"
Williams and Wilkins Co., Baltimore, 1925.
- Creighton, H. Jermain "Electrochemistry, Volume I, Principles"
John Wiley and Sons, New York, 1924.
- Fales, Harold A. "Inorganic Quantitative Analysis"
The Century Company, New York, 1925.
- Kolthoff, Dr. I. M. & Furman, N. Howell "Potentiometric Titrations"
John Wiley and Sons, New York, 1926.
- Popoff, Stephen "Quantitative Analysis"
Blakiston's Son and Co., Philadelphia, 1927.
- Thompson, Maurice deK. "Applied Electrochemistry"
Macmillan Company, New York, 1911.