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# The ionization of silicic acid

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A thesis, presented to the Department of Chemistry, in partial fulfillment of the requirements for the Degree of Bachelor of Science with a chemistry major.

By Robert E. Carpenter

Approved Charles B. Hurd

June 1948



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Bindery, January 29, 1949.

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## INTRODUCTION

The purpose of this research was to gain further knowledge of the ionization of silicic acid. Silicic acid is a weak polybasic acid which changes its molecular complexity on standing. The mechanism of this change is probably a condensation although it is not definitely known. By titrating a solution of sodium silicate with acid, we hoped to get a better idea of the ionization of the silicic acid.

The acids used in this research were nitric, hydrochloric and sulphuric, all strong acids. The sodium silicate used was diluted from standard solution. The titrations were run with indicator, with the quinhydrone potentiometer, and with the Fisher junior titrimeter.



## HISTORICAL

Quite a little work has been done on silicic acid or hydrated silicic in the last twenty or twenty-five years. Colloidal silicic acid has been known for about two hundred years. Most of the recent work has been done on the silicic acid gels. A number of contributions have come from this laboratory.

There are several different ways to prepare the silicic acid. The most common method consists of the addition of an acid to a solution of sodium silicate. It is also possible according to some observers (1) to use an ammonium salt instead of an acid.

Another possible method to prepare the acid sol is the hydrolysis of the sodium silicate solution followed by electrolysis by Treadwell and Wieland (2). This method removed most of the sodium hydroxide and left fairly stable sols.

The hydrolysis of different silicon compounds has also been used to prepare the colloidal silica. Included among these are the chloride (3) the fluoride (4) and the sulphide (5).

All the methods have one objection viz. that other substances besides silicic acid are formed. These may be partially removed by dialysis but not completely.

When the silicic acid is first formed, it appears to be in the form of simple molecules of low molecular weight. The molecular weight increases rapidly with time. In these determinations of molecular weight, allowance for the other electrolytes present must be made and the values obtained are not very accurate.

Bradfield (6) found the pH of a pure silicic acid sol to be 6.5 but earlier observers found it to be lower. These measurements unfortunately give the pH of the sol after it has stood for a while during which time some condensation has taken place.

There is not much data on either acid or the basic ionization constants of silicic acid or silicon hydroxide. Because of the immediate condensation, it is almost impossible to measure either of them accurately. Treadwell (7) believes that  $2 \times 10^{-10}$  is a reliable value for the acid ionization constant but there is no confirmatory evidence. The acid ionization is slightly stronger than the basic ionization.

R. W. Harmon (8) used the hydrogen ion concentration of a solution of sodium silicate to get the hydroxyl ion concentration and from the latter calculated the degree of hydrolysis. He found that the indicators were unsatisfactory because different results were obtained with different indicators. The method he



used was the hydrogen electrode. He made a hydrogen cell from purified hydrogen and platinized platinum and used a saturated calomel cell for a standard cell. He used a Cambridge and Paul potentiometer and an accumulator to supply current.

Bogue (9) previously had used the method of the hydrogen cell to measure the hydrogen ion concentration and Harman's results checked his quite well.



## EXPERIMENTAL

The nitric, sulfuric, and hydrochloric acids used in this research were made up by dilution of the concentrated acids to approximately one normal. These acids were standardized against oxalic acid, exactly one normal, made up as a primary standard. The sodium hydroxide used was not free from sodium hydroxide and the effect of this was minimized by bringing the mixture of sodium hydroxide and acid to a boil while there is just one or two drops excess acid to drive off the carbon dioxide. The mixture is then cooled. Next the sodium hydroxide needed to effect completely neutralization is added. The end point with phenolphthalein is extremely sharp after boiling off the carbon dioxide. There will be a little carbonate in the last two or three drops added by this has little or no effect. The driving off of the carbon dioxide has to be accomplished in acid solution because it forms carbonic acid in acid solution which dissociates with heat and the carbon dioxide escapes. The carbon dioxide was driven off by heating every time that sodium hydroxide was used in a titration. The carbonate in the sodium hydroxide changed the normality of the acids about five parts in a thousand.

The sodium silicate solution used in this research was diluted from a solution made up previously and was made up approximately one normal with respect to sodium hydroxide. A large volume was made up to insure a uniform concentration in each titration. The exact concentration of the sodium silicate solution is not necessary because it has to be mixed with water to reduce the concentrations so the mixture will not gel as the acid is added.

The procedure used in the titration of the sodium silicate solution with strong acid was to pipette exactly 25 cc. of the silicate into an Erlenmeyer flask and then add three times the volume of the silicate or 75 cc. of distilled water. The exact amount of diluent is not important but should be approximately the same in all cases. Then two drops of methyl orange indicator was added. The acid was then introduced quite rapidly and the mixture swirled. The number of milliliters of acid added at the end point was observed and recorded. It was necessary to add the acid rather rapidly in order that the silicic acid formed would not polymerize and gel. The water also was added to lessen the possibility of the formation of a gel. If necessary the temperature of the titration could be reduced to further decrease the possibility of a gel formation. With the decreased temperature and the decreased concentration the silicic acid did not gel. This procedure was followed exactly the same with all the acids used.



The quinhydrone potentiometer was also used as a measuring device for the titration of sodium silicate with strong acid. This apparatus was not very successful, however, because it does not work well with solutions of pH over eight. Consequently the acid had to be titrated with the silicate instead of the other way around as was done with the other methods.

The procedure used in the quinhydrone potentiometer method was to prepare a normal calomel electrode and also a platinum wire electrode. A large porcelain evaporating dish was found to work very well as a receptacle. It was wide enough for the electrodes and the burette and the solution was easily stirred. Twenty-five cc. of the 1N. acid were pipetted into the evaporating dish and then distilled water was added to cover the electrodes. The potentiometer was then wired to a dry cell and to the calomel and platinum electrodes. The galvanometer of the potentiometer was adjusted to zero. A pinch of quinhydrone was added to the acid and the voltage of the acid measured and recorded. The silicate solution was added from a burette and the voltage recorded again. More silicate was added and the voltage taken again until the voltage goes from negative through zero to positive. When there was little change in voltage a large volume of silicate can be added but near the end point a small change of volume produced a large change in potential. All the strong acids were used in the titration, the procedure being the same for all the acids.

A third device used in the titrations to measure the end point was the Fisher Junior Titrimeter. With this instrument it was possible to get the alkaline part of the curve which the quinhydrone potentiometer could not measure. With the use of this instrument it was necessary to dilute the solution and also to keep it in an ice bath during the titration so that the silicic acid formed would not set.

The procedure for the use of the titrimeter is first to bring the instrument into adjustment. Then exactly twenty-five cc. of sodium silicate solution was pipetted into a beaker with about seventy-five cc. of distilled water and this beaker was placed in a larger beaker containing ice water. This beaker was adjusted so that the electrodes of the titrimeter were completely under the surface of the solution. The motor to the stirrer was started and when the solution was thoroughly mixed, the selector on the titrimeter was turned to position three or four and when the galvanometer needle rested on the red line the dial reading was recorded. Sometimes the zero reading was on the three scale and sometimes on the four. The zero end of the scales join each other i.e. zero on the three scale equals zero on the four scale.



Therefore, in plotting the readings on the three scale could be regarded as minus numbers. A little of the 1 N. acid was added from the special burette, a galvanometer adjusted, in the dial read and recorded. This addition of acid, large amounts at first gradually decreasing and then increasing again as the end point was reached and passed, was continued until about twice the volume of silicate or fifty cc. of acid had been added. Because of the drifting of the galvanometer, it was considered desirable to take two runs with each acid. In one run the dial was read immediately after the introduction of the acid and in the other the dial was read two minutes after the addition of the acid. Essentially this same procedure was used with all three acids.

Besides the above methods phenolphthalein was used as an indicator in the titration. Phenolphthalein was used to detect a bisilicate or a sodium acid silicate if such a compound exists. With sodium carbonate which is analagous to sodium silicate, there are two end points, one when the sodium carbonate is changed to sodium bicarbonate and the second when the sodium bicarbonate is changed to the carbonic acid.



# RESULTS

Table I

	Methyl Orange Indicator	Quinhydrone Potentiometer	Titrimeter
Hcl	.9058	.9250	.9540
H <sub>2</sub> SO <sub>4</sub>	.9051	.9210	.9210
HNO <sub>3</sub>	.9054	.9130	.9280
Ave.	.9054	.9197	.9245*

\* Disregarding N with Hcl

This table gives the normality of sodium silicate in equivalents of sodium hydroxide.



## DISCUSSION OF RESULTS

The results obtained by titrating sodium silicate with strong acid were slightly different depending on the measuring device. The results with methyl orange indicator were lower than those with titrimeter and the quinhydrone potentiometer. The results for the three strong acids also checked better with indicator than with the instruments.

The results using methyl orange indicator checked very close with all three strong acids. Using methyl orange as indicator the end point was the complete conversion to silicic acid comparable to the complete conversion of sodium carbonate to carbonic acid. With phenolphthalein and bron thymol blue as indicators no reliable results were obtained showing that there is no evidence of a partial conversion to sodium acid silicate such as is the case with sodium carbonate.

The results using the quinhydrone potentiometer did not check as well as those with methyl orange. The results were reproducible and the curves produced practically coincided.

The results using the titrimeter were the most erratic. With hydrochloric acid the normality was extremely high. Aside from this the other acids gave results close to the ones for the quinhydrone potentiometer.



## EXPLANATION OF GRAPHS

The graph of the potentiometer reading against cc's. of sodium silicate solution added to twenty-five cc of acid consists of a long relatively flat horizontal beginning and a sharp vertical rise which indicates the end point. The second run has been plotted with the first run and the points from the second run fell on top of the curve.

Because the instrument could not produce the more alkaline portion of the curve, the end of the curve only begins to level off. The inability of the instrument to work above a pH of nine also made it necessary to add the sodium silicate to the acid instead of vice versa as in the case of the other instruments.

The graph of the titrimeter reading against cc's. of acid added to twenty-five cc. of sodium silicate is not nearly as regular as that of the potentiometer. This is partly because of the drifting of the galvanometer needle. Two curves were plotted, one with the titrimeter reading taken immediately after the addition of the acid and the second with the titrimeter reading taken two minutes after the addition of the acid. The major difference between the two curves is that the second with the reading taken after two minutes is sharper at the end point and the end point is reached with slightly less acid than the curve with the immediate reading.



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- (6) Bradfield - J. Am. Chem. Soc. 44, 965 (1922)
- (7) Treadwell - Trans. Faraday Soc. 31, 297 (1935)
- (8) Harman - J. Phys. Chem. 30, 1100 (1926)
- (9) Bogue - J. Am. Chem. Soc. 42, 2575 (1920)



25 ML.  $\text{Na}_2\text{SiO}_3$   
TITRATED WITH  $\text{HCL}$  (N=1.020) USING TITRIMETER

TITRIMETER READING

40

30

20

10

0

10

20

30

40

50

ML.  $\text{HCL}$  ADDED

A

C

D

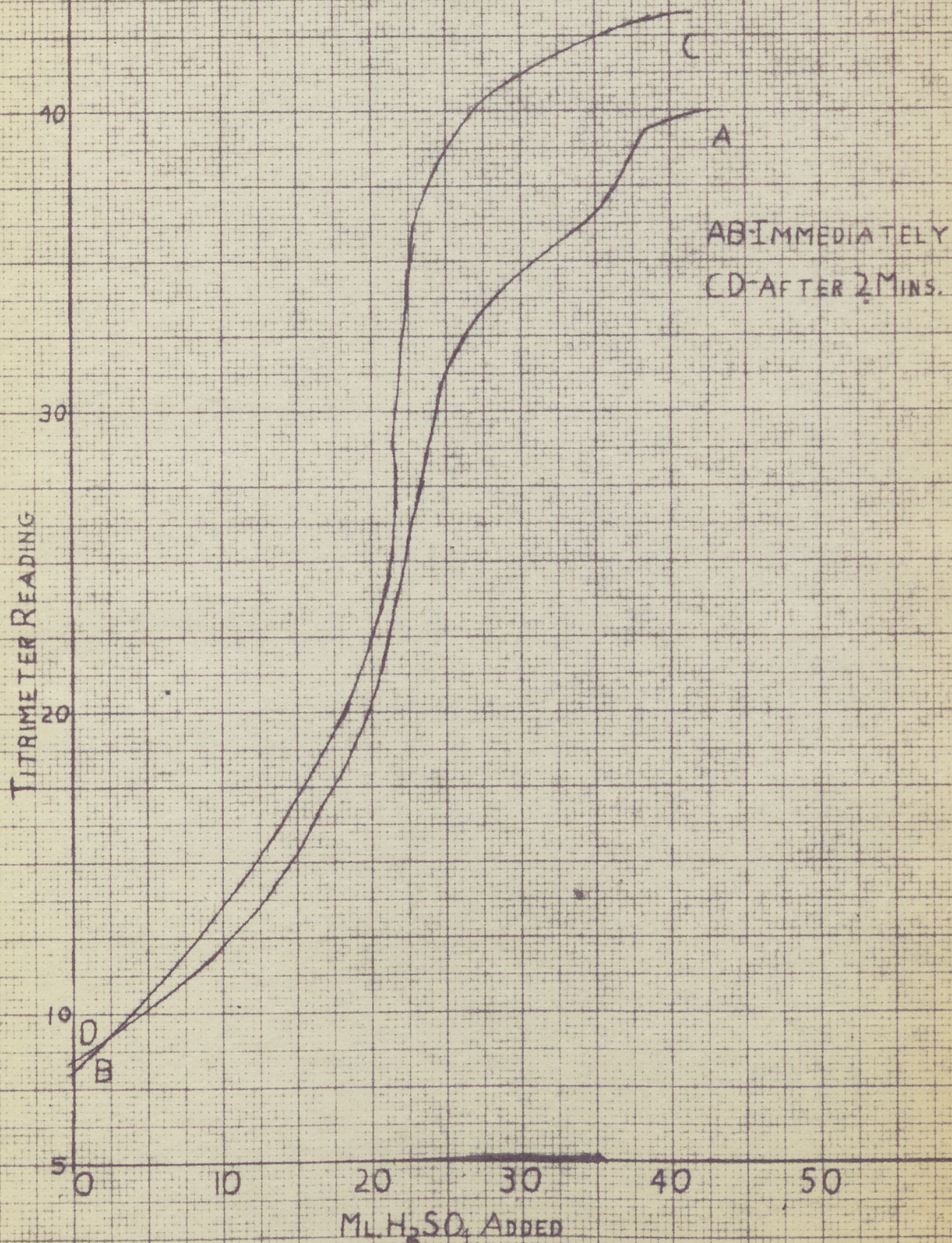
B

AB - IMMEDIATELY  
CD - AFTER 2 MINS.

RECEIVED BY KESSLER CO., N. Y., NO. 38913  
10 x 10 in. low by (left), 200 (right) - 10 x 10 in.  
MADE IN U. S. A.



25 ML.  $\text{Na}_2\text{SiO}_3$   
TITRATED WITH  $\text{H}_2\text{SO}_4$  (N=1.0205) USING TITRIMETER





25 ML.  $\text{Na}_2\text{SiO}_3$   
TITRATED WITH  $\text{HNO}_3$  (N=.9465) USING TITRIMETER

TITRIMETER READING

40

30

20

10

D

B

10

20

30

40

50

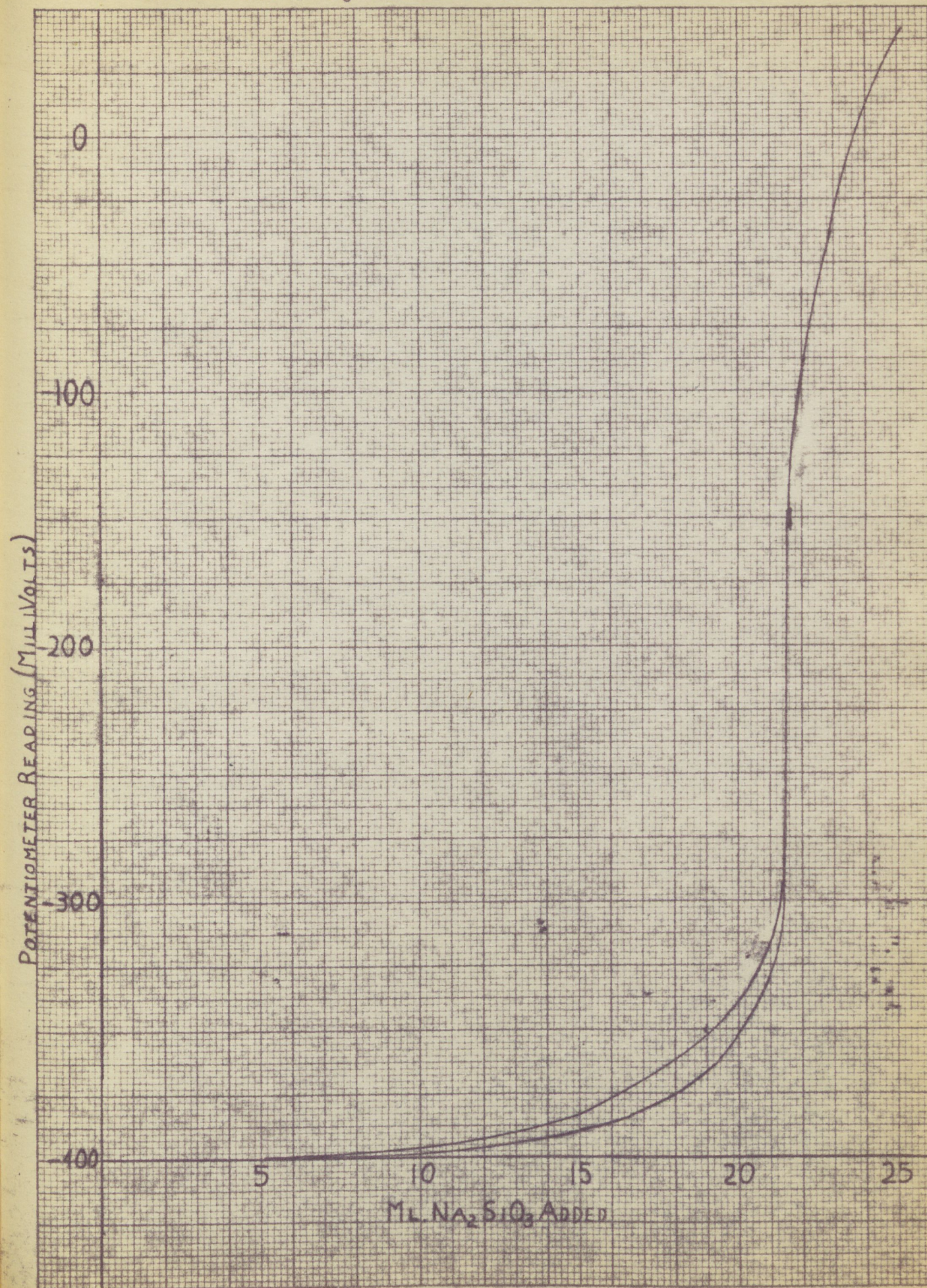
ML.  $\text{HNO}_3$  ADDED

AB - IMMEDIATELY  
CD - AFTER 2 MINS.



25 ML. HCL -  $N = .8057$

TITRATED WITH  $Na_2SiO_3$  USING QUINHYDRON POTENTIOMETER





25 ML.  $\text{HNO}_3$  -  $N = .9530$

TITRATED WITH  $\text{Na}_2\text{SiO}_3$  USING QUINHYDONE POTENTIOMETER

