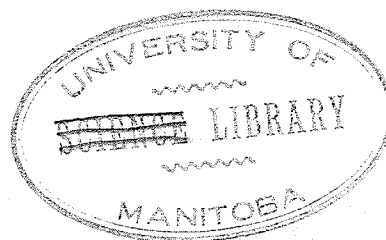


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A THESIS
PRESENTED TO THE FACULTY OF ARTS AND SCIENCES
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THE EQUILIBRIUM BETWEEN
CALCIUM CARBONATE, CALCIUM SULPHATE AND CARBON DIOXIDE
IN WATER SOLUTIONS AS DETERMINED BY
ELECTROMETRIC TITRATIONS.

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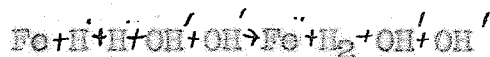
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INTRODUCTORY.

1.

The numerous recent researches on the corrosion of iron have proved beyond a doubt that the process of corrosion is an electrochemical phenomenon, and the mechanism of the reaction is essentially the same whether due to a stray current of electricity or to corrosion in the absence of any impressed E.M.F. (1).

It is a well known fact that Iron dissolves readily in an acid, that Iron has a high solution tension with respect to hydrogen, and even in pure water Iron has a definite solution tension. The Iron goes into solution as the ferrous ion according to the equation,



a corresponding negative charge being assumed by the hydroxyls. In presence of dissolved oxygen the ferrous hydroxide is oxidized to the insoluble ferric hydroxide or rust.

Many salts when dissolved in water undergo hydrolysis, (Hydrolysis is discussed more fully later on) and this hydrolysis may be acidic or basic, i.e. we may have H^+ ion present in a larger, or lesser concentration than in water. If we have a salt dissolved in water which undergoes an acidic hydrolysis then the H^+ ion will be increased, and if a piece of iron be immersed in this solution it will dissolve more rapidly than in the case of pure water.

Carbon dioxide dissolved in water gives rise to Carbonic acid

1.-- Corrosion and Preservation of Iron and Steel." Cushman & Gardner."



2.

the carbonic acid ionizes and would increase the rate of solution of iron, due to the increased H concentration.

Investigations on the corrosion of cast iron pipes lines in the vicinity of Winnipeg (1) and analysis of soil waters have shown that Calcium Sulphate, Calcium Carbonate and free Carbon Dioxide are held in solution in such waters. The soils of the Winnipeg District are rich in lime, and at depths of from four to twelve feet aggregations of crystals of Calcium Sulphate (Gypsum) and Magnesium Sulphate frequently occur, usually in a highly calcareous layer several inches thick.

P. Hedinger has carried out investigations on solutions of calcium sulphate, calcium carbonate and carbon dioxide in water and the following quotation from his paper (2), "On the Destruction of Gas and Water Systems in Clay Soil containing Gypsum", accounts for the increased hydrogen ion contents of such water.

"Of essentially greater and more determinative significance, is however on the other hand, the operation of gypsum as determined by, me upon the dissociation.

1.--J. Am. Inst. Elec. Eng. 40,642(1921)

" W. Nelson & J.W. Shipley."

2.--Journal fuer Gasbeleuchtung und verwandte Beleuchtungsarten
sowie fuer Wasserversorgung-- Berlin Feb. 16 and 23, 1918.

of free carbon dioxide in water. As I have proved 3.
 in my work mentioned on the rusting of iron, in the determination of the activity of a water upon iron, whether it be the ground water or the water system itself, it is a question practically simply and solely of the concentration of the hydrogen ions of the water. And in water, the hydrogen ion concentration is practically exclusively conditioned by the dissociation of the free carbonic acid therein contained. The activity of the water rises and falls also with the dissociation of the free carbonic acid. This decomposes in water in part according to the equation.



From this results according to the law of Mass operation.

$$\frac{(H^+) (HCO_3')}{(H_2 CO_3)} = K \quad (1a)$$

If water contains besides, bicarbonates, let us say Calcium bicarbonate, then this is for the most part dissociated according to the equation.



from which follows.

$$\frac{(Ca_{\frac{1}{2}}) (HCO_3')}{(Ca_{\frac{1}{2}} HCO_3)} = K_2 \quad (2a)$$

The Calcium bicarbonate accordingly brings a quantity of new HCO_3' ions into solution. Thereby in equation (1a) the numerator becomes greater; in order that K remain constant, the denominator must become greater; and hence the quantity of undissociated carbonic acid increases. That is to say, the dissociation of the

free carbonic acid is strongly suppressed, the H ion concentration decreases; the water becomes "less acid". Let us now add gypsum to this water. This for its part becomes in a high degree dissociated according to the equation.



Since in addition, gypsum is rather soluble in water, we thereby bring a greater quantity of new Ca ions into the solution, and it is obvious from what has been said above; that equation (2) must be displaced from right to left, and the dissociation of the bicarbonate must thus decrease.

Thereby however, their obstructive operation upon the dissociation of the free carbonic acid (equation 1) also decreases, and we have, through the addition of a completely neutral salt, calcium sulphate, made the water sourer more active.

The corrosion of iron being due to the activity acidity of solutions in contact with it, and the increased corrosion of cast iron pipe lines in soils containing gypsum (CaSO_4), a very interesting, and important subject for research presented itself i.e. to determine by means of the hydrogen electrode the acidity of solutions of calcium sulphate, calcium carbonate and carbon dioxide in water solution, and also of mixtures of calcium sulphate and calcium carbonate both in the presence of, and without dissolved carbon dioxide.

The results which follow have been deduced from a consideration of the titration curves obtained experimentally by means of the hydrogen electrode.

5.

I wish to take this opportunity of thanking Dr. J.W. Shipley for the interest he has shown in the investigation, and for his valuable suggestions in the interpretations of the results obtained.

Concentration Cell(1).

If we pass a current through two silver electrodes immersed in a solution of a silver salt a change in concentration around the electrodes will be brought about. Such a process may be performed reversibly, i.e. if we change the concentration around the electrode by reversible freezing or evaporation of the solvent or by use of a semipermeable membrane there will be a difference of potential between the two electrodes.

It is thus evident that we can obtain a relation between osmotic work and electrical energy, by changing the concentration first by means of a semipermeable membrane, and then bringing the system back to its original condition reversibly by the passage of an electric current. The osmotic work and electrical energy will here be equal to one another, since mechanical energy may be readily converted to electrical energy. Assuming the gas laws for very dilute solutions osmotic work may be very simply determined, and thus the electrical energy, and from that the electromotive force of any concentration cell may be deduced.

For simplicity of calculation consider a binary electrolyte with univalent cation and anion, e.g. Silver Nitrate. Let there be two solutions of the salt of osmotic pressure P & $P + dP$. The number of cubic centimeters in which one gram molecule of the salt is dissolved will be expressed by V , and $V - dV$ respectively. If u and v are the rate of migration of the cation and anion then the passage of one Faraday of Electricity through the solution will necessitate the passage of

$$\frac{u}{u + v}$$

1. (a) Theoretical Chemistry--"W. Nernst."
- (b) "Helmholtz"-Phil. Mag. (5), 5, 348, 1878.
- (c) Outlines of Theoretical Chemistry--"Getman".
- (d) Text Book of Electro-Chemistry.--"Le Blanc."
- (e) Electro-Chemistry.--"Lohfeldt".
- (f) Introduction to Physical Chemistry.--"Jas. Walker."

gram molecules of cation through the liquid junction of the solutions, and of $\frac{u}{u+v}$ gram molecules of the anion in the other direction.

The anode dissolves to supply cation to replace that which leaves the anodic compartment and to neutralize the anion which arrives. There will be on the whole an increase of concentration of $\frac{v}{u+v}$ gram molecules of the salt in the anodic compartment; and an equal diminution in the Cathodic compartment. The passage then of one Faraday of electricity is equivalent to the transference of $\frac{v}{u+v}$ gram molecules of the salt from cathodic to anodic compartment.

Let us consider the osmotic work which would have to be done on the supposition that the solution in the anodic compartment is the more concentrated.

Cut off from the more dilute solution of osmotic pressure P , a portion containing $\frac{v}{u+v}$ gram molecules. Concentrate the portion cut off by forcing water through the semipermeable membrane into the rest of the more dilute solution until the osmotic pressure in the separated portion reaches the value $P+dP$. It is assumed that the total bulk of the original solution is so great, that the addition or removal of the quantity of water containing $\frac{v}{u+v}$ gram molecules has no appreciable effect on the dilution or osmotic pressure.

The degree of dilution of osmotic pressure P , is V , and of $P+dP$ is $V-dV$. The process of concentrating one gram molecule of the salt, from the first to the second dilution would involve the

removal of dV cubic centimeters of water. The concentration of $\frac{V}{u+v}$ gram molecules necessitates the expulsion of $\frac{V}{u+v} \cdot dV$ cubic centimeters through the osmotic membrane. This volume has been moved against an osmotic pressure rising uniformly from 0 to dP , the average being $\frac{1}{2}dP$. The osmotic work done would be

$$\frac{1}{2}dP \cdot \frac{V}{u+v} \cdot dV \text{ ----- (1)}$$

The separate portion of the solution, being now of the same osmotic pressure as the more concentrated anodic solution, may be mixed with it.

To restore the more dilute solution the $\frac{V}{u+v}(V-dV)$ cubic centimeters of water necessary to bring it back to the original volume, may be forced through the semipermeable membrane separating the solutions. The difference of the osmotic pressure on the two sides is, and remains dP . The osmotic pressure work done then is equal to,

$$dP \cdot \frac{V}{u+v} \cdot (V-dV) \text{ ----- (2)}$$

On the whole $\frac{V}{u+v}$ gram molecules of dissolved salt have been transferred $u+v$ to the concentrated, from the dilute solution at an expenditure of work equal to.

$$(1)+(2) \cdot \frac{1}{2}dP \cdot \frac{V}{u+v} \cdot dV + dP \cdot \frac{V}{u+v} \cdot (V-dV) \cdot \frac{V}{u+v}$$

or $dP \cdot \frac{V}{u+v} \cdot (V - \frac{1}{2}dV)$ gram centimeters ----- (3)

Since the difference of dilution dV is very small in comparison with V the total work, L may be equated

$$L = \frac{V}{u+v} \cdot dPV \text{ ----- (4)}$$

without sensible error.

In order to evaluate in quantities which may be measured we are

make use of the Gas Law as applied to dilute solutions.

For one gram molecule of dissolved salt, the Van't Hoff coefficient of which is i , we have.

$$PV = iRT$$

$$dP = d\left(\frac{iRT}{V}\right).$$

and by differentiating

$$dP = \left(\frac{-idV}{V^2} + \frac{di}{V} \right).$$

Substituting this value for dP in (4)

$$L = RT \cdot \frac{v}{u+v} \left(\frac{-idV}{V} + di \right) \text{-----(5)}$$

If the same transference were carried out electrically, the electrical energy would be CdE , dE equals the E.M.F. due to the difference of dilution dV , which must overcome the E.M.F. of the concentration cell. If we measure R in electrical units the work done and the electrical energy are equal.

Then

$$dE = \frac{RT}{C} \cdot \frac{v}{u+v} \left(\frac{-idV}{V} + di \right).$$

In very dilute solutions $i=2$

$$\text{Then } dE = \frac{-2 RT}{C} \cdot \frac{v}{u+v} \cdot \frac{dV}{V} \text{-----(6)}$$

For finite differences of dilution, we may imagine a great number of concentration cells of this kind arranged in series, and the finite E.M.F. will be obtained by integration between the extreme dilutions.

$$\text{Then } E = \frac{-2 RT}{C} \frac{v}{u+v} \cdot \log_e \frac{V_1}{V_2}$$

We can substitute the inverse ratio $\frac{C_2}{C_1}$ for the ratio of dilution, and

$$E = \frac{-2 RT}{C} \frac{v}{u+v} \cdot \log_e \frac{C_1}{C_2} \text{------(7)}$$

Let us now calculate, from the osmotic theory, the diffusion E.M.F. existing at the junction of two differently concentrated solutions of the same electrolyte.

Let u and v equal the speed of the cation and anion, the ions being univalent and the salt completely ionized. Let the osmotic pressure of each ion be P_1 in one concentration and P_2 in the other. Let C Coulombs of electricity be passed, so that the cation is transferred from higher pressure P_1 to lower pressure P_2 . The amount of cation which will pass the junction from P_1 to P_2 will be $\frac{u}{u+v}$ gram molecules; the amount of anion passing from P_2 to P_1 , will be $\frac{v}{u+v}$ gram molecules.

From the Gas Laws, we find that when a gas is isothermally expanded, the work it does per gram molecule is.

$$L = RT \log_e \frac{V_2}{V_1}$$

Applying Boyle's Law which is true here

$$L = RT \log_e \frac{P_1}{P_2}$$

Consequently for the transference of $\frac{u}{u+v}$

gram molecules of cation from P_1 to P_2 we have.

$$L_c = \frac{u}{u+v} RT \log_e \frac{P_1}{P_2},$$

and for the transference of $\frac{v}{u+v}$ gram molecules of anion from P_2 to P_1 we have

$$L_a = \frac{v}{u+v} RT \log_e \frac{P_1}{P_2},$$

The total work.

$$L = L_c + L_a = \frac{u-v}{u+v} RT \log_e \frac{P_1}{P_2}.$$

This work is equivalent to electrical energy and

$$E^1 = \frac{1}{C} \frac{u-v}{u+v} RT \log_e \frac{P_1}{P_2} \quad \text{or, substituting the ratio of the concentration } \frac{C_1}{C_2} \quad \text{for the osmotic pressure.}$$

$$E^1 = \frac{RT}{C} \frac{u-v}{u+v} \log_e \frac{C_1}{C_2} \quad \text{Volts-----(8)}$$

Since the net E.M.F. is expressed by equation (7) and the diffusion E.M.F. at the junction of liquids by equation (8), the E.M.F. due to the electrode potentials must equal the sum.

(7) + (8)

$$\begin{aligned} E + E^1 &= \frac{RT}{C} \left(\frac{2v}{u+v} + \frac{u-v}{u+v} \right) \log_e \frac{C_1}{C_2} \\ &= \frac{RT}{C} \log_e \frac{C_1}{C_2} \quad \text{-----(9)} \end{aligned}$$

Where R gas constant measured in electrical units.

T the absolute temperature.

C one Faraday of electricity.

In deriving the equation for a concentration cell, we have considered it to be composed of silver nitrate solutions, and metallic silver electrodes; but it is possible to have such a cell, in which a gas may function as an electrode. Platinum has the property of absorbing hydrogen, and if we immerse a strip of platinum, saturated with hydrogen, in a solution containing H^+ ion a difference of potential is obtained between the platinum and the solution. Platinum is inert chemically towards the solution, and serves as a mechanical device to give rigidity to the electrode. The difference of potential is due to the dissolved hydrogen ion, and thus giving rise to a change of potential between the hydrogen saturated platinum and the solution.

Equation (9) is the fundamental equation for the hydrogen electrode. The concentration C_1 is expressed as normal with respect to hydrogen ion, and the equation thus becomes.

$$E = \frac{RT}{C} \log_e \frac{1}{C_x} \quad (10)$$

where C_x is the unknown hydrogen ion concentration, and is less than normal.

In order that equation (10) may be put into working form, electrical equivalents have to be found for R and C .

Before deriving these, since measurements of potential are made in terms of the international volt, this, the ampere, and Ohm will be defined (Bureau of Standards Circular No. 60.1916.)

International Ohm is, "the resistance offered to an unvarying

electric current by a column of mercury at the temperature of melting ice, 14.4521 grams in mass, of a constant cross sectional area and of a length of 106.300 cm."

International Ampere is " the unvarying electric current which, when passed through a solution of nitrate of silver in water in accordance with specification 2, (of the 1908 London Conference), deposits silver at the rate of 0.00111800 of a gram per second."

International volt is " the electrical pressure which, when steadily applied to a conductor the resistance of which is one international Ohm, will produce a current of one international ampere."

C. the faraday is derived as follows. The international ampere deposits silver at the rate of 0.00111800 grams per second. The atomic weight of silver is 107.88. A gram equivalent would be deposited in one second by $\frac{107.88}{0.00111800} = 96494$ amperes.

A coulomb is the quantity of current transferred by a current of one international ampere in one second. Hence 96494 coulombs are carried by a gram equivalent of silver or one faraday 96494 coulombs.

R is derived from the gas equation

$$\text{i.e.} \quad PV = \frac{P_0 V_0}{273.09} \times T, \text{ where } \frac{P_0 V_0}{273.09} = R$$

273.09 being the absolute temperature. V_0 the volume of 1 gram molecule of an ideal gas at a pressure of one atmosphere and 0° C.

is 22412 ccs. (Berthelot, 28 1904).

P_0 = one atmosphere or 76 cm. of mercury at 0°C . and 45° latitude. The acceleration of gravity at 45° latitude is 980.665 cm. per second. One cc. of mercury under the gravitational pull weighs 13.59545 grams then $P_0 = 980.665 \times 76 \times 13.59545 = 1013276$ dynes per square centimeter.

$$\text{Hence } R = \frac{1013276 \times 22412}{273.09} = 8315773.9.8 \text{ ergs}$$

10^7 ergs = 1 joule absolute, and one joule absolute = .99966 international joule from which $R = 8.3129446$ international joules or volts coulombs.

Substituting the values of R and C in equation (10) we have

$$E = \frac{8.3129446}{96494} T \log_e \frac{1}{C_x}$$

Transposing to logarithms to base 10, y dividing by 0.43429 we have $E = 0.00019837 \cdot T \cdot \log_{10} \frac{1}{C_x} \text{ ----- (11)}$

In making measurements with the concentration cell, or gas chain it is possible impossible to prepare a solution which is normal with respect to hydrogen ion concentration, and even if it were possible to prepare such a solution, its value in making such measurements would be doubtful, owing to the difficulty of maintaining a constant hydrogen ion concentration over any length of time. The working standard used is the calomel electrode, (a more complete description of which is given later on) and the difference of potential between the calomel electrode, and the theoretical normal hydrogen electrode is calculated from measurements made between the calomel electrode,

and a hydrogen electrode in some fractional normal hydrogen ion concentration.

An absolute standard of reference has been chosen (suggested by Nernst 1897) and this is that the potential difference between a hydrogen electrode under one atmosphere pressure of hydrogen, and a solution normal with respect to the hydrogen ions shall be defined as zero, then the E.M.F. of a hydrogen electrode gas chain composed of a normal hydrogen electrode, and a hydrogen electrode in hydrogen ion normality C_x will be the potential difference at this last named electrode.

The Mercury of the calomel electrode, ~~is diagrammatically~~ is positive to the platinum of the normal hydrogen electrode, then diagrammatically the following relation exists.

$$\begin{array}{l} \text{absolute} \\ \text{potential} \nearrow \searrow \\ \text{unknown} \end{array} \begin{array}{c} \left\{ \begin{array}{l} \text{Mercury of calomel electrode} \\ 0 \\ \text{Pt. of normal hydrogen electrode} \\ \text{Pt. of fractional normal} \\ \text{hydrogen electrode.} \end{array} \right. \\ \text{Total E.M.F.} \end{array}$$

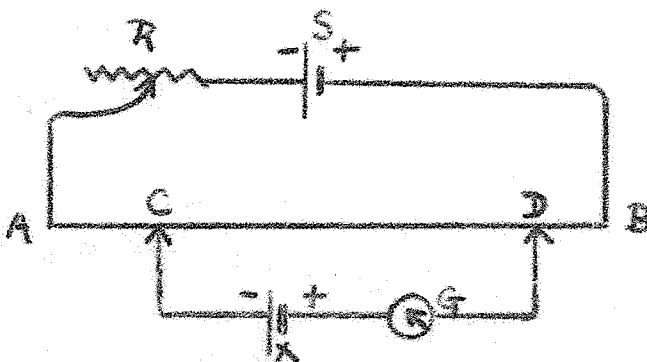
If we give to the value of the potential difference between the mercury of the calomel electrode, and the platinum of the normal hydrogen electrode a positive sign, this value must be subtracted from the total E.M.F. to give the potential difference between the platinum of the normal hydrogen electrode, and the platinum of the fractional normal hydrogen electrode, and equation (11) becomes

$$\frac{\text{E.M.F. (observed)} - \text{E(calomel electrode)}}{0.0001983 T} = \log \frac{1}{\log (H)} = \text{pH} \quad \text{--- (12)}$$

Equation (12) defines what is known as the pH value used for expressing hydrogen ion concentration. The chief reason for using the pH value in place of the (H^+) concentration is one of convenience in plotting results on ordinary cross section paper. If we had say a (H^+) of 1×10^{-4} , and another of 4×10^{-4} , and attempted to plot these along with other values, such as 2×10^{-8} to show any variation in the first two concentrations, the graph paper would necessarily have to be extended beyond bounds, but by using the logarithmic function, this difficulty is obviated. It being a comparatively simple matter to plot such values as 4, 5.4 and 7.7 which are the approximate pH values of the (H^+) cited above.

The Potentiometer method of measuring.

Among the numerous methods of measuring potential differences, the Poggendorff compensation method, or the potentiometer method, is usually employed for measuring the E.M.F. of a concentration cell or gas chain. In brief it consists in balancing the potential difference against a known opposing potential difference. When the balance is so obtained, no current can flow through the circuit, and this point is determined by placing a current indicator, such as a galvanometer, in the circuit.



The diagram illustrates the potentiometer method. S is a cell producing a current of electricity, which flows through A B. A B is a uniform wire, and we therefore have a uniform fall of potential from A to B. Let us lead in at C and D the ends of the wires of another cell (unknown) X, having the positive and negative lead as indicated in the diagram. When C and D span such a length of A B, that the fall in potential is the same as the potential difference between C and D, then no current will flow from X, this will be indicated by the Galvanometer G.

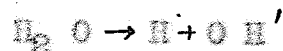
If we then know the fall of potential per unit length of A B we can determine the potential difference between C and D, or the E.M.F. due to the cell X.

The potential difference per unit length of A B can be found by inserting a standard Weston cell in place of X, and the position of C and D adjusted until the null point is attained as indicated by the galvanometer. The fall of potential between C and D is then equal to the E.M.F. of the standard Weston cell, and it is a comparatively easy matter to calculate the fall of potential per unit length of A B. It is evident that between the operation of standardization and measurement, the current in the potentiometer circuit supplied by S must remain constant.

This simple potentiometer has of course been rendered more convenient and sensitive, but in principle the operation is identical. The arrangement for measuring by means of a potentiometer will be given in detail under the description of the apparatus.

Theory of Hydrolysis.

In considering solutions, water itself is usually considered as inert, but water ionizes, according to the equation,



and due to these ions in the solution, in so called hydrolytic reactions, water takes a stoichiometric part.

The dissociation constant for water would be given by the equation,

$$\frac{(\text{H}) (\text{OH}')} {(\text{H}_2\text{O})} = K$$

the terms bracketed being ionic concentrations, at equilibrium, but the value (H_2O) is so large in relation to the ionized portion, that it may be considered constant, and the ionic product of water is given by the equation.

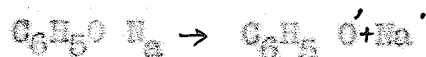
$$(\text{H}') (\text{OH}') = K_w$$

The numerical value of (H') and (OH') will be the same in pure water, and the value for either concentration has been found to be 1×10^{-7} (1). K_w then is equal to 10^{-14} . This means 1×10^{-7} gram molecules of water are ionized in one liter of pure water.

The phenomenon of hydrolysis takes place, when a salt, the acidic or basic component of which is weak, is dissolved in water. If sodium phenate be dissolved in water it largely dissociates into its ions, since all salts dissociates very largely.

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- 1.-(a) "Ostwald" Zeitsch physik. Chem. 11, 521, (1893)
 (b) "Arrhenius" " " 11, 323, (1893)
 (c) "Hernst" " " 14, 155, (1894)
 (d) "Falkousch & Heydmeiller" physik Chem. 14, 330, (1894)
 (e) "A.A. Noyes & Kanolt" Carnegie Inst. Pub. 63, 297, (1907)
 (f) "Hudson" J. Am. C.S. 29, 1571, (1907)

according to the equation.



then momentarily we have a very large concentration of $\text{C}_6\text{H}_5\text{O}^-$ ion.

Phenol is an acid which dissociates according to the equation,



the dissociation constant is given by

$$\frac{(\text{C}_6\text{H}_5\text{O}^-) (\text{H}^+)}{(\text{C}_6\text{H}_5\text{OH})} = 1.3 \times 10^{-10}$$

$$(\text{C}_6\text{H}_5\text{OH})$$

This means that only a very small quantity of $\text{C}_6\text{H}_5\text{O}^-$ ion can exist in presence of H^+ ion, without continuing to give undissociated $\text{C}_6\text{H}_5\text{OH}$.

In solution we have momentarily a larger concentration of $\text{C}_6\text{H}_5\text{O}^-$ ion, and a concentration of H^+ ion, due to the solvent (water), which is too great to allow these ions to remain uncombined, and consequently undissociated $\text{C}_6\text{H}_5\text{OH}$ is formed until the expression,

$$\frac{(\text{C}_6\text{H}_5\text{O}^-) (\text{H}^+)}{(\text{C}_6\text{H}_5\text{OH})}$$

$$(\text{C}_6\text{H}_5\text{OH})$$

has reached its necessary value. H^+ is removed from solution and the concentration has been reduced, a further quantity of hydroxyl ions must be formed from the solution, in order that the ionic product $(\text{H}^+) (\text{OH}^-)$ remain constant. Hence we have a preponderance of OH^- over the H^+ , and as a result the solution reacts alkaline.

If, on the other hand, we have a salt composed of a weak base, and a strong acid such as AlCl_3 the resultant reaction is acid. The dissociation constant of $\text{Al}(\text{OH})_3$ given by

$$\frac{(Al''') (OH')^3}{(Al (OH)_3)} = K$$

20.

is very small. When $AlCl_3$ is dissolved in water, it dissociates largely into Al''' and Cl' ions. Momentarily, we have a larger concentration of Al''' in presence of OH' from the water, than will permit of them remaining uncombined, and consequently they unite to form undissociated $Al(OH)_3$ (1) until the equation

$$\frac{(Al''') (OH')^3}{(Al (OH)_3)}$$

has reached its constant value. Thus OH' is removed from the solution, and since $(H') (OH') = \text{a constant}$, more H' must be produced from the water. We then have a preponderance of H' over OH' and consequently the solution is acidic. A solution of any salt which gives a rise to a base MOH which is only slightly dissociated removes OH' to form the undissociated molecules consequently in order that the product $(H') (OH')$ be constant H' must be produced from the water and the resulting reaction is acidic.

Since the ionic product for water is always a constant

$$(H') (OH') = 10^{-14}$$

it is possible to express either acidity or basicity in terms of the H ion concentration. A neutral solution is a solution,

1.--- Denham (Loc cit) and Ley (Zeitsch physik Chem. 30, 222, 1918) have shown that $AlCl_3$ probably undergoes hydrolysis according to the equation.



in which the concentration of H^+ is equal to the concentration of OH^- or giving the numerical value 1×10^{-7} . If we have a solution of a salt, the H^+ ion concentration of which is less than 1×10^{-7} , the solution will be alkaline, since in order that $(H^+)(OH^-)$ be constant there must be a corresponding increase in the OH^- concentration and we would have a preponderance of OH^- and the solution would react alkaline.

On the other hand if the (H^+) is increased above 1×10^{-7} , the hydroxyl will be correspondingly decreased, and the solution, will be acidic.

Since we can express alkalinity as well as acidity, in terms of hydrogen ion concentration, and the hydrogen electrode, is used to measure the concentration of hydrogen ion, it is but a short step to determining the degree of hydrolysis by this means. Its use however is limited to salts which are less noble than hydrogen, since metals which are more noble, would plate out on the platinum electrode, an equivalent amount of hydrogen passing into the ionic state; nor can it be used in presence of reducible anions such as NO_3^- , ClO_3^- etc. Denham(1) has employed the hydrogen electrode to measure hydrolysis, and the calculation of the degree of hydrolysis from the measurements of the hydrogen ion concentration is perhaps more simply explained by referring to his measurements on Aniline hydrochloride.

The solution used contained one gram molecule dissolved in

1.--- Denham. J.C.S. (trans.) 41, 1908.

32 liters. The hydrogen ion concentration was found to be 0.000807 gram ions per liter. If the emiline hydrochloride has completely hydrolysed (assuming complete dissociation) for the hydrochloric acid) the value would have been $\frac{1}{32}$ gram ions per liter. The percentage hydrolysis is then given by.

$$\frac{0.000807 \times 100}{\frac{1}{32}} = 2.58 \%$$

A definite concentration of OH' is established in such solutions at equilibrium, due to hydrolysis, but if we disturb the equilibrium by adding, say an acid, to a salt, such as Na_2CO_3 , which, in water solutions reacts alkaline or has a basic hydrolysis, the increased concentration of H' will tend to remove a corresponding amount of OH' until the value $(\text{H}')(\text{OH}')$ is a constant. Sodium carbonate undergoes hydrolysis according to the equation.



both products of hydrolysis are highly dissociated in solution, and the H' concentration of the solution must be due to the further dissociation of the HCO_3' ion,

$$\text{then } \frac{(\text{H}')(\text{CO}_3'')}{(\text{HCO}_3')} = K$$

The constant K would be very small. Now the addition of H' would have a tendency to remove OH' until the concentration of the two ions were equal to that of pure water, but the constant K is very small, and we would have a higher concentration of H' and CO_3'' than could exist dissociated, and they would unite to form HCO_3' ion, thus removing H' from solution, then OH' would be produced from the

water until the value $(H^+)(OH^-)$ was satisfied.

Hydrolysis then is progressive, and if we continued to add an acid to Na_2CO_3 the salt would continue to undergo hydrolysis, producing OH^- . If we had used hydrochloric acid the process would cease when, the total amount of Na_2CO_3 had undergone progressive hydrolysis, and the OH^- produced had been removed by addition of H^+ until the concentration of H^+ = the concentration of OH^- . Although the original concentration of OH^- may be small, the potential amount may be large. A salt which undergoes acid hydrolysis, may have a very small concentration of H^+ , but as this is removed equilibrium conditions may again increase the concentration of the H^+ , and the salt may exhibit the characteristics of a weak acid.

Colorimetric Method of determining pH.

Hydrogen ion concentration may be measured by means of the colour changes produced in an indicator. The method is however a comparative method with hydrogen electrode measurements as calibration, and with a series of standard "buffer" solutions indicators may be arranged empirically without involving an theory whatsoever.

There are numerous coloured compounds occurring in nature or produced synthetically which might be used as indicators, and the number of available indicators soon become burdensome. The first selection of indicators for measuring pH values was due to Sørensen(1) in connection with his work on enzyme chemistry, in

1.-- "Sørensen". Compt. Rend. Lab. Carlsberg Biochemical Z.

this was followed by a selection due to Clark and Lubs(1) covering a range of values from pH 1.2 to pH 9.8.

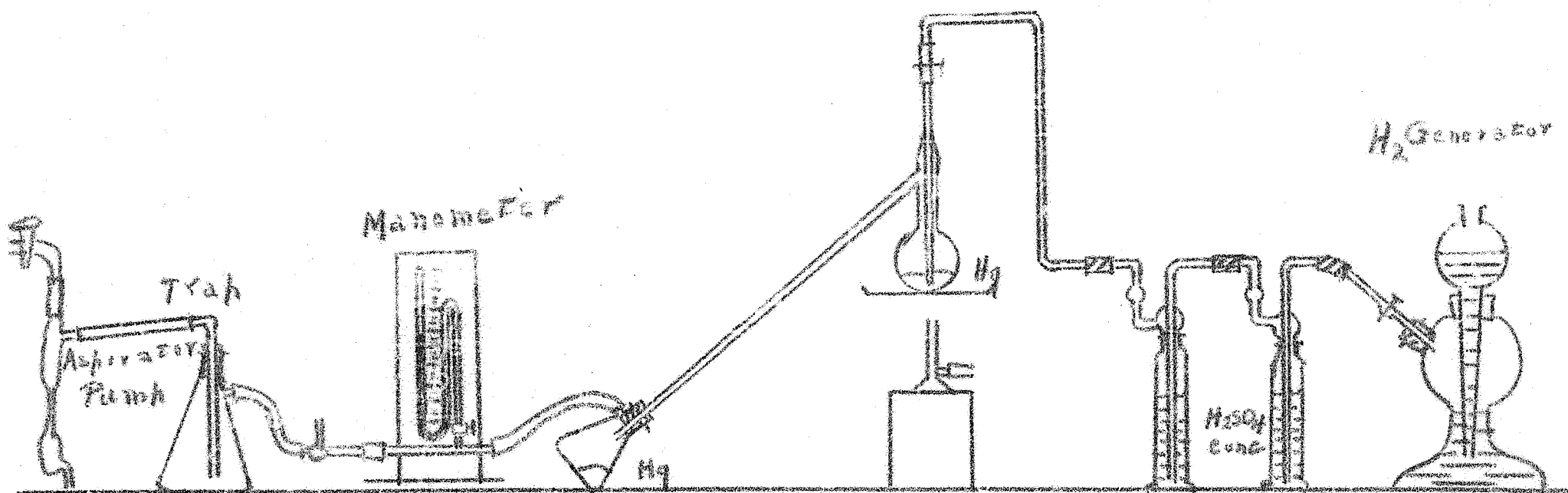
In determining pH values by indicators a series of standard "buffer" solutions whose pH values are known are prepared, and to these are added a definite amount of the corresponding indicator. The colours so produced are a standard for comparing colours produced in solutions of unknown pH value. A list(2) of indicators and of standard buffer solutions are given both by Sørensen and Clark and Lubs.

What is meant by buffer action is explained by referring to the consideration of Na_2CO_3 . Due to hydrolysis a definite H^+ concentration is produced. If to this solution we add hydrochloric acid there is a tendency to increase the H^+ concentration, but as has been indicated this would be removed to form HCO_3^- , accompanied by an increase of OH^- concentration, and although a considerable amount of H^+ might be added to the solution the increase of H^+ concentration would be comparatively very small. This power of certain solutions to resist change in H^+ concentration has been termed buffer action.

The colorimetric method is a secondary method of determining pH values, and at best is only accurate to the first decimal place. For any work requiring a higher degree of accuracy, or in plotting titration curves, the indicator method would be impracticable.

1.--- "Clark and Lubs." J. Biol. 2, 1, 109, 191, (1917).

2.--- "The Determination of Hydrogen Ions." W. Mansfield Clark."



Distillation of Mercury
Diagram I

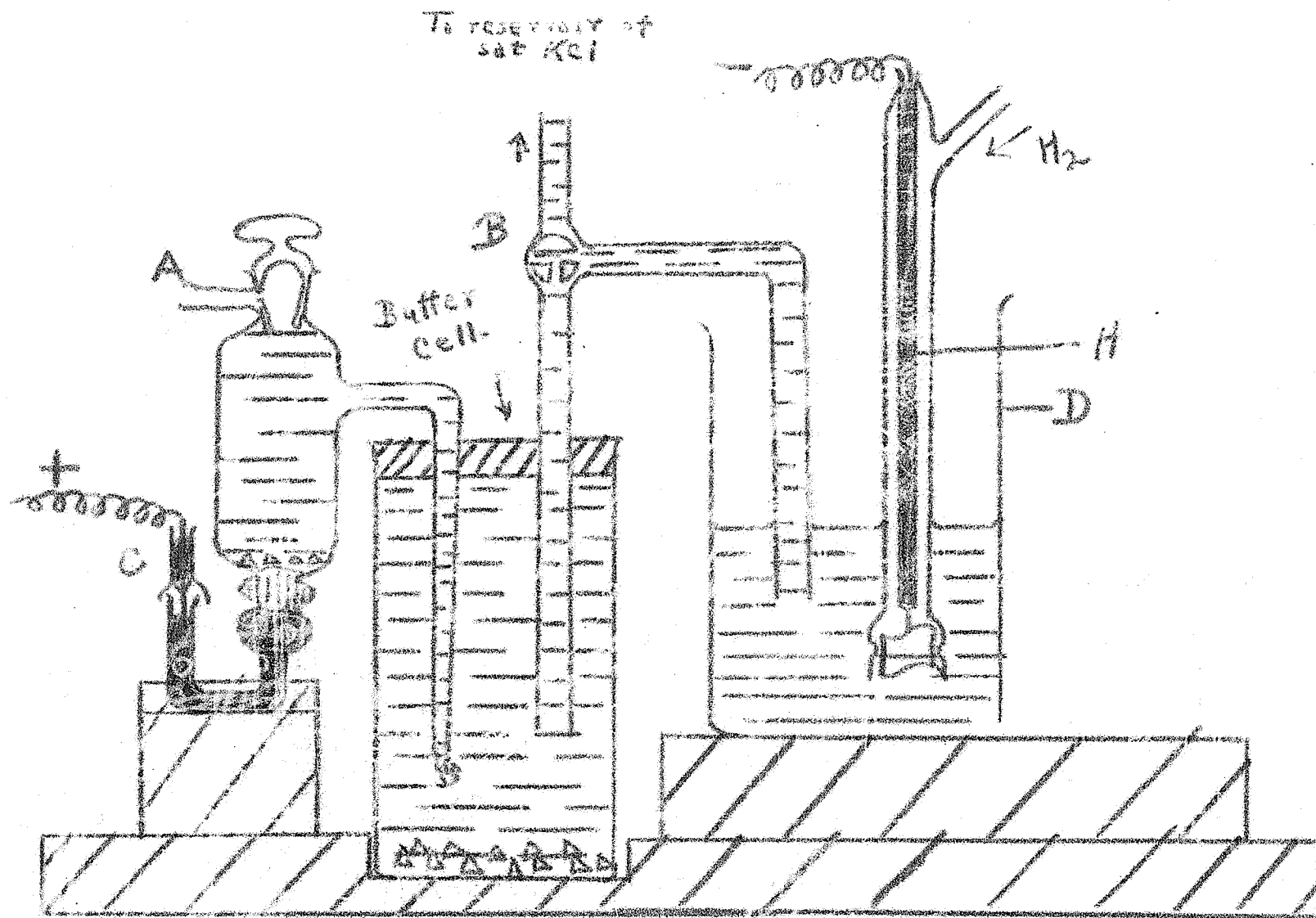
The hydrogen electrode used was that known as the Hildebrand bubbling type(1). Such an electrode is adapted for use in an open vessel, and is admirably adapted for measuring hydrogen ion concentration during a titration.

The saturated calomel cell was used to compare the potential of the hydrogen electrode, with that of the theoretical normal hydrogen electrode.

This type was chosen, because the temperature coefficient is very low, also slight changes in the concentration of the KCl solution do not effect the voltage readings to such an extent, as would corresponding changes in the concentration of a N/1 or N/10 electrode. The resistance of the gas chain is also lowered by using a saturated KCl solution, and hence the sensitivity is increased; and when using a saturated KCl solution in the buffer cell, connecting the calomel with the hydrogen electrode, no special precaution to avoid diffusion need be taken.

The mercury used in the calomel cell was purified by washing with dilute nitric acid, and then distilling, under reduced pressure, in a current of hydrogen. The accompanying diagram(1) shows the apparatus used in this distillation.

The calomel was Kahlbaum's analyzed. It was washed several times with distilled water, ground in an agate mortar with 1 cc. of the pure mercury, placed in a well washed bottle, and shaken on a shaking machine, with saturated KCl for three hours, the calomel being allowed to settle at hourly intervals, the super-

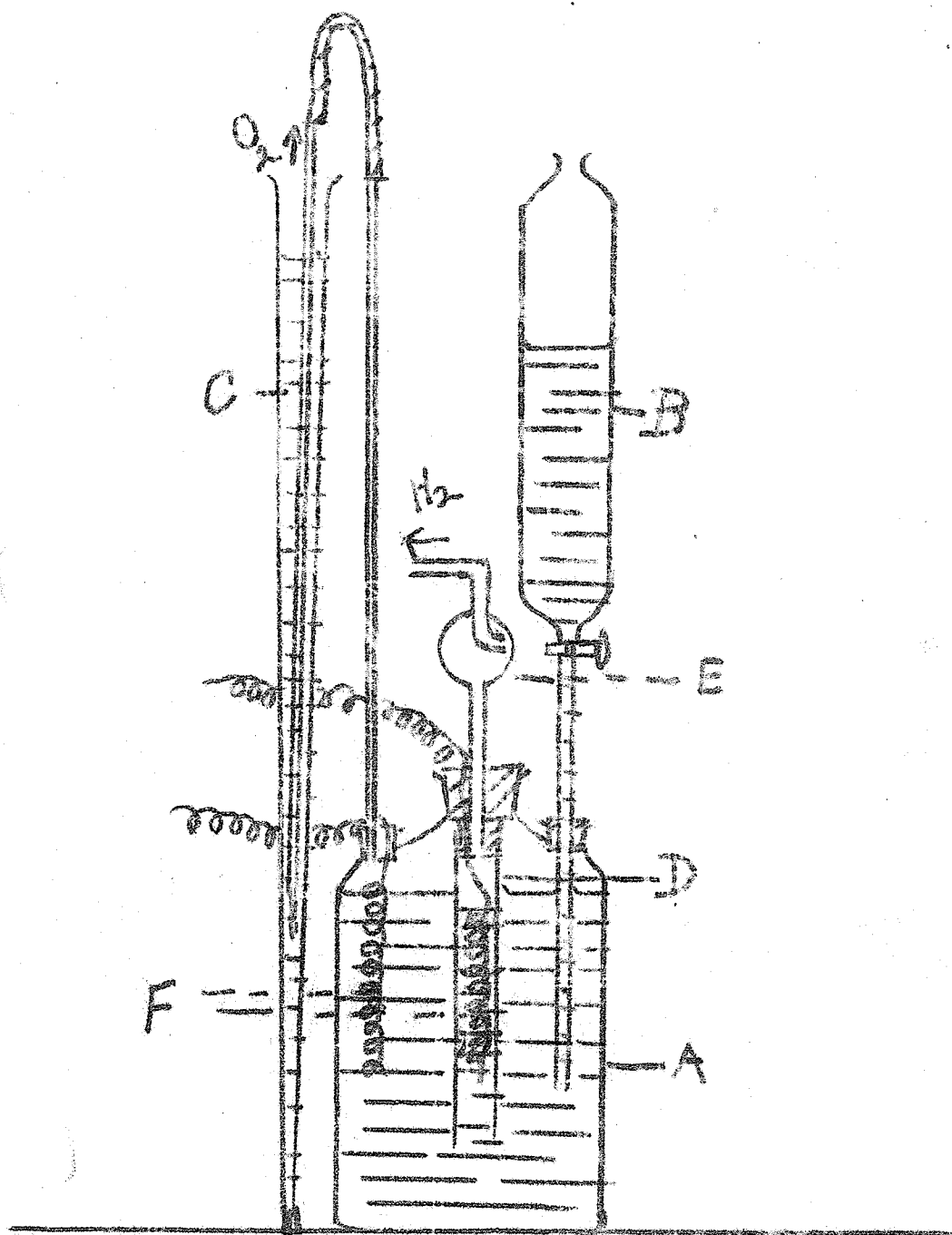


The Gas Chain
Diagram II

matant liquid decanted off, and fresh saturated KCl being added. To the calomel paste fresh saturated KCl was added, and the whole shaken for three hours, so that the solution was thoroughly saturated with Calomel. The KCl used was a sample of Baker's analyzed. The solution was prepared by shaking an excess of salt with distilled water for three hours.

The calomel cell was then filled by pouring ⁱⁿmercury (the type of cell used, and the amount of mercury are shown in diagram (2)). this was covered with a fairly thick layer of the calomel paste, a few crystals of KCl were added to maintain saturation, and the cell was finally filled by attaching a piece of rubber tubing to the glasstube at A, opening the combined stopper and stop cock, immersing the end of the side arm in the solution, saturated with KCl and Calomel, and sucking the solution into the cell until it was filled to the bottom of the stop cock.

A large sized straight walled weighing bottle of about 150ccs capacity was used as a buffer cell. The side arm of the calomel electrode vessel, and the siphon arm, which completed the connection to the solution being measured, passed through a cork previously immersed in melted paraffin. The cell was filled with saturated KCl, a layer of KCl crystals placed in the bottom, and the cork finally made tight with sealing wax. The siphon arm was provided at B, with a three way stop cock, by which connection could be made to a reservoir (not shown in the diagram) of saturated KCl, permitting the open end of the tube to be washed with KCl, in order to remove any liquid which may have entered by diffusion during a measurement. D is a 150 ccs. beaker



An Electrolytic Hydrogen
Generator
Diagram III

containing the solution whose pH value is to be determined. The whole was mounted on a wooden base, to which a support for the hydrogen electrode was also attached, binding posts being provided for the leads. C is a glass cover for the calomel electrode vessel, making connection with the mercury by means of a platinum wire fused through the bottom. The upper portion is filled with mercury to provide contact with the copper wire leading to the potentiometer.

The hydrogen used was obtained from an electrolytic generator (Diagram (3)) constructed from a large jar provided with three openings the centre opening being large enough to admit a piece of hard glass tube about 3cm. in diameter. This opening was fitted with a large rubber stopper through which passed a glass tube provided with a trap E to prevent the electrolyte from being carried over. The tube passed through a smaller cork which fits tightly into the end of a hard glass tube D. B is a large sized separatory funnel, which serves as a reservoir for the electrolyte, and also a pressure column, in order to force the gas through the washing bottles. The outlet for the Oxygen C is immersed in a tall narrow cylinder of water, in order to provide an outlet with sufficient back pressure.

The electrodes F are coils of nickel wire, the coil in D was surrounded by a rubber ring at either end the free end of the wire being bent so as to be free from the glass tube, thus preventing breakage due to the heat produced should the current form an arc between the electrode and the electrolyte.

Holes were punched in the rubber stoppers through which the

leads to the electrodes were passed as shown in the diagram. In operation the electrode in D is made the Cathode. The hydrogen liberated passes up through the trap E as indicated. The oxygen escapes through the tube U. The oxygen cannot escape until the pressure is equal to that of the column of water from the open end of C to the surface of the liquid in the tall cylinder. The Oxygen then exerts a pressure on the surface of the liquid in A, forcing it up into B until the difference in the levels in D and B is equal to the pressure at C. If the outlet for hydrogen be closed the pressure of gas forces the electrolyte in D away from the electrode and the current is automatically controlled.

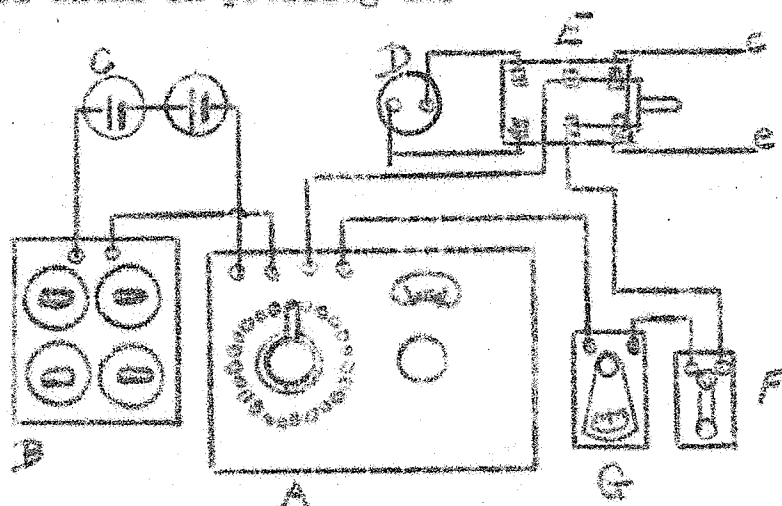
The generator was connected by means of a T tube to a large hydrogen Kipp which served as a ~~manometer~~ reservoir to store the gas. The other arm of the T tube was connected to the chain of washed bottles.

The gas was washed by passing successively through alkaline potassium permanganate, alkaline pyrogallate, and distilled water.

The Students Potentiometer.

(Loeds and Northup Coy.) was used to measure the E.M.F. of the gas chain. Diagram(4) shows the potentiometer set up. A is the combined bridge and slide wire; B a rheostat to regulate the current flowing through A from the battery C; D is a standard cadmium cell; E a double throw switch connecting either the standard cell or the gas chain to the potentiometer. The lead C is connected with the calomel electrode, e with the hydrogen electrode. F is a single contact key; G is an enclosed lamp and

scale galvanometer having a resistance of 1000 ohms. To measure an unknown E.M.F. A is set at the voltage of the standard cell, the switch E is then thrown over towards the standard cell D, and then tapping the key F, the resistance B varied until the Galvanometer indicates that no current is flowing through the circuit. E is then thrown over towards the E.M.F. to be measured, A adjusted until on pressing the



The Potentiometer Set-up
Diagram IV

key F no current flows through the Galvanometer. The voltage is then read off directly.

A stirrer directly connected to an electric motor, mounted on a stand so that adjustments both vertically and horizontal could be made, and a specially constructed burette completed the apparatus. The burette was modified by sealing on, in place of the ordinary stop cock, a piece of glass tube about 12 inches long provided with a stop cock at the centre. This was bent at right angles above the stop cock, and again bent vertically below the stop cock, to provide an set off of about five inches.

so that the electric stirrer could be placed directly over the beaker D (diagram 2). The free end was drawn out to provide a suitable tip.

The Method of making an electrometric titration curve.

(a) The solution to be titrated, or in the case of a substance only slightly soluble in water, e.g. CaCO_3 , the suspension was placed in the beaker D (diagram 2) which was removed from its position for this purpose. The beaker was half filled with the solution or suspension. The acid solution poured into the burette, and the meniscus adjusted to zero in the usual manner. The strength of the acid solution was adjusted so that the titration was complete within one filling of the burette. The stop cock at B was turned to connect the reservoir of saturated HCl with the open end of the siphon arm, and sufficient HCl run through it to wash it out thoroughly. The stop cock was turned to connect the siphon to the buffer cell. D was placed in position, the supporting block having been removed, so that the siphon arm was not immersed in the solution. The hydrogen electrode was immersed in the solution, and hydrogen bubbled through it until the platinum black was saturated; saturation was attained in about fifteen minutes. The block was placed beneath D, so that the siphon arm was immersed, the electric stirrer placed in position and set in operation, the battery (diagram 4) C balanced against the standard cell D, the switch thrown over to the gas chain and the E.M.F. measured. Sufficient acid was run in from the burette to give a change of 0.005x to 0.010 volts, and the number of ccs. added and the voltage noted. As the

"neutral" point was approached as a drop of acid added was sufficient to cause a large change in voltage. The titration was continued until the voltage readings approached a constant value.

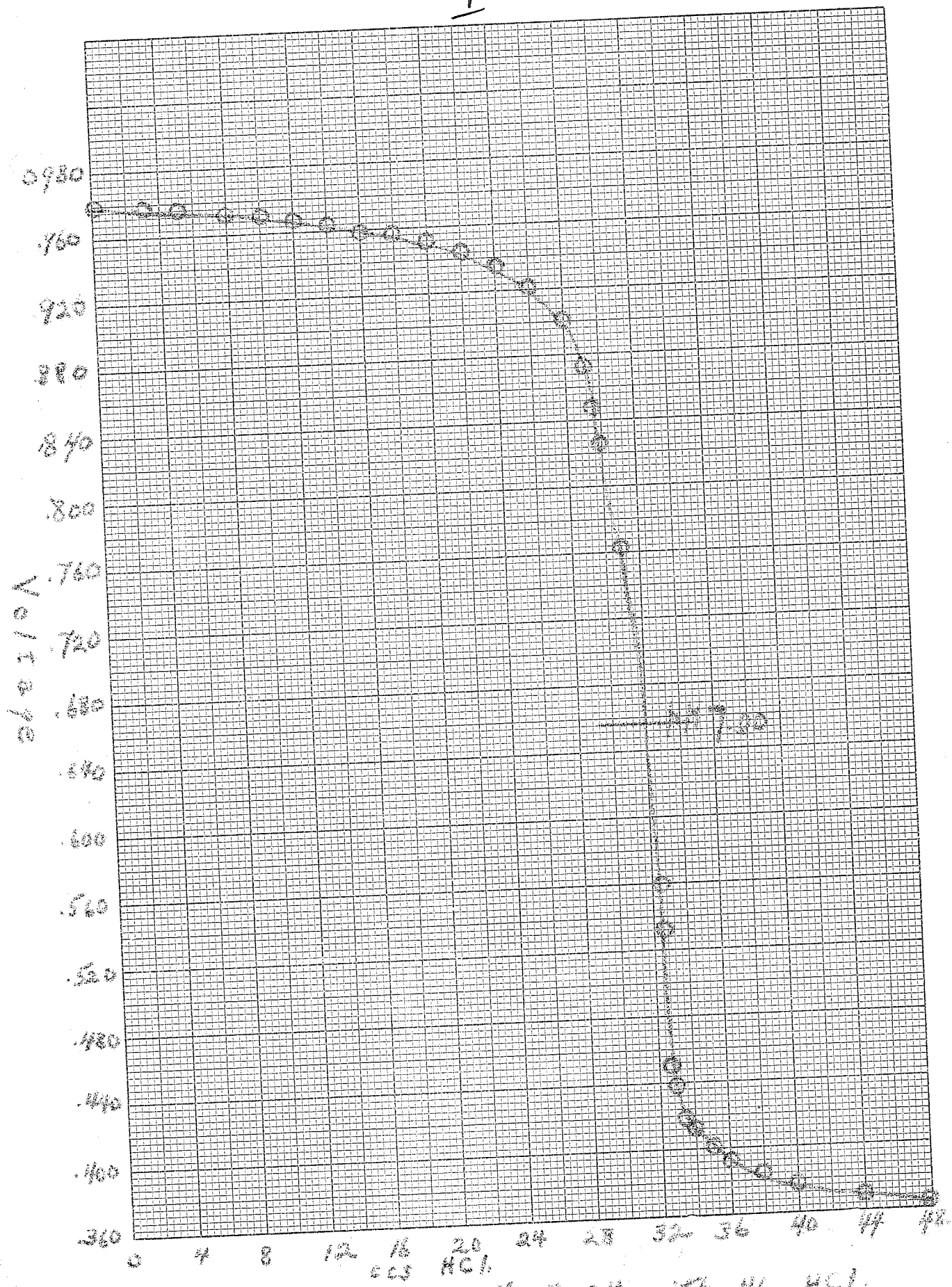
The voltage readings were plotted as ordinates, and the cc. of acid added as abscissae.

(b) Titration with CO_2 or carbonic acid.

It was desired to plot titration curves in which carbonic acid was used to neutralize the base. It was impracticable to use a solution of CO_2 in water, because the strength of solution would not remain constant. The titration was carried out in the following manner. It is not necessary to know the exact amount of acid added, but it is essential that the unit or fractional amount be known. This was accomplished by bubbling a constant stream of CO_2 through the solution, and noting the readings at regular intervals of time. The procedure until the addition of acid is identical with that described. ^{was} A stop watch used to check the time. When the initial reading had been obtained the CO_2 was bubbled through the solution, and as soon as the first bubble appeared the stop watch was set in operation. By constantly tapping the key F, (diagram 4) and adjusting the combined bridge and slide wire so that no current was indicated flowing through the circuit, readings at intervals of one or even of half a minute could be obtained.

The time was plotted as abscissae and the voltage readings as ordinates.

I



Titration Curve of $N/10$ KOH with $N/10$ HCl.

Limit of Accuracy.

The titrations were made in a room thermostated to 20°C with a variation from 19° to 21°C . This variation of temperature (1) would cause a variation of 0.0006 volts. The variation due to change in barometric pressure would be 0.0004 volts.

The saturated KCl used was considered to eliminate the liquid junction potential.

The slide wire of the potentiometer was graduated to 0.0005 volts. A variation of this amount gave a variation of 4 mm millimeters either side of the zero point of the galvanometer. Readings accurate to one millivolt could be made.

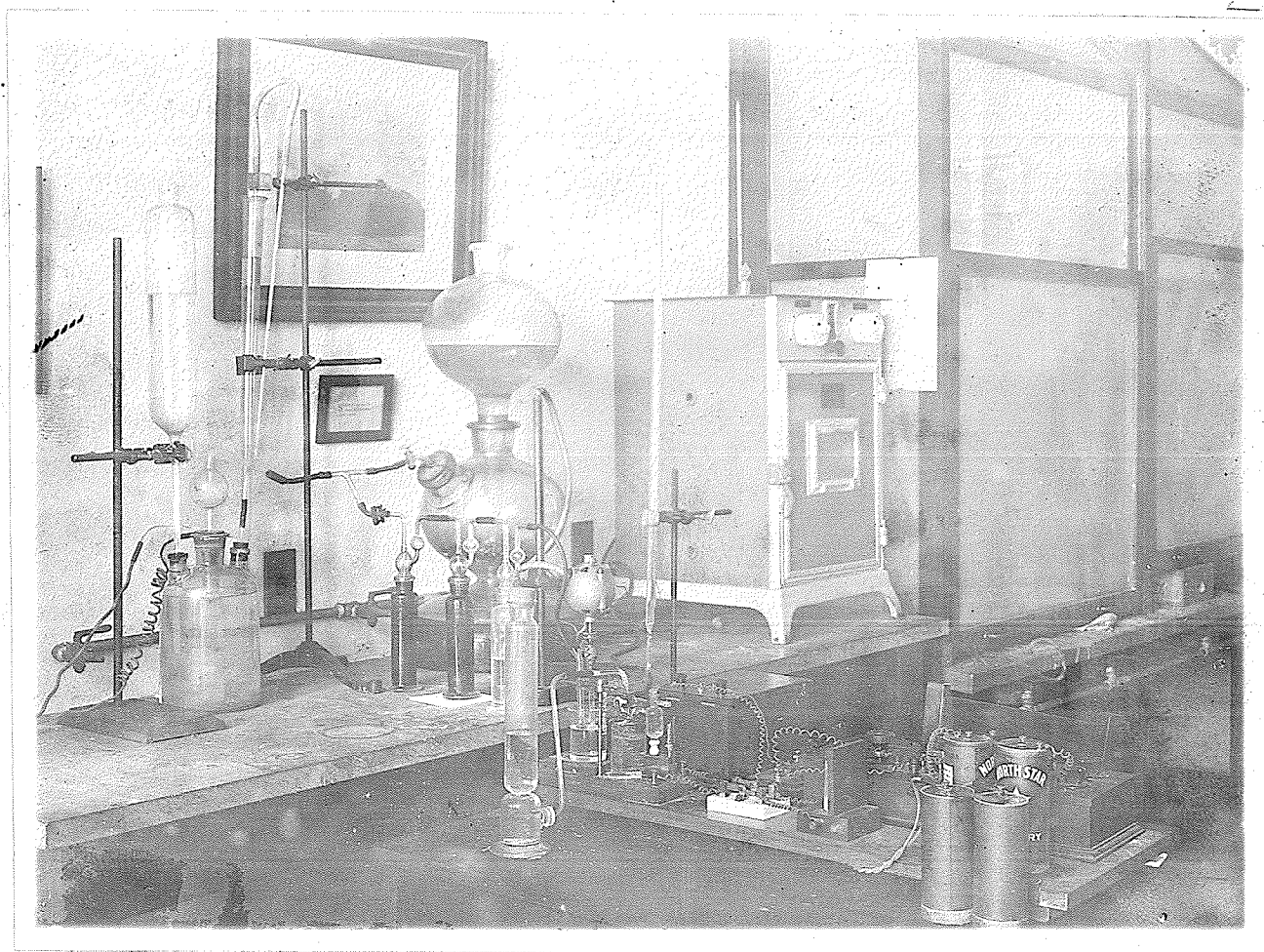
The limit of accuracy is then 0.001 volts.

A titration curve for NaOH and HCl was measured and plotted to determine the degree of accuracy of the calomel electrode. Examination of the curve No. 1 shows that the neutral point agrees with the theoretical pH value of 7.00.

Wherever possible the pH value of the solution was determined colorimetrically and in each case the values agreed to 0.1 of the pH value, e.g. SrCO_3 colorimetrically determined gave a pH of 9.2 the voltage of the gas chain gave a value of 9.1.

An indicator was present in each titration and the colour change agreed with the theoretical pH value for such a change. The curves can only be plotted accurately to 0.004 volts. Readings accurate to 0.001 volts are sufficiently accurate for the plotting of such curves.

1.--Die Wasserstoffionenkonzentration Berlin, "L. Michaelis" (1914).



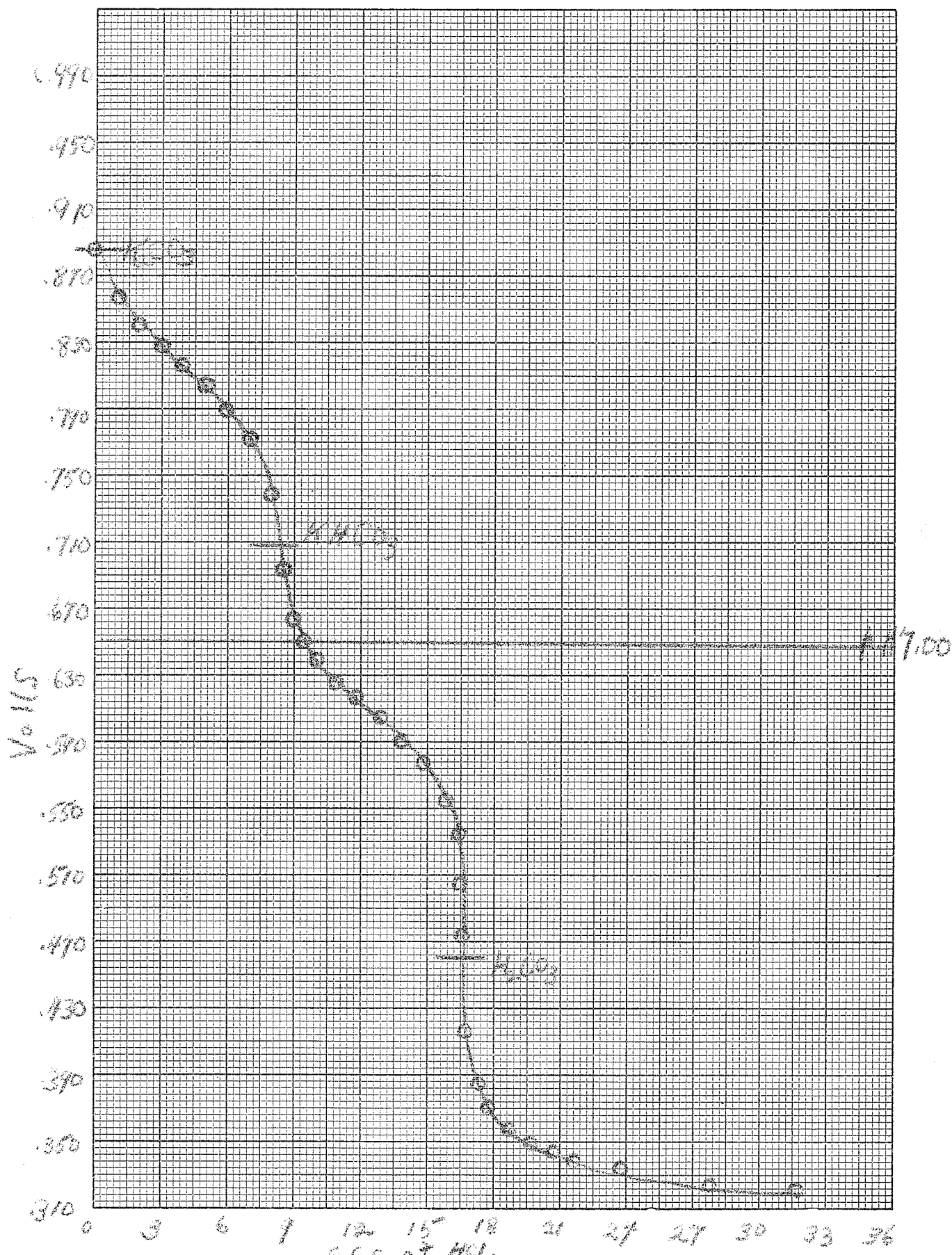
*The Electrometric Titration Apparatus
Used in this Research.*

TWENTY THREE

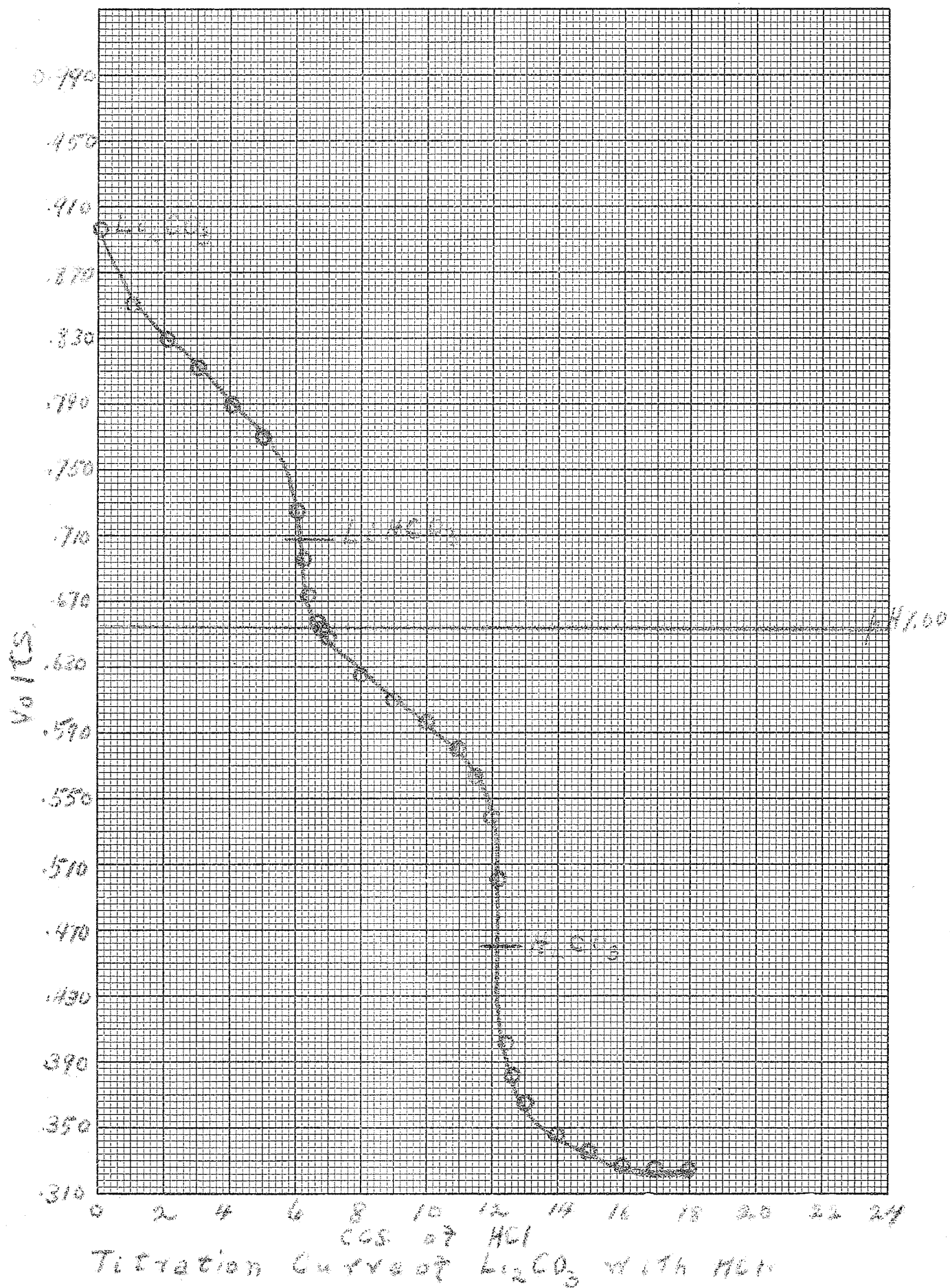
The determination of the equilibrium existing between solutions of Calcium Sulphate, Calcium Carbonate and Carbon Dioxide in water, and admixtures of these entailed the determination of the degree of hydrolysis of the salts concerned. Hydrolysis can be measured by means of electrometric titrations. Curve No. 1 is a typical electrometric titration curve. The first measurement noted was that for the pure base NaOH. On addition of acid very little change was produced in the voltage readings, or the product of the (H) (1) due to the acid added, and the (OH) , due to the base, is greater than 10^{-14} and consequently they unit to form H_2O , but the original concentration of OH is so much greater than that of the H added that the amount of OH removed is very small compared to the amount present, consequently the ratio change of (H) to (OH) would be very slight this is shown on the curve by the upper portion remaining almost horizontal. As more and more hydrogen ion is added the increase becomes more apparent, and eventually a point is reached where the addition of a very small amount of acid causes a large decrease in the voltage of the gas chain, indicating a marked increase in the (H) . There is then a gradual falling off of the (H) as the concentration approaches that of the acid used, voltage readings of the gas chain become more or less constant, and the curve again approaches the horizontal. It can be shown mathematically (2) that the center point of the "drop" on the curve indicates the point at which an equivalent amount of acid has been added to the amount of base present. This point will be

1. Ions which are enclosed in brackets such as (H) indicate ionic concentration.
2. J. Am. Chem. Soc. 35, 847, (1913).

II



III



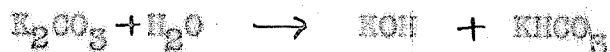
termed the end point for the salt produced, e.g. in Curve No. I it would be the end point for NaCl. The term neutral Point will be used for that point on the curve which has a pH. value of 7 or a(H) of 1×10^{-7} indicating the voltage reading which would be obtained from pure water. In curve No. I the end point for NaCl corresponds with the neutral point. If we had used a weak acid, such as acetic acid, the end point for sodium acetate would not correspond with the neutral point, (1) but would correspond to a much higher voltage reading of the gas chain, indicating a lower(H) than pure water, or the salt would have undergone a basic hydrolysis.

It is also possible to obtain a titration curve for a carbonate titrated with an acid.

Curve no. II was obtained by titrating K_2CO_3 with HCl and no. III. by titrating $LiCO_3$ with HCl.

The initial reading indicates a(H) much lower than that of pure water, i.e. the salt in solution undergoes a basic hydrolysis.

Potassium Carbonate undergoes hydrolysis according to the equation.



then if H be added (page 28) part is removed to form more HCO_3 as shown by the consideration of the progressive hydrolysis of Na_2CO_3 . When sufficient H has been added to convert all the $CO_3^{''}$ into HCO_3' a rapid decrease in the voltage readings of the gas chain is noted, and an almost vertical drop occurs on the curve. The center point of this drop is the end point for $KHCO_3$, that is sufficient acid has been added to satisfy the equation.



The KHCO_3 produced undergoes hydrolysis according to the equation

$$\text{KHCO}_3 + \text{H}_2\text{O} \rightarrow \text{KOH} + \text{H}_2\text{CO}_3$$

As H^+ is added it unites with the OH^- present produced from the dissociated KOH to form H_2O . In order that the ionic product for water remain constant more H^+ must be produced from the water, at the same time H^+ unites with HCO_3^- to give undissociated H_2CO_3 .

We have in solution the following equilibria.

$$\frac{(\text{H}^+)(\text{HCO}_3^-)}{(\text{H}_2\text{CO}_3)} = K_1 \text{-----(1)}$$

$$\frac{(\text{K}^+)(\text{HCO}_3^-)}{(\text{KHCO}_3)} = K_2 \text{-----(2)}$$

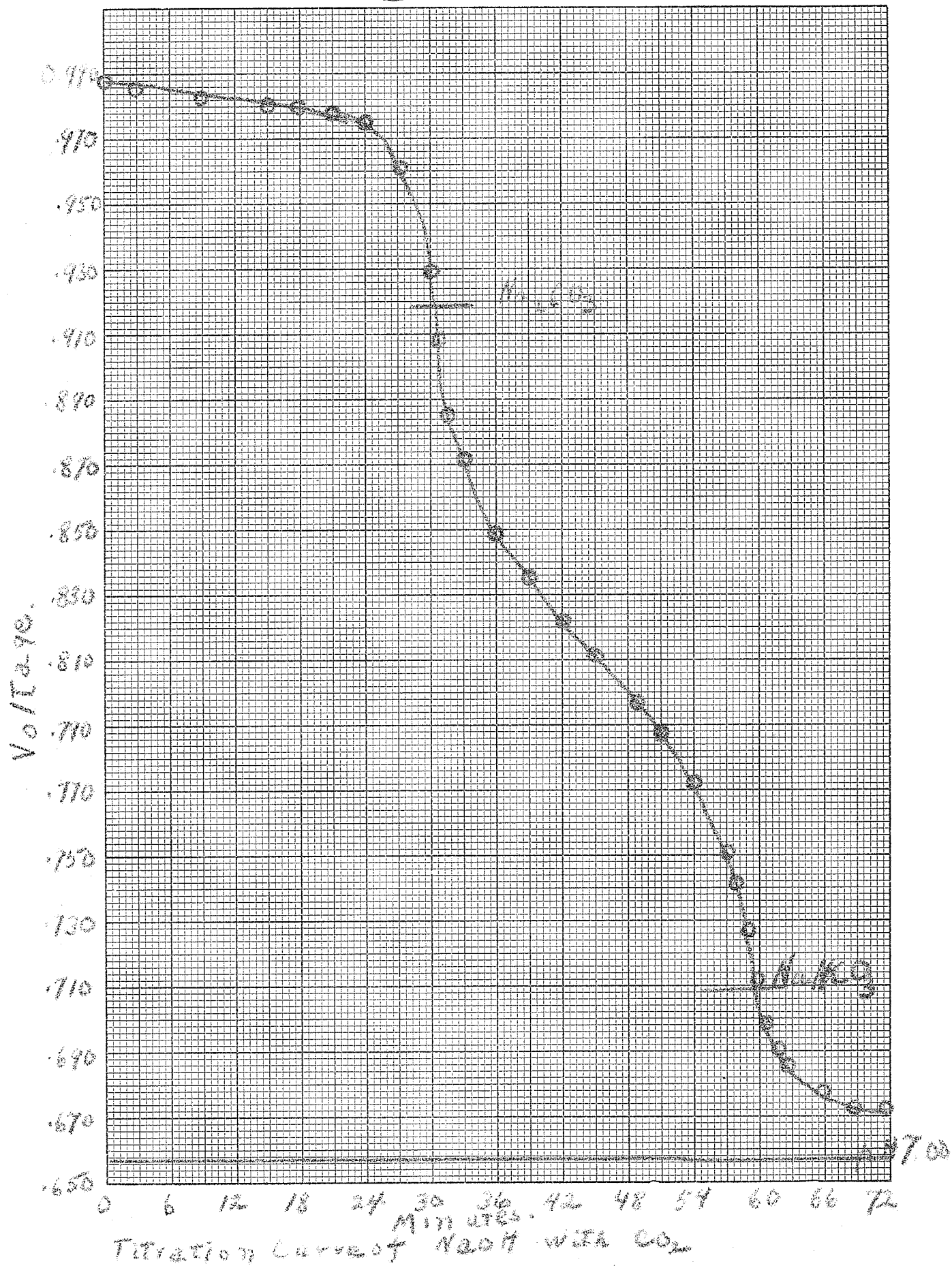
At first there is a large amount of KHCO_3 present. Consequently (HCO_3^-) in (2) will be large, and by increasing this concentration in (1) the concentration of H^+ will diminish so that K remains constant; but by increasing the (H^+) by addition of acid we may reach a point (since K is very small) where the carbonic acid present is practically undissociated, and as we approach this point the increase of (H^+) as shown, by a rapid decrease in voltage of the gas chain, is rapid, and we have a second drop in the curve. The center point of this drop is the point at which sufficient acid has been added to satisfy the equation



This point is the end point for carbonic acid, since KCl does not hydrolyse. Sufficient HCl has been added to convert all of the CO_3^{--} present at the beginning to H_2CO_3 .

The consideration of the curve for LiCO_3 is identical with that for K_2CO_3 .

IV

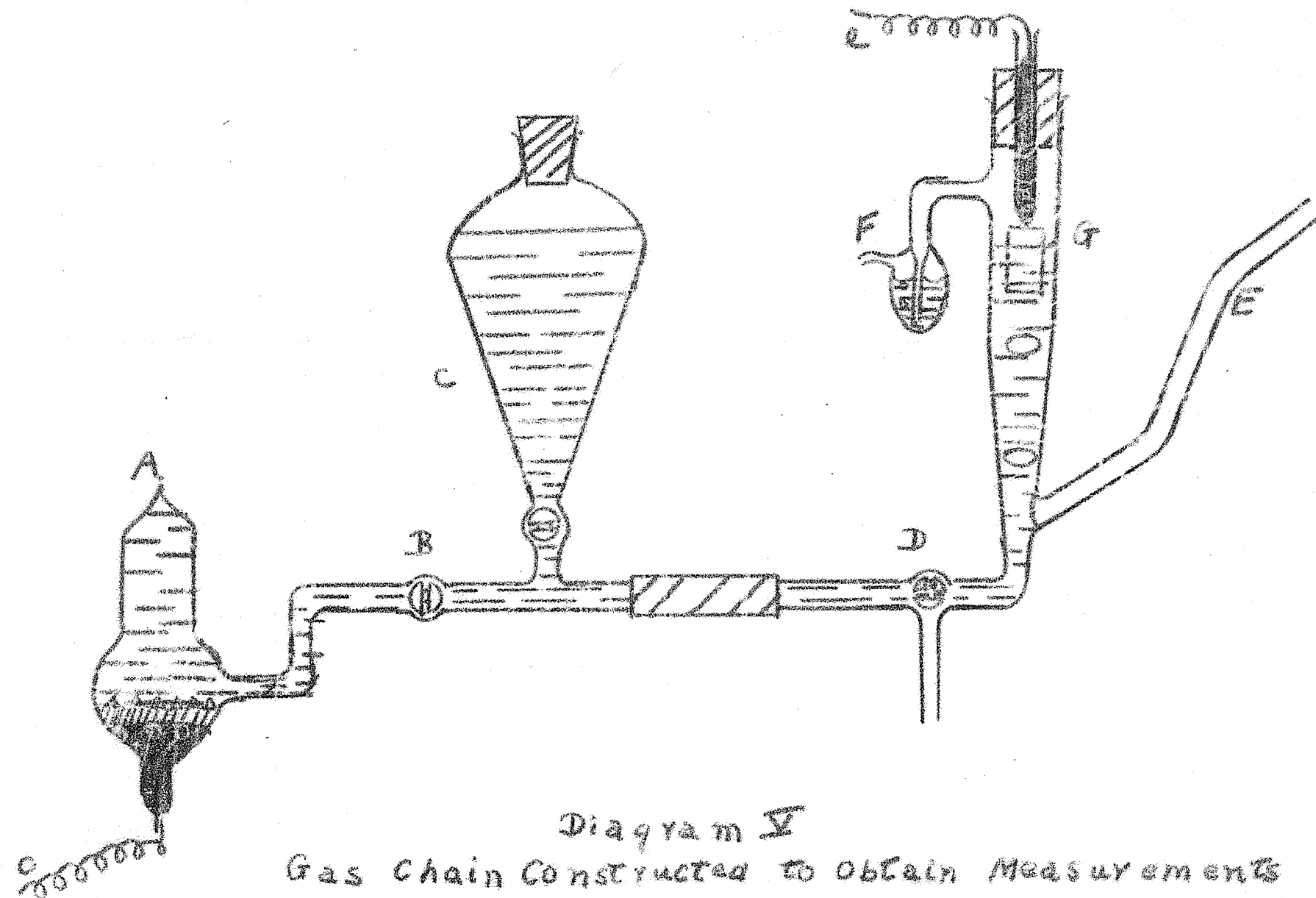


At the end point for KHCO_3 and LiHCO_3 only half as much acid need be added as for the end point for H_2CO_3 . Referring to curve no. II. we find that to reach the end point for H_2CO_3 16.8 ccs. were added; and for NaHCO_3 8.4 ccs; in no. III. 6.1 ccs. were added to attain the end point for LiHCO_3 , and 12.2 ccs. for H_2CO_3 .

If we can obtain an end point for KHCO_3 and for H_2CO_3 then it should be possible to obtain end point for Na_2CO_3 and NaHCO_3 if a solution of NaOH be titrated with CO_2 in the manner described (page 31).

Curve no. IV. shows the result obtained in such a titration. At the beginning, as CO_2 is bubbled through the solution, there is only a slight increase in H^+ , but finally there is a rapid increase, again a gradual falling off of the rate of increase, and a second drop. The first drop is the end point for Na_2CO_3 the second drop for NaHCO_3 . A constant current of CO_2 was obtained from a cylinder of compressed gas, and the rate of flow regulated by a valve. It required 30 minutes to reach the end point for Na_2CO_3 , and 60 minutes to reach the end point for NaHCO_3 , which from a theoretical consideration is exactly what would be expected.

An attempt was made to discover end points for the carbonates of Calcium by titration of Ca(OH)_2 with CO_2 , but the curve instead of resembling no. IV. resembled no. I, indicating that the normal carbonate alone existed. This possibility of the non existence of bicarbonates carried the research beyond the original problem and numerous electrometric titrations were made in an endeavor to ascertain whether an end point for the bicarbonate could be obtained, but as will be shown later no such end points



†

appeared on the curves. The research was then extended to include the carbonates of Magnesium barium and strontium.

The electrometric titration of calcium hydroxide with sulphuric acid shows calcium sulphate to be a ~~neutral~~ neutral salt; but if a solution of calcium sulphate be prepared, the voltage readings of the gas chain indicates an acidic hydrolysis. The colorimetric method however shows that a solution of CaSO_4 has the same (H) as pure water.

An enclosed type of hydrogen electrode was constructed in order that more accurate measurements could be made on CaSO_4 solutions. Diagram No. V illustrates the type of electrode. A is a saturated calomel electrode, B a stop cock greased at both ends which is closed. Electrical contact is secured through the film of saturated KCl surrounding the ungreased portion of the stop cock. C is a reservoir ~~off~~ of saturated KCl solution.

The calomel electrode is connected to the hydrogen electrode vessel by means of a short piece of rubber tubing. D is a three way stop cock which provides a means of emptying the electrode vessel, F is a liquid valve providing an escape for the H_2 lead in through E, G is the platinum electrode coated with platinum black and partly immersed in the ~~ex~~ solution as shown. The electrode vessel is provided with a one holed rubber stopper through which a glass tube filled with mercury passes providing electrical connection to the platinum plate in the usual manner. The leads c and e are connected to the corresponding positions on the potentiometer (Diagram IV.). In

operation the hydrogen electrode vessel is filled with the solution to be measured, hydrogen is bubbled through E, and the amount of liquid adjusted by running the excess out through D. The stop cock connecting the reservoir of saturated HCl is opened, and the rubber tubing pressed together forcing a small amount of the liquid into G. This stop cock is closed and D is turned as indicated in the diagram. On releasing the rubber tubing the solution from the electrode vessel passes through the stop cock producing the liquid junction in the wide part of the tube thus avoiding undue potential due to junctions in capillary tubes.

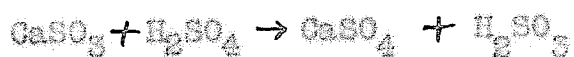
A saturated solution of CaSO_4 was placed in the hydrogen electrode vessel, and the voltage of the gas chain noted at frequent intervals as hydrogen was bubbled through the electrode vessel. The voltage readings increased rapidly until saturation was attained, and then more slowly, and remained constant at .701 volts. This voltage indicates that CaSO_4 undergoes a basic hydrolysis.

The anomalous behaviour is explained by the fact that the SO_4^{--} may be reduced by hydrogen under certain conditions. Hydrogen absorbed in platinum black is very active chemically, and should SO_4^{--} be reduced an oxidation reduction potential would be established. This would have a tendency to lower the voltage of the gas chain, the amount of lowering depending on the ease with which the radicle is reduced. The reduction of calcium sulphate would proceed as indicated by the following equation

$$\text{CaSO}_4 + 2\text{H} \rightarrow \text{CaSO}_3 + \text{H}_2\text{O}$$

When all of the CaSO_3 present had been reduced the readings of the gas chain would be an indication of the (H) of the solution of CaSO_3 . Sulphurous acid is weak acid, whereas $\text{Ca}(\text{OH})_2$ is a strong base, consequently, as would be expected, CaSO_3 undergoes a basic hydrolysis.

In the electrometric titration of $\text{Ca}(\text{OH})_2$ with sulphuric acid fresh SO_4^{2-} ions is being constantly added, and any CaSO_3 that might be formed would be again converted to the sulphate according to the equation.



In solution then an equilibrium would be established between H_2SO_3 , H_2O and SO_2 (produced from H_2SO_3). The H_2 gas passing through the solution would remove the SO_2 thus decreasing the amount of H_2SO_3 produced, and as this amount is at any time very small it would be removed completely from solution, and the (H) would be due only to the equilibrium established between $\text{Ca}(\text{OH})_2$ and H_2SO_4 .

Hence the electrometric titration confirmed by the colorimetric determination of the (H) concentration of solutions of CaSO_4 is a reliable measurement of the (H) concentration of solutions of CaSO_4 .

The experimental results which follow have all been verified by duplicate measurements, but only in a few instances has it been practicable to plot duplicate curves.

Preparation of a solution of $\text{Ca}(\text{OH})_2$ in H_2O .

A solution of $\text{Ca}(\text{OH})_2$ was prepared by igniting a pure sample of calcium oxide at the temperature of the blast lamp for five hours, and dissolving it in conductivity water prepared by the

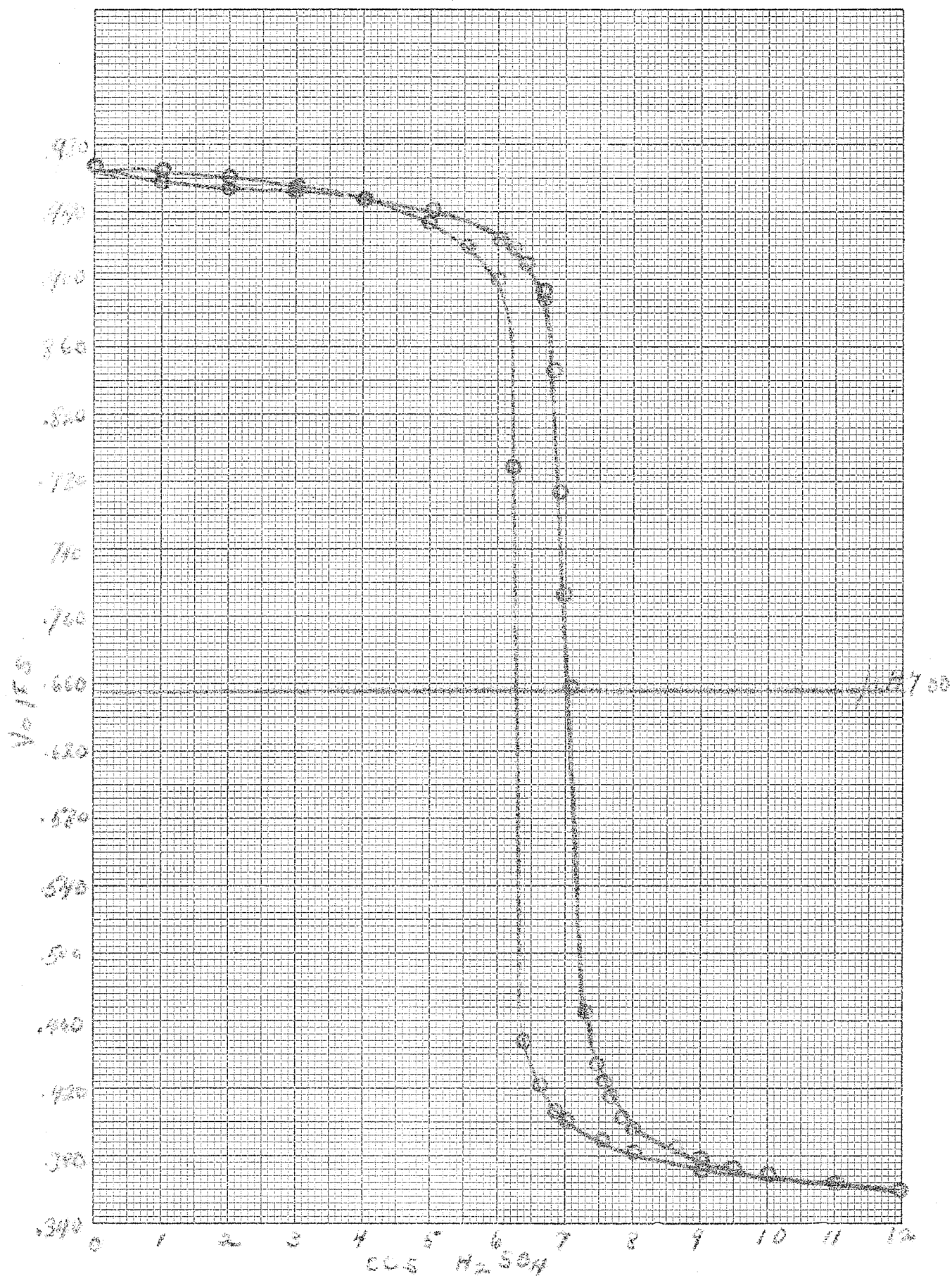
Electrometric Titration of $\text{Ca}(\text{OH})_2$ with H_2SO_4 .

No. 1

No. 2

ccs.	volts.	ccs.	volts.
0	.968	0	.969
.2	.958	1.0	.964
1.0	.957	2.0	.961
2.0	.955	3.0	.958
3.0	.953	4.0	.947
4.0	.948	5.0	.935
5.0	.942	5.5	.919
6.0	.925	6.0	.880
6.2	.920	6.2	.790
6.4	.880	6.4	.449
6.6	.895	6.6	.422
6.7	.878	6.8	.408
6.8	.858	7.0	.400
6.9	.775	7.5	.389
7.0	.714	8.0	.381
7.2	.661	9.0	.372
7.3	.464	10.0	.367
7.4	.433	11.0	.364
7.5	.422	12.0	.361
7.6	.415		
7.8	.403		
8.0	.396		
8.2	.391		
8.6	.385		
9.0	.378		
9.5	.373		
10.0	.369		
12.0	.358		

V



Titration Curves of $\text{Ca}(\text{OH})_2$ with H_2SO_4

method described by Boysfield.(1)

The Electrometric Titration of $\text{Ca}(\text{OH})_2$ with H_2SO_4 .

An electrometric titration of $\text{Ca}(\text{OH})_2$ with H_2SO_4 was carried out, and the results are shown graphically in curve NO.V. The high initial reading is due to the small (H) of the solution of $\text{Ca}(\text{OH})_2$. Examination of the curve shows that the end point for CaSO_4 corresponds with the neutral point. Consequently Calcium Sulphate is to be considered as a neutral salt.

Titration of $\text{Ca}(\text{OH})_2$ with CO_2 .

An electrometric titration of $\text{Ca}(\text{OH})_2$ with CO_2 was made to determine the degree of hydrolysis of the carbonates of Calcium. The results are shown graphically on curve no. VI. #1 was obtained by titrating a solution of CaO in distilled water with CO_2 , #2 and #3 by titrating a solution of CaO (prepared as described) in conductivity water.

The shape of the curve is similar to no. I and differs entirely from those of the alkali carbonates in which a definite flexure is obtained for the bicarbonates, as well as for the normal carbonates. This was the first indication that $\text{Ca}(\text{HCO}_3)_2$ did not exist in solution. As CO_2 is bubbled through into lime water CaCO_3 is precipitated, and until all of the hydroxide is converted into the normal carbonate no bicarbonate could be formed. At the end point for CaCO_3 the ions in solution omitting those concerned in the products of hydrolysis would be Ca^{++} and CO_3^{--} .

Then as we pass this point as more H is added, due to the reaction

1.---"Boysfield". J. Chem. Soc. 37,740, (1905)

Electrometric Titration of $\text{Ca}(\text{OH})_2$ with CO_2 .

NO. 1		NO. 2		NO. 3	
Minutes	Volts.	Minutes	Volts.	Minutes	Volts.
0	.956	0	.969	0	.968
4.0	.927	1.0	.957	2.0	.964
5.0	.911 2	5.0	.947	4.0	.959
7.0	.813	6.0	.935	6.0	.953
8.0	.775	7.0	.918	7.0	.945
9.0	.728	8.0	.842	8.0	.934
10.0	.674	8.5	.733	9.0	.919
11.0	.658	9.0	.746	10.0 9.5	.876 .900
12.0	.644	9.5	.702	10.0	.876
14.0	.630	10.0	.693	11.5	.856
15.0	.624	10.5	.687	12.0	.785
16.0	.621	11.0	.680	12.5	.737
20.0	.617	12.0	.672	13.0	.714
22.0	.616	13.0	.665	13.5	.703
24.0	.615	14.0	.660	14.0	.692
26.0	.611	15.0	.655	15.0	.679
30.0	.611	16.0	.651	16.0	.666
		18.0	.645	18.0	.647
		22.0	.634	20.0	.635
		26.0	.627	22.0	.628
		28.0	.625	24.0	.627
		30.0	.624	30.0	.624

Bubbling CO_2 through a Saturated solution of CaCO_3 and CaCO_3 suspended in water.

NO. 4.

Minutes Volts.

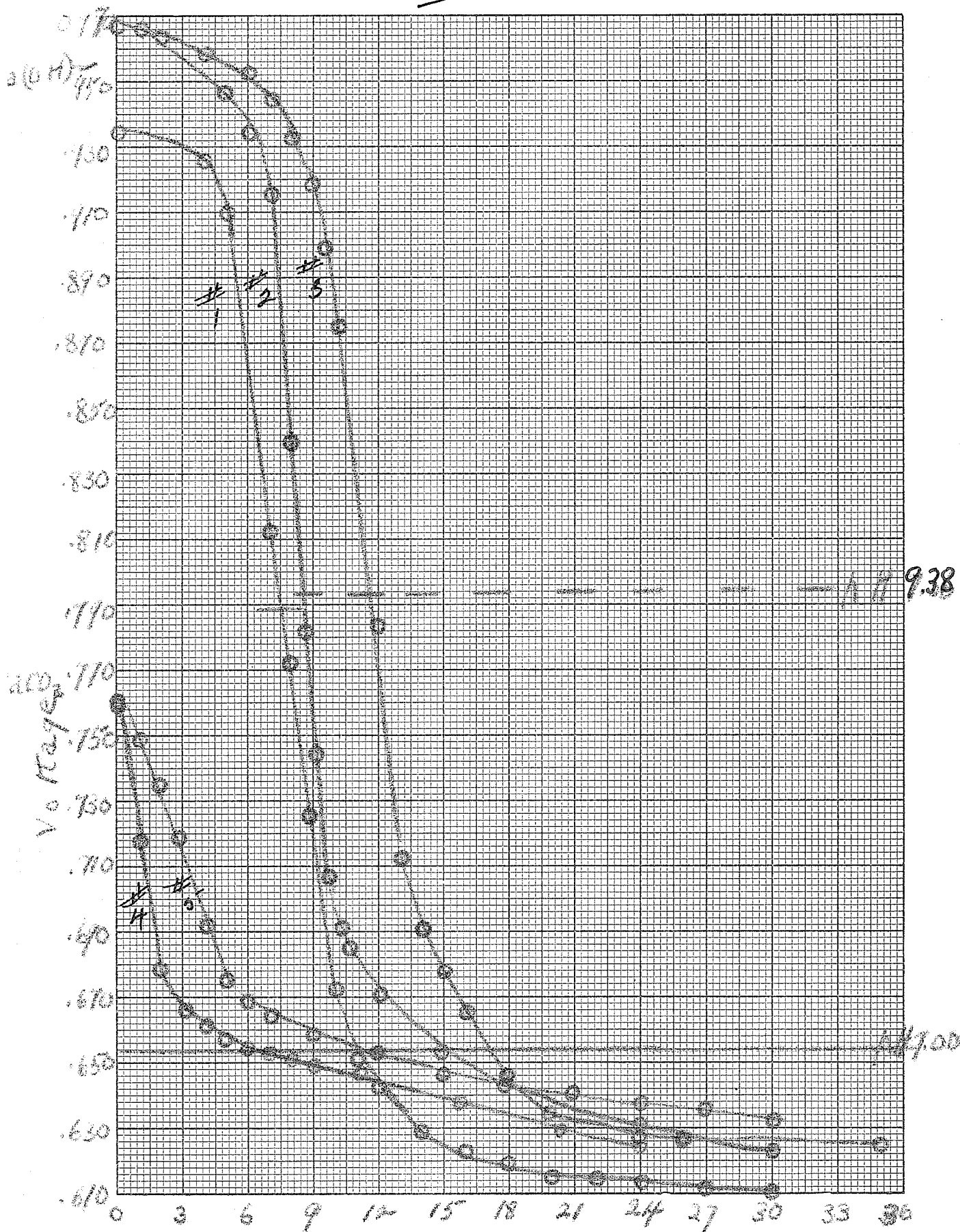
0	.765
.5	.743
1.0	.721
1.5	.690
2.0	.681
2.5	.674
3.0	.668
3.5	.666
4.0	.663
4.5	.661
5.0	.659
6.0	.657
7.0	.654
8.0	.653
10.0	.651
12.0	.650
14.0	.648
16.0	.645
18.0	.635
20.0	.629
24.0	.627

NO. 5.

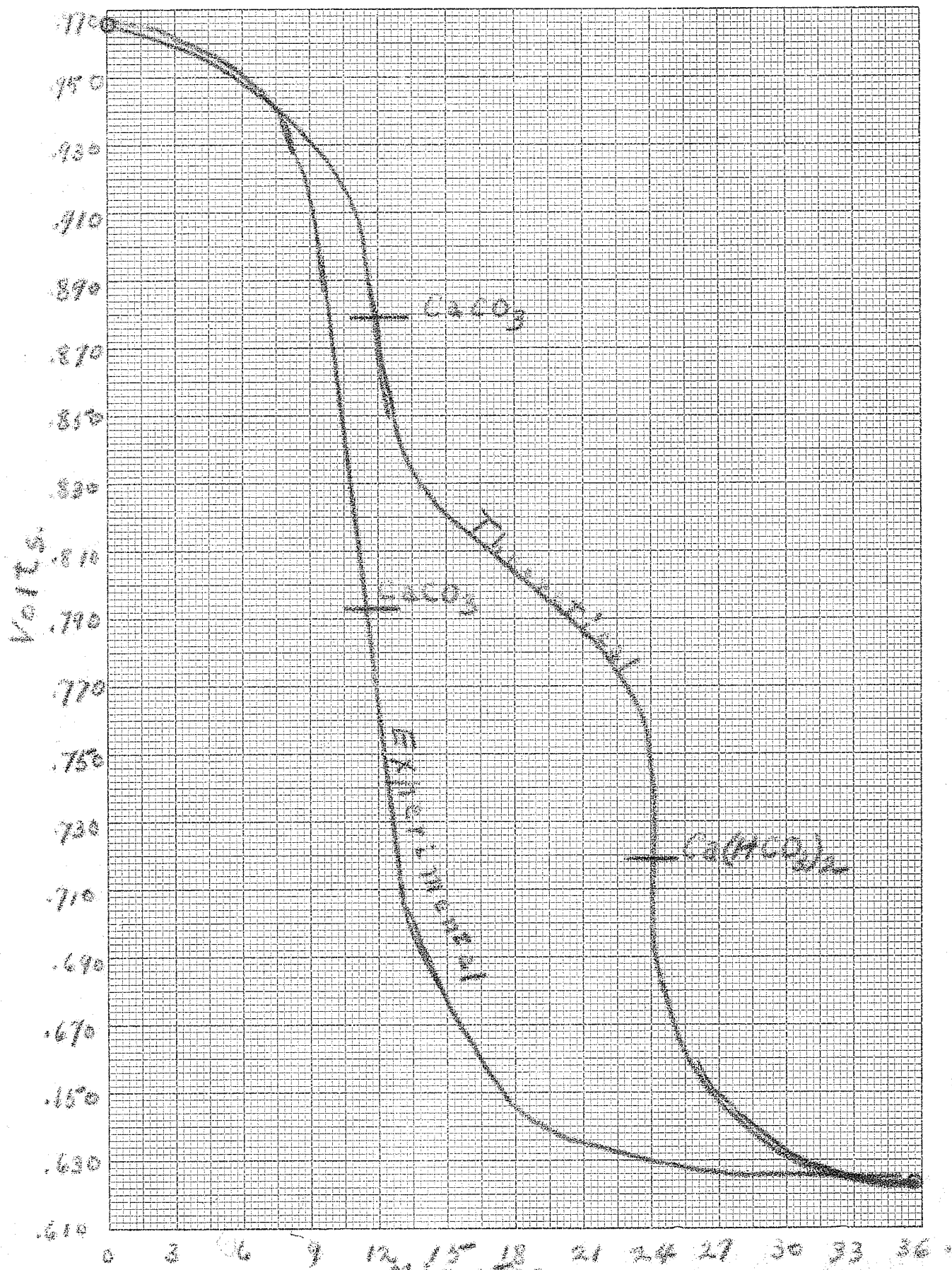
Minutes Volts.

0	.764
.5	.755
1.0	.750
1.5	.744
2.0	.737
2.5	.730
3.0	.721
3.5	.706
4.0	.694
4.5	.683
5.0	.677
5.5	.673
6.0	.670
6.5	.669
7.0	.666
8.0	.665
9.0	.661
10.0	.658
12.0	.655
14.0	.650
16.0	.645
18.0	.644
20.0	.643
22.0	.640
24.0	.639
26.0	.637
28.0	.637
30.0	.636

VI



$$\sqrt{V/2}$$

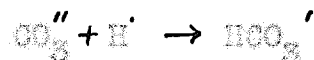


The Theoretical and Experimental Titration Curves of $\text{Co}(\text{OH})_2$ with CO_2



41.

and the ionization of carbonic acid, we should have a reaction represented by the equation.



i.e. H would be removed from the solution to form HCO_3' . This reaction would ~~xxx~~ be indicated by a flattening of the curve followed by a second "drop" giving an end point for ~~xxxxx~~ $\text{Ca}(\text{HCO}_3)_2$. No. VIa. is the theoretical titration curve of such a titration plotted from the data ~~xxx~~ McCoy, (2) Seyler and Lloyd, (3) and Engel (4) calculating from their percentage of hydrolysis of CaCO_3 the (H) which would exist in such a solution, and also the (H) concentration due to the bicarbonate.

Let us consider the equilibria present in a solution of CaCO_3 . The hydrolysis would be given by the equation.



Consequently in ~~solution~~ solution we would have the following:

$$\frac{(\text{Ca}) (\text{CO}_3'')}{(\text{CaCO}_3)} = K_1 \text{-----(1)}$$

$$\frac{(\text{Ca}) (\text{OH}')^2}{(\text{Ca}(\text{OH})_2)} = K_2 \text{-----(2)}$$

$$\frac{(\text{H}) (\text{HCO}_3')}{(\text{H}_2\text{CO}_3)} = K_3 \text{-----(3)}$$

2.--- "McCoy and Smith", J. Am. Chem. Soc. 33, 468, (1911).

3.--- "Seyler and Lloyd", J. Chem. Soc. 95, 1347. (1909).

4.--- "Engel", Ann. chim. phys. (6) 13, 348, (1838).

$$\frac{(H') (CO_3'')}{(HCO_3')} = K_4 \text{-----(4)}$$

42.

$$\frac{(H') (OH')}{=} = K_w \text{---(5)}$$

Equation(1) is the solubility product for $CaCO_3$ consequently the concentration of CO_3'' will be low. If H' be added it will increase the (H') in (5) thus decreasing the (OH') which will necessitate a decrease of (OH') in no.2 thus decreasing the (Ca') . Increasing this concentration in (1) will decrease the (CO_3'') in order that K_1 remain constant. Decrease of (CO_3'') in(4) will be accompanied by an increase of (H') concentration, or a decrease of (HCO_3') .

Experimentally the (H') concentration only increases very slightly. Since K_4 is large at this dilution (as will be shown later), and (H') is small as well as (CO_3'') the amount of HCO_3' will be very small, and can be neglected at the commencement of the titration. The (H') concentration at the end of the titration of $Ca(OH)_2$ with CO_2 is only slightly larger than that of pure water, and although more of the solid $CaCO_3$ produced in the titration goes into solution in the presence of CO_2 the dissolved salt may not be completely ionized, and the (CO_3'') may not be materially increased, the (H') is also small, and referring again to equation (4) the (CO_3'') and of (H') may not be large enough to produce any HCO_3' , that is to say there may be a minimum product of $(H') (CO_3'')$ necessary in order that the HCO_3' ion may exist. This explanation of the absence of an end point for $Ca(HCO_3)_2$ will be considered more fully under the dilution effect produced on the titration of Na_2CO_3 with HCl .

Curves (4) and (5) were obtained by bubbling CO_2 through a saturated solution of CaCO_3 no.(4) and through a suspension of CaCO_3 no.(5) in water. The solutions were prepared by bubbling CO_2 through a suspension of CaCO_3 in water, allowing the excess of carbonate to settle, and removing the supernatant liquid by a pipette. The saturated solution was obtained by boiling this liquid and filtering free from precipitated CaCO_3 . The suspension was prepared by expelling the CO_2 by boiling, and then ^{cooled} ~~was~~ titrating directly with CO_2 . Both were ~~warmed~~ rapidly to room temperature to avoid as far as possible the effect of absorption of CO_2 from the air.

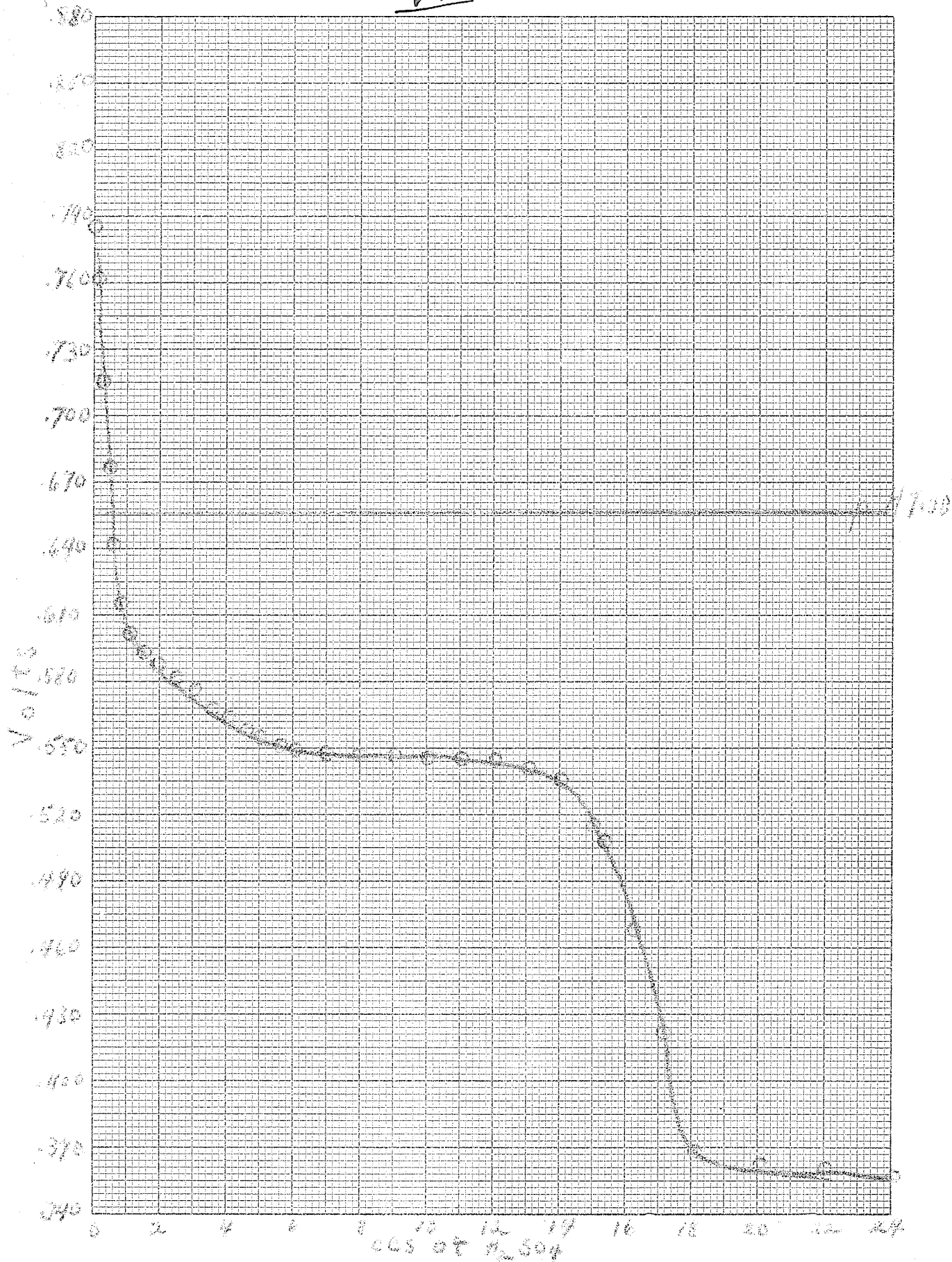
The initial reading does not agree with the end point for CaCO_3 in nos.(1) (2) (3), but a very small amount of CO_2 present would give a relatively large increase in (H^+) , and the difference in voltage readings is to be expected in an electrode in which the solution is exposed to the action of the air. The shape of the curve again suggests the non existence of HCO_3^- . If such an ion had been produced the (H^+) produced from the carbonic acid would have united with the CO_3^{--} present to form HCO_3^- , and in place of the rapid increase in voltage readings the increase should have only been slight. This would be shown on the curve by more or less flattening of the curve from the initial reading followed by an almost vertical drop, and again a gradual flattening as the voltage readings approached a constant value.

Let us consider the equilibria existing in these. The products of hydrolysis would be the same in both cases and for the present may be neglected. The following equilibria are subject to change.

Electrometric Titration of CaCO_3 with H_2SO_4 bubbling in CO_2
during titration.

ccs.	volts.
0	.785
.1	.765
.2	.712
.4	.677
.6	.642
.8	.616
1.0	.601
1.4	.600
1.8	.592
2.0	.590
2.4	.587
2.8	.577
3.2	.574
3.6	.568
4.0	.567
4.8	.559
5.0	.554
6.0	.548
7.0	.547
8.0	.546
9.0	.546
10.0	.546
11.0	.545
12.0	.545
13.0	.540
14.0	.535
15.0	.514
15.4	.507
15.7	.495
16.2	.467
17.0	.420
18.0	.388
20.0	.363
22.0	.360
24.0	.356

VII



Titration Curve of $CaCO_3$ with H_2SO_4
 Bubbling in CO_2

$$\frac{(H)^2 (CO_3'')}{(H_2 CO_3)} = K_6 \text{ ----- (6).}$$

$$\frac{(Ca) (CO_3'')}{(Ca CO_3)} = K_7 \text{ ----- (7).}$$

In curve no.(4) the amount of $CaCO_3$ in solution is constant through out, and the (H) concentration attained was only slightly higher than that of pure water. In no.(5) however the amount of $CaCO_3$ in solution was increased a great deal. Now if this had ionized the (CO_3'') would have been greatly increased and consequently in order that K_6 be constant the (H) would be greatly diminished. But in this instance the (H) is only slightly less than in no.(4) indicating that the amount of $CaCO_3$ dissolved in no.(5) during the titration exists very largely in the undissociated condition. If we assume bicarbonate to be formed equations nos.(6) and (7) become

$$\frac{(H) (HCO_3')}{(H_2 CO_3)} = K_3 \text{ ----- (3).}$$

and

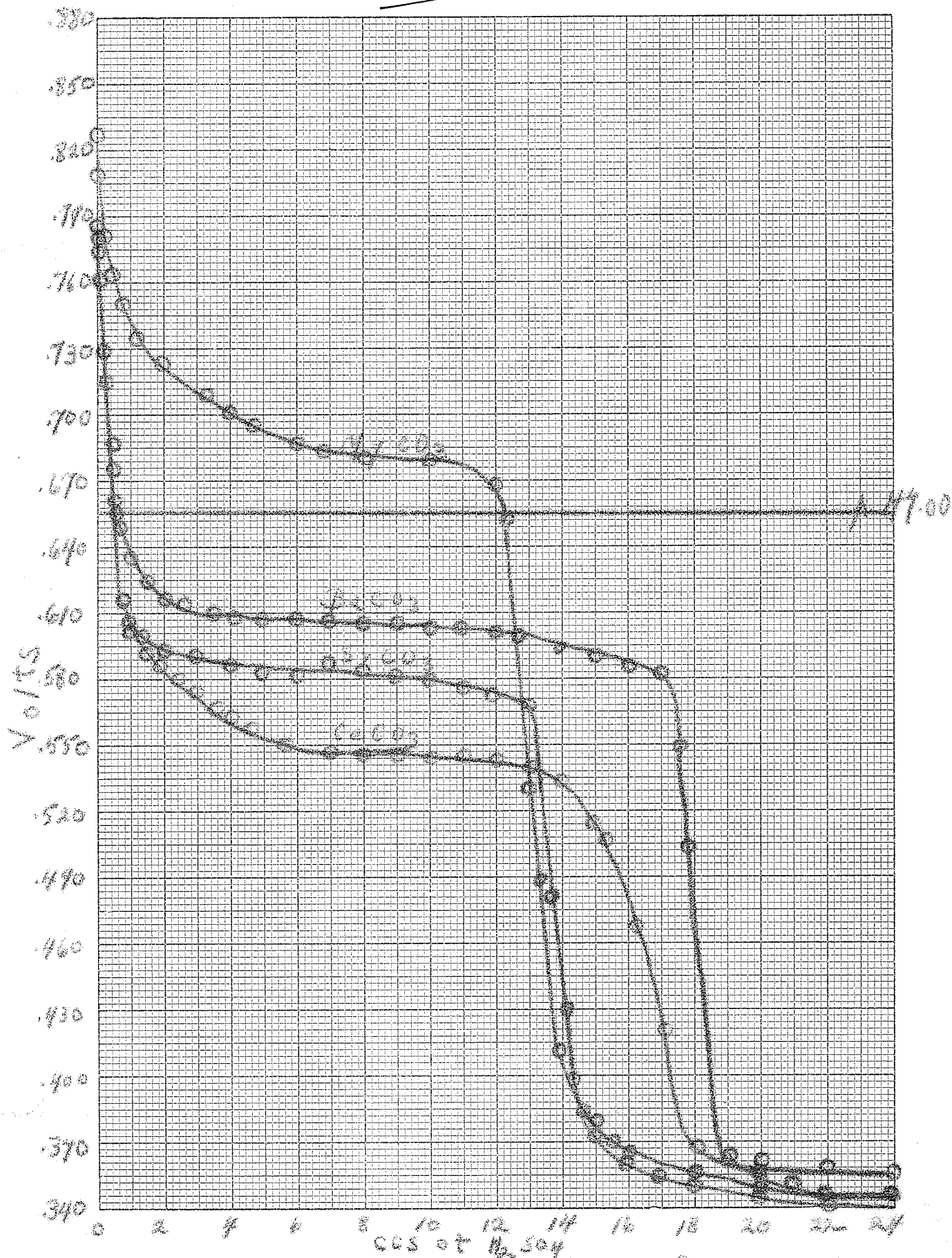
$$\frac{(Ca) (HCO_3')^2}{(Ca(HCO_3)_2)} = K_8 \text{ ----- (8).}$$

and again the decreased (H) between the solution and suspension is not sufficient to admit of the $Ca(HCO_3)_2$ in no.(5) being completely dissociated.

Electrometric Titration of $CaCO_3$ with H_2SO_4 bubbling CO_2
through the solution during the titration.

The end point for a bicarbonate can be obtained also by titrating the normal carbonate with an acid, and in order to determine if such a point existed a suspension of $CaCO_3$ was titrated with H_2SO_4 . The results are shown on curve no. VII.

VIII



Titration curves of $MgCO_3$, $BaCO_3$, $SrCO_3$ and $CaCO_3$
with H_2SO_4 Bubbling in CO_2 .

The suspension was prepared as described in the previous titrations (no. 3). The initial reading is in fair agreement with the end point obtained for CaCO_3 (no. VI). As successive amounts of acid are added there is a rapid increase in the (H) indicated by a rapid decrease in the voltage of the gas chain, and graphically by an almost vertical drop in the curve. Towards the end of this vertical drop the voltages of the gas chain become very irregular. This irregularity was due to the removal of liberated CO_2 from the solution by the H_2 gas bubbling through the electrode accompanied by a decrease in the (H) as the equilibrium $\text{CO}_2 \rightleftharpoons \text{H}_2\text{CO}_3$ was readjusted. This removal was compensated for by constantly bubbling CO_2 through the suspension during the remainder of the titration. The voltage readings approached a constant value, and then as the point was approached where all of the CaCO_3 was converted to CaSO_4 the voltage of the gas chain decreased rapidly, and a drop was produced on the curve, the readings again becoming constant. The center of this drop is as before the end point for H_2CO_3 since CaSO_4 does not undergo hydrolysis. If bicarbonates had been produced during the titration the curve instead of having a vertical drop from the initial reading should have (by analogy from the curve for K_2CO_3) flattened out and then dropped vertically, flattening again and giving a second drop. There is no point on the curve which can be definitely designated as an end point for the bicarbonates of Calcium.

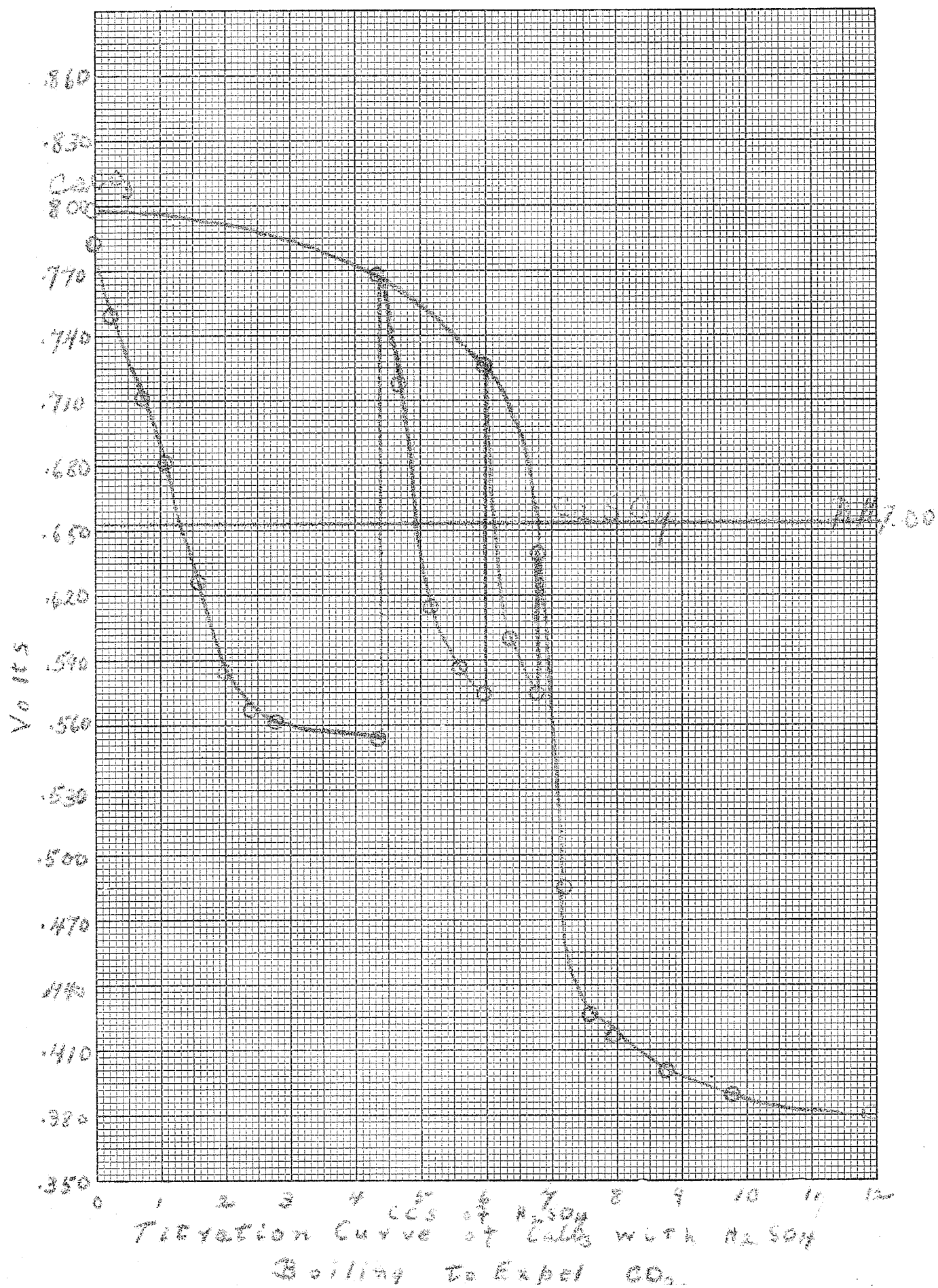
Electrometric Titration of MgCO_3 , BaCO_3 and SrCO_3 with H_2SO_4 .

Electrometric titrations were made of MgCO_3 , BaCO_3 and SrCO_3 with H_2SO_4 . The procedure was identical with that of CaCO_3 . The samples used were "Baker's" Analyzed, and duplicate measurements

The Electrometric Titration of CaCO_3 with H_2SO_4 boiling
to expel CO_2 .

ccs.	volts.
0	.780
.1	.742
.2	.732
.4	.714
1.0	.585
1.2	.568
1.4	.565
1.6	.563
2.2	.558
Boiled	
2.2	.767
2.4	.720
2.6	.615
2.8	.586
3.0	.575
Boiled	
3.0	.726
3.2	.600
3.4	.575
Boiled	
3.4	.640
3.6	.485
3.8	.425
4.0	.417
4.9	.390
6.0	.360

1X



were made on the carbonates precipitated from solutions of the salts by pure K_2CO_3 and washed by decantation until samples of the supernatant liquid showed a constant (H^+) concentration as determined by the colorimetric method. The results shown on No. VII. are those for the freshly precipitated carbonates, and are in good agreement with the titration made using commercial samples of these salts.

The initial readings are in the order of their basicity $MgCO_3$, $BaCO_3$, $SrCO_3$, $CaCO_3$. From the solubilities of the carbonates, and the arrangements in the present periodic classification of Ba, Sr, and Ca, we would expect the hydrolysis to be as indicated by the readings.

Examination of the curves show that from the initial reading until the various equilibria between the carbonates sulphates and carbonic acid have been established, the readings coincide. The shape of the curve again indicates the non existence of the HCO_3 in solutions of $MgCO_3$, $BaCO_3$ and $SrCO_3$, as well as in solutions of $CaCO_3$.

Titration of $CaCO_3$ with H_2SO_4 boiling at intervals to expel CO_2

An electrometric titration of $CaCO_3$ with H_2SO_4 was made. When the voltage readings became very nearly constant the solution was removed and boiled to expel the CO_2 produced in the reaction.



The solution was then cooled rapidly to room temperature, ($20^\circ C$) replaced in the gas chain and again titrated. Curve no. IX. shows the results obtained. From the initial reading the curve drops sharply, flattening to nearly constant voltage values. At the first boiling, indicated by the vertical rise, the voltage

readings increased almost to the initial reading. On adding acid there is again a sudden drop and a flattening of the curve. A second boiling increased the voltage readings but to a lower value than the first boiling. Addition of acid again gave a sudden drop in the voltage readings of the gas chain, and a third boiling increased the voltage readings only a slight amount. On further addition of acid the voltage of the gas chain decreased rapidly, indicating that all of the CaCO_3 has been converted to CaSO_4 . As voltage readings again become constant (at about .410 volts) the solution was again removed and boiled, but no appreciable change in the voltage readings occurred.

As acid is added carbonic acid is produced in the solution, and at each boiling it is decomposed according to the equation



the CO_2 being removed from solution. Consequently there would be a decrease of (H^+) accompanied by an increase in the voltage of the gas chain. Along the flat portion of the curve (at .410 volts) the (H^+) ~~at this solution~~ is so large that any H_2CO_3 existing would be in the molecular condition, and consequently boiling would not affect the (H^+) of the solution, hence there would not be a change in the voltage of the gas chain. The sudden drop in the voltage readings of the gas chain on addition of acid after boiling and cooling the suspension again points to the non existence of the HCO_3 . If each succeeding drop in the curve could be continued experimentally the voltage of the gas chain would decrease, and the constant value (slightly below .550 volts) would have been obtained, that is to say each "drop" would have produced a curve similar to curve no. VII.

Electrometric Titration of H_2O with CO_2 .

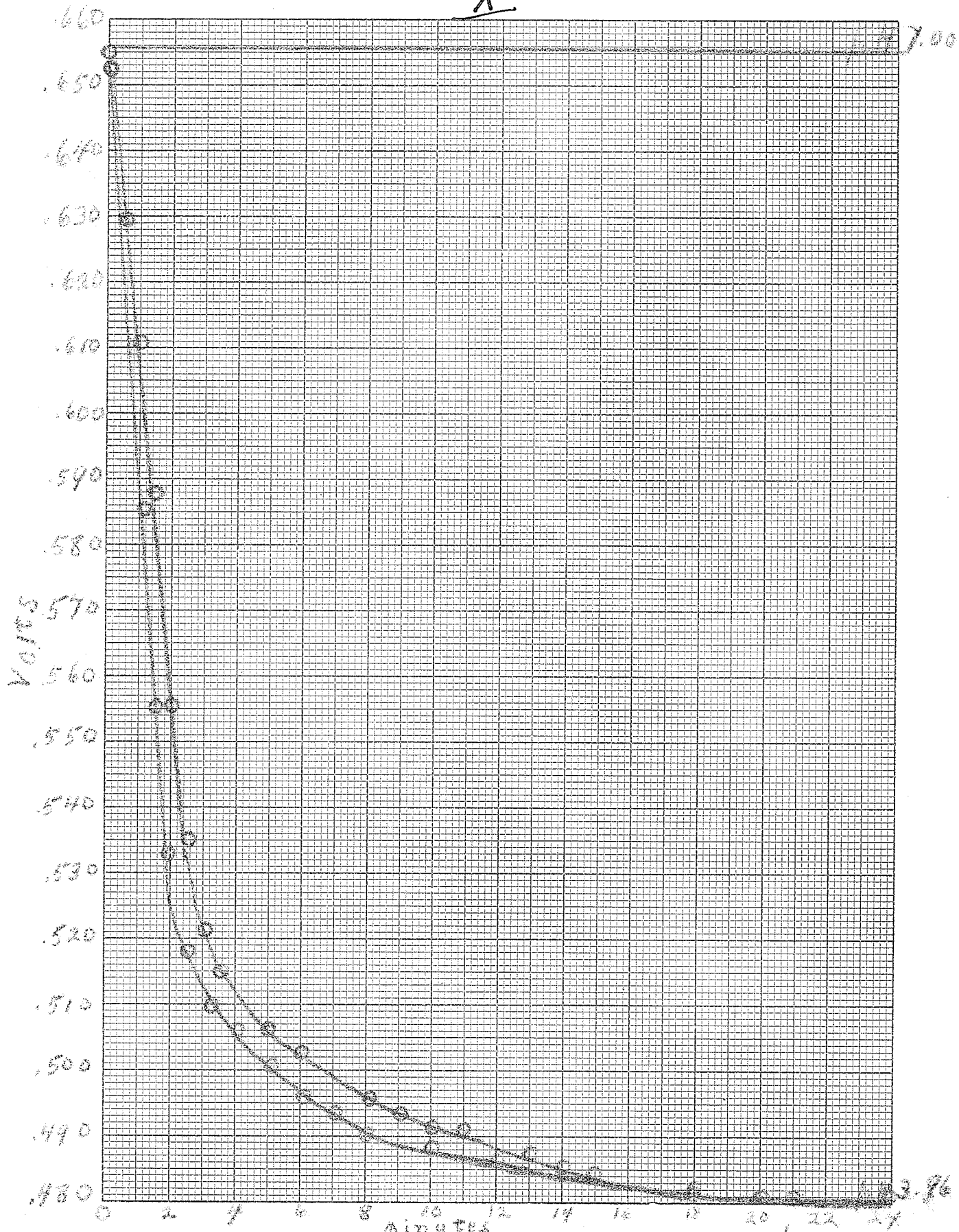
NO. 1

NO. 2.

Minutes	Volts.
0	.652
.5	.629
1.0	.610
1.5	.588
2.0	.565
2.5	.535
3.0	.521
3.5	.514
4.0	.509
5.0	.505
6.0	.503
7.0	.496
8.0	.495
9.0	.493
10.0	.491
12.0	.489
14.0	.485
16.0	.483
18.0	.481
20.0	.481
22.0	.480
24.0	.480

Minutes	Volts.
0	.655
1.0	.585
1.5	.555
2.0	.533
2.5	.513
3.0	.519
4.0	.506
5.0	.500
6.0	.495
7.0	.493
8.0	.490
10.0	.486
12.0	.487
14.0	.485
18.0	.482
20.0	.480
22.0	.480
24.0	.480

X



Curves Showing Change in pH Value
as CO_2 is Bubbled through H_2O

If as the initial value we take the end point for CaCO_3 (no. VI) and draw a curve through the vertices a regular curve is produced. Since we are titrating CaCO_3 with H_2SO_4 , at the beginning of the titration we have a (H^+) due to the CaCO_3 alone. At the end the (H^+) concentration is due to CaSO_4 and a small amount of H_2CO_3 which had not been removed. (Since CaSO_4 does not hydrolyze in solution the neutral point shall be considered as the end point for this titration). Intermediate between these then we have a mixture of CaCO_3 and CaSO_4 , since the CO_2 has been expelled by boiling. The curve so produced is then a measure of the (H^+) of various proportions of CaCO_3 and CaSO_4 in solution.

At the commencement of the titration shown by curve no. VII. we have CaCO_3 , at the end we have CaSO_4 and H_2CO_3 . This curve then is a measure of the (H^+) of mixtures of CaSO_4 , CaCO_3 and CO_2 in solution.

Curve no. VII. and no. IX. are then closely related. If we take voltage readings along the curve through the vertices (no. IX.) and saturate with H_2CO_3 the curve produced would be no. VI. The voltage readings between the curves are therefore a measure of all the possible (H^+) concentrations due to the mixtures of CaCO_3 , CaSO_4 and CO_2 in water solution.

Change produced in (H^+) as CO_2 is bubbled through H_2O .

The starting point in the titration, if it may so be termed, was conductivity water, further freed from absorbed gases by boiling and cooling quickly to 20° . The hydrogen electrode, siphon arm, stirrer and beaker were thoroughly washed with conductivity water before the measurements were begun. A steady current of CO_2 , regulated by a valve, was bubbled through the water, and voltage

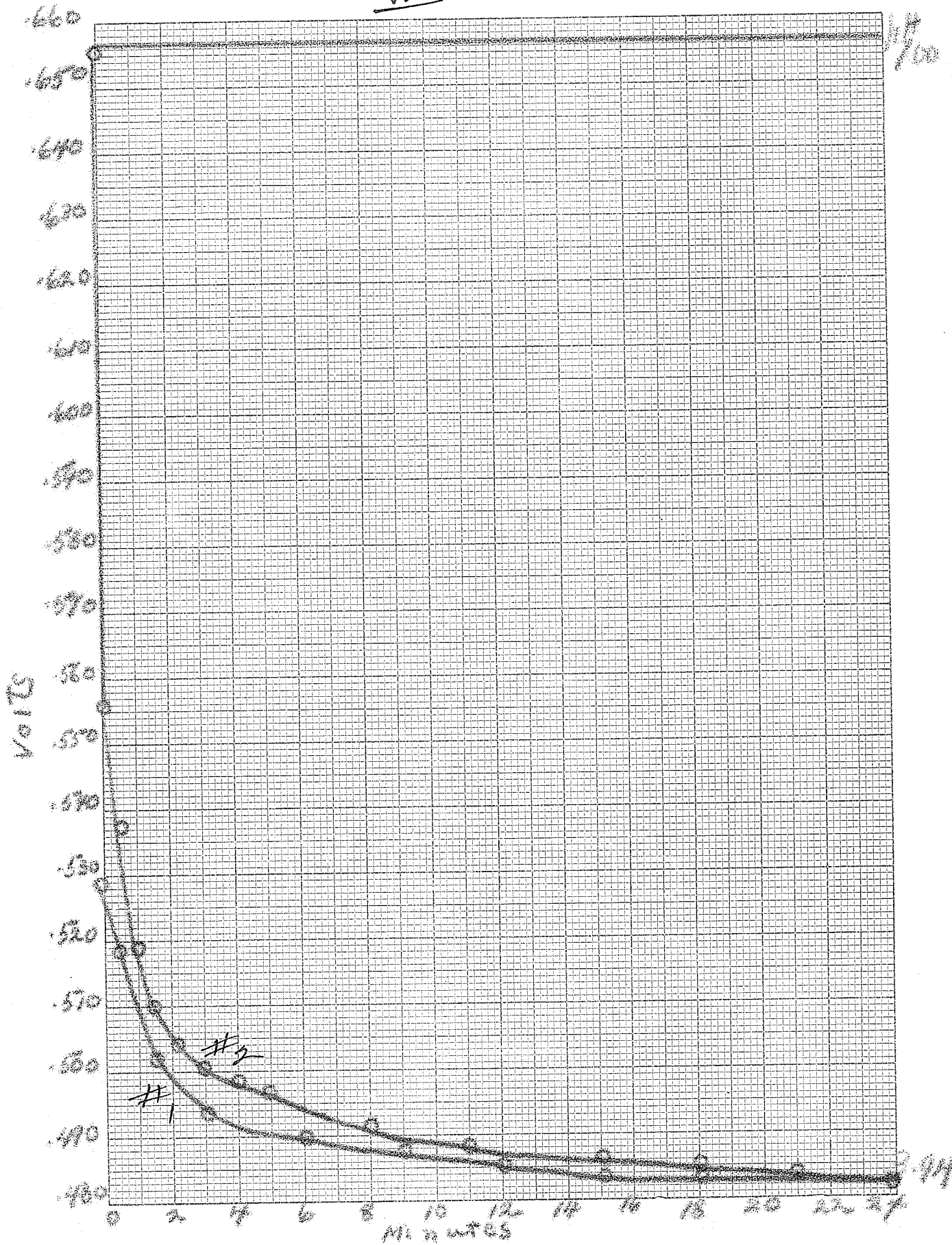
The Electrometric Titration of CaSO_4 with CO_2 .

NO. 1

NO. 2

<u>ccs.</u>	<u>volts.</u>	<u>ccs.</u>	<u>volts.</u>
0	.528	0	.655
.5	.518	CaSO_4 (solid) added.	
1.0	.501	0	.555
2.0	.492	.5	.537
3.0	.491	1.0	.518
4.0	.489	1.5	.509
5.0	.488	2.0	.502
6.0	.487	3.0	.500
7.0	.484	4.0	.498
8.0	.484	5.0	.496
9.0	.483	8.0	.490
10.0	.483	11.0	.487
11.0	.482	15.0	.485
12.0	.482	18.0	.484
13.0	.482	21.0	.483
16.0	.481	24.0	.481
18.0	.481		

XI



Titration Curve of CaSO₄ with CO₂

readings were made at regular intervals of time. Curve no. X. shows the results obtained. The initial ^{voltage} readings agree very closely with the theoretical value for pure water. This is followed by a sudden drop in the curve, indicating a rapid increase of (H^+) as the CO_2 unites with the water to produce H_2CO_3 , and subsequent ionization producing H^+ . As the waterx nears the saturation point for CO_2 (at .530 volts) the curve gradually flattens out, and after 20 minutes the voltage readings become constant at a pH value of 3.96. ~~This value then is as a~~ ^{or} (H^+) of 1.10×10^{-4} gm. ions per liter. This value then is the maximum (H^+) that can be produced by CO_2 dissolved in water at 20°C. and at a partial pressure of one atmosphere.

Electrometric Titration of $CaSO_4$ with CO_2 .

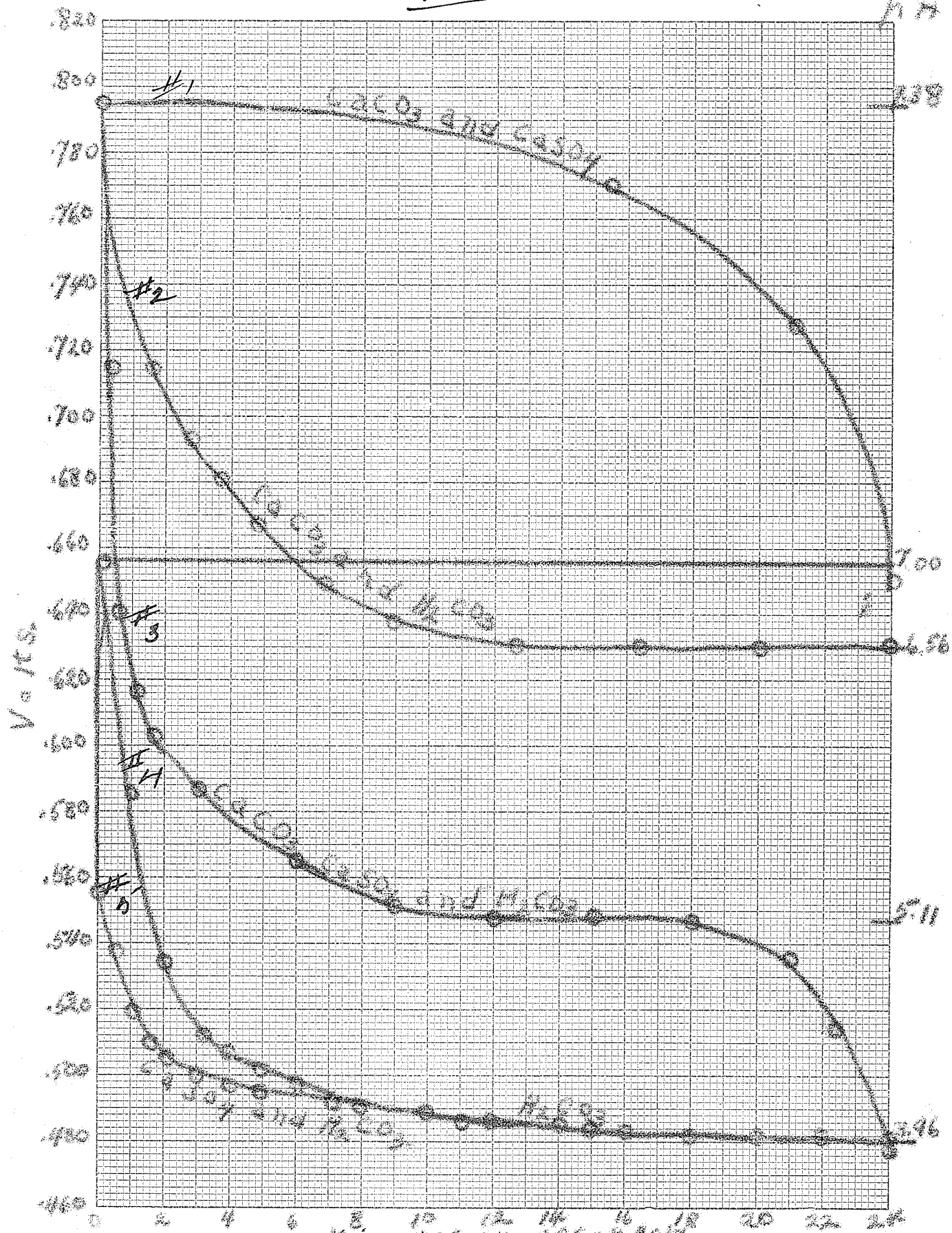
An electrometric titration of a saturated solution of $CaSO_4$ with CO_2 was made. The results are shown on curve no. XI. (1). The initial voltage of the gas chain is .528 volts. This voltage would indicate a (H^+) much greater than that of pure water (.6557 volts). Calcium sulphate however does not undergo hydrolysis in solution, and the low voltage of the gas chain is probably due to an oxidation-reduction potential brought about by the reduction of the SO_4^{--} by occluded H in the platinum black of the electrode. As CO_2 is bubbled through the solution a rapid decrease occurs in the voltage of the gas chain, shown by the sudden drop of the curve, which flattens out to a constant voltage similar to that of pure water.

Curve no. II. was obtained by using the conductivity water prepared as described in no. X. When the voltage of the gas chain becomes constant (.655 volts) $CaSO_4$ (solid) was added. The voltage dropped to .555 volts. CO_2 was then bubbled through the solution.

A sudden decrease of voltage occurred as shown by the drop of the curve, and the constant values obtained were again the same as those for pure water saturated with CO_2 .

Since in solutions of CaSO_4 when their (H) is measured by means of the hydrogen electrode we probably have an oxidation-reduction potential as well as the potential of the electrode, such measurements alone could not be taken as an accurate determination of the (H) ; but on the completion of the titration a colorimetric determination of the solution, now saturated both with respect to CaSO_4 and CO_2 , was made, and the pH value so determined was 4.00, in good agreement with that obtained from the voltage of the gas chain 3.96. The bubbling of CO_2 through the solution overcomes in some unaccountable manner the oxidation-reduction potential produced by CaSO_4 , and the constant value obtained (pH. 3.96) is a measure of the maximum (H) that can be obtained when a solution of CaSO_4 is saturated with CO_2 at a partial pressure of one atmosphere. Since CaSO_4 does not hydrolyze in solution, from theoretical consideration we would expect this value to be the same as that obtained for pure water.

E. Wilke Z. Anorg Chem. 119, 365, (1921) has shown that in concentrated salt solutions the (H) due to carbonic acid increases with increasing concentration. Since CaSO_4 is only slightly soluble in water this effect would not occur.



Curves Showing pH Values of Solutions of CaCO_3 , CaSO_4 and CO_2 in H_2O .

(1)

The (H) Due to Admixtures of $CaSO_4$, $CaCO_3$ and CO_2 in solution in H_2O .

From a consideration of the electrometric titration curves obtained we can discuss the (H) found in solutions of various concentrations of $CaSO_4$, $CaCO_3$ and CO_2 in H_2O . The results obtained are shown graphically on Curve no. XII. The voltage readings have been plotted as ordinates, and the cc. of acid added or minutes, when titrating with CO_2 , as abscissae. The cc. or minutes have been extended so that the portions of the curves related to the equilibria under discussion extend completely across the squared paper. This is in effect reducing the strength of the acid added or the rate of flow of CO_2 through the solution and the (H) indicated are fundamentally the same. No. 1 is reproduced from no. IX., and is the curve through the vertices, and a measure of the (H) due to the mixtures of $CaCO_3$ and $CaSO_4$ in solution in H_2O . No. 2 is reproduced from no. VI. the portion of curve no. 3 below the end point for $CaCO_3$ has been taken, since this curve is a better representation of the (H) due to dissolved $CaCO_3$ and CO_2 than no. 4 or no. 5. No. 3 is reproduced from no. VII. and has only been plotted as far as the end point for H_2CO_3 , since voltage readings lower than this point correspond to a (H) of the H_2SO_4 added. No. 4 is the curve produced as CO_2 is bubbled through H_2O (no. X.), and no. 5 as CO_2 is bubbled through a saturated solution of $CaSO_4$ (no. XI, no. 2).

No. 1 has an initial reading of .794 giving a pH. value of 9.38 or a (H) of 4.17×10^{-10} gm. ions per liter. That is to say a sat-

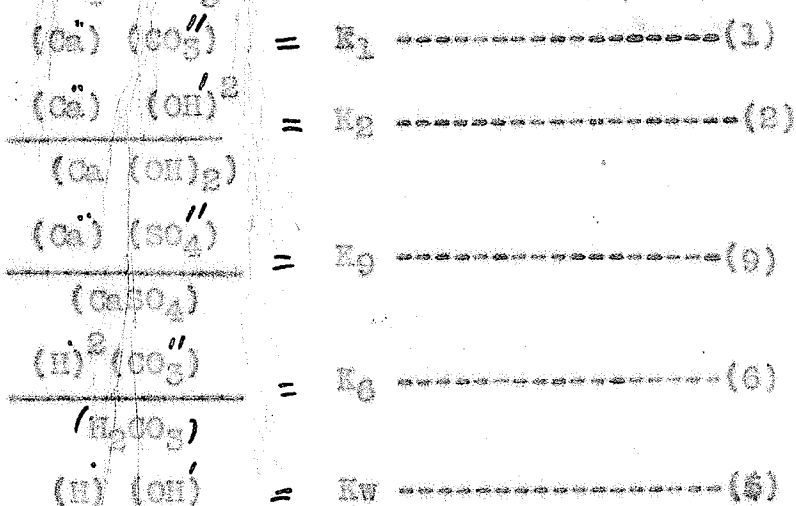
1.--- CO_2 in solution shall be referred to as carbonic acid H_2CO_3

urated solution of CaCO_3 gives a very small concentration of H^+ much smaller than that of pure water. At infinite dilution the (H^+) concentration of a solution of CaCO_3 would be that of pure water or 1×10^{-7} gm. ions per liter. All possible (H^+) concentrations then of the solutions of CaCO_3 lie between the values 4.17×10^{-10} and 1×10^{-7} gm. ions per liter.

Since CaSO_4 does not hydrolyze in solution the (H^+) in solution in H_2O at all possible dilutions will be 1×10^{-7} .

From no. 1 it is evident that all possible (H^+) due to various mixtures of CaCO_3 and CaSO_4 lie between 4.17×10^{-10} and 1×10^{-7} gm. ions per liter.

In such mixtures we have the following equilibria between CaSO_4 , CaCO_3 , and its products of hydrolysis, in solution in H_2O .



If (1) (2) (3) and (5) are all in equilibrium in the same solution at the same time, and CaSO_4 (3) be added, then the (Ca^{++}) will be increased in (2), this increase will cause a decrease of (OH') , and decreasing (OH') in (5) will increase the (H^+) of the solution.

Also increase of (Ca^{++}) in (1) will cause a decrease of (CO_3^{--}) , and decreasing (CO_3^{--}) in (4) will increase the (H^+) concentration

or the addition of the "neutral" salt CaSO_4 to a solution of CaCO_3 would increase the (H^+) of the solution, and consequently curve no. 1 drops more rapidly than would a curve showing the increase of (H^+) of solutions of CaCO_3 on dilution.

Curve no. 2 shows all possible (H^+) concentrations as H_2CO_3 is added to a saturated solution of CaCO_3 . The initial reading of the gas chain is again .794 volts corresponding to a (H^+) of 4.17×10^{-10} gm. ions per liter. The greatest (H^+) obtained when the solution is saturated with respect to H_2CO_3 is shown by a pH value of 6.56 or a (H^+) of 2.75×10^{-7} . That is, if we have a saturated solution of CaCO_3 , and add to this H_2CO_3 we can increase the (H^+) from 4.17×10^{-10} to 2.75×10^{-7} gm. ions per liter.

No. 3 has an initial value of .794 volts or a (H^+) of 4.17×10^{-10} , and by adding CaSO_4 and H_2CO_3 to a saturated solution of CaCO_3 the ultimate pH value is 3.96 or a (H^+) concentration of 1.10×10^{-4} .

It will be noticed that the curve shows a constant value for several varying amounts of CaSO_4 and CaCO_3 saturated with H_2CO_3 at a pH value of 5.11. This indicates that mixtures of CaSO_4 and CaCO_3 in solution saturated with respect to H_2CO_3 will show a strong buffer action at a (H^+) of 7.77×10^{-6} gm. ions per liter.

Here again the addition of the "neutral" salt CaSO_4 has increased the (H^+) concentration. The equilibria concerned are identical with no. 1, and the reason for the increase is also similar. We have however in the latter case much higher (H^+) in the solution before CaSO_4 is added, since it is saturated with respect to H_2CO_3 .

Curve no.4 shows the maximum (H^+) concentration obtained when water is saturated with CO_2 , the voltage of the gas chain indicates a pH value of 3.96 or a (H^+) concentration of 1.10×10^{-4} gm. ions per liter. The addition of $CaSO_4$ to such a solution has no effect on the (H^+) concentration as no.4 and no.5 coincide.

A saturated solution of $CaCO_3$ has a (H^+) of 4.17×10^{-10} , and if to this solution H_2CO_3 be added the (H^+) increases to 2.75×10^{-7} . The (H^+) concentration at this point is determined by the equilibria between the (OH^-) due to the hydrolysis of $CaCO_3$, and the (H^+) due to the ionization of H_2CO_3 . Now if $CaCO_3$ be removed from the solution, still saturated with respect to H_2CO_3 , the (OH^-) will decrease, then in order that the ionic product for water (5) remain constant the (H^+) must increase, and at infinite dilution the (OH^-) concentration due to hydrolysis would be the same as pure water. The (H^+) would be identical with that obtained when pure water is saturated with H_2CO_3 or 1.10×10^{-4} . All (H^+) concentrations due to the various mixtures of $CaCO_3$ and H_2CO_3 in water are between 4.17×10^{-10} and 1.10×10^{-4} gm. ions per liter.

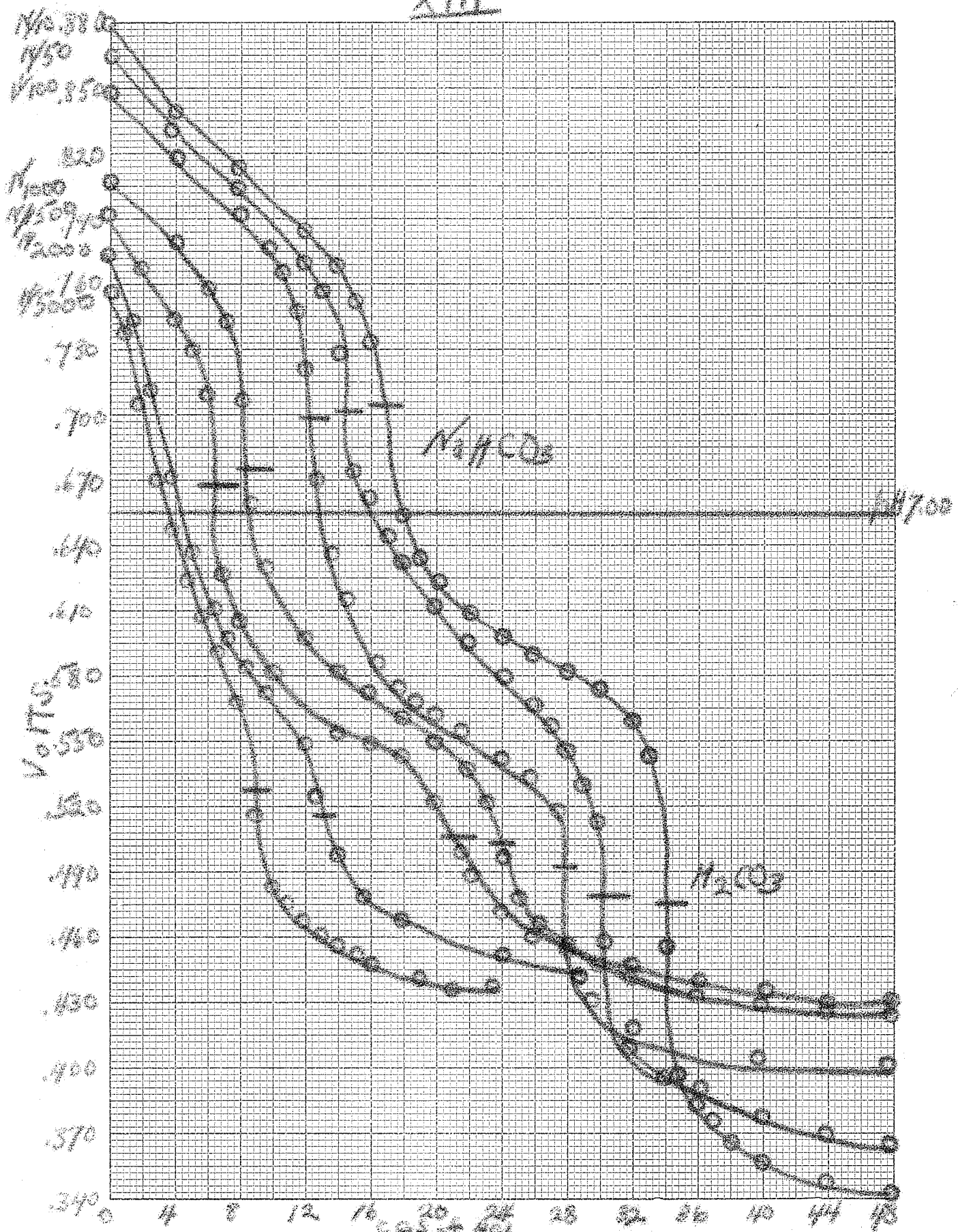
If to a solution saturated with $CaCO_3$ and H_2CO_3 , $CaSO_4$ be added then the (H^+) will be increased, and when the solution is saturated with respect to all three the pH of the solution will be 5.11 or a (H^+) of 7.77×10^{-6} gm. ions per liter. Consequently if we have a solution saturated with $CaCO_3$ and H_2CO_3 , having a (H^+) of 2.75×10^{-7} , the addition of $CaSO_4$ can only increase the (H^+) to 7.77×10^{-6} gm. ions per liter.

Now if the amount of $CaCO_3$ present be reduced, and the solution be still saturated with $CaSO_4$ and H_2CO_3 , the (H^+) will

increase and ultimately reach the same value as when water is saturated with carbonic acid. Again if the amount of H_2CO_3 present be reduced the (H^+) will be reduced, and no. 1 is an indication of the values so produced or if CaSO_4 be reduced there will also be a decrease in the (H^+) concentration until the value represented by no. 2 are reached.

The (H^+) of all possible proportions of CaSO_4 , CaCO_3 and H_2CO_3 in solution in H_2O lie between the values 4.17×10^{-10} and 1.10×10^{-4} gm. ions per liter.

XIII



Titration curves of Na_2CO_3 with HCl showing variation with dilution.

The Relation of the Equilibria between CaSO_4 , CaCO_3 , CO_2 and H_2O to the Self Corrosion of Cast Iron in Alkaline Soils referred to the soils of the Winnipeg District.

The investigations(1) on the self corrosion of Cast Iron pipe lines in the Winnipeg district, and examination of the soils surrounding corroded pipes has shown that corrosion is most rapid close to deposits of Magnesium and Calcium Sulphate. In some instances crystals of these salts were in contact with the corroded pipe. The presence of these crystals can only mean that the ground water in contact with the pipe was a concentrated ~~an~~ solution of these salts. Present also in the soils are large amounts of calcium and magnesium carbonates. The ground water contains CO_2 in solution giving rise to carbonic acid. The present investigation deals only with the Calcium salts in presence of CO_2 . Investigations on the effect of the Magnesium salts will be carried out at an early date.

The corrosion of iron may proceed from the iron in contact with water solutions displacing the H^+ present, due to its being more electro positive than hydrogen. The dissolved Fe^{++} is then precipitated from solution as $\text{Fe}(\text{OH})_2$ or if oxygen be present, as it often is, in solution in the ground water the ferrous ion may be oxidized to the ferric ion and $\text{Fe}(\text{OH})_3$ would be precipitated.

If CaSO_4 , CaCO_3 and CO_2 be dissolved in water then in the solution the following equilibria are established,

1.---"W. Nelson Smith & J. . Shipley", J. AM. Inst. Elec. Eng. 40, 642, 1921.

$$(\text{Ca}^{++}) (\text{CO}_3^{--}) = K_1 \text{ ----- (1)}$$

$$\frac{(\text{Ca}^{++}) (\text{OH}')^2}{(\text{Ca}(\text{OH})_2)} = K_2 \text{ ----- (2)}$$

$$\frac{(\text{Ca}^{++}) (\text{SO}_4^{--})}{(\text{CaSO}_4)} = K_3 \text{ ----- (3)}$$

$$\frac{(\text{H}')^2 (\text{CO}_3^{--})}{(\text{H}_2 \text{CO}_3)} = K_4 \text{ ----- (4)}$$

$$(\text{H}') (\text{OH}') = K_w \text{ ----- (5)}$$

and it has been shown that the addition of CaSO_4 increases the (H') concentration of the solution.

The (H') of the solution determines the rate at which the iron in contact with it will be dissolved; the potential amount of H' , the amount which can be produced by the readjustment of the equilibria in the solution as iron displaces the H present, determines the amount of iron which the solution is capable of dissolving.

The ground waters are probably in constant motion, and consequently the dissolved iron might be carried away in solution, and fresh H' would be brought in contact with the cast iron pipes; but let it be considered that the ground water is not free to move. Then as iron displaces the H' from solution the hydrogen gas produced escapes from the solution into the surrounding soils. A new equilibrium is introduced into the solution.

$$\frac{(\text{Fe}') (\text{OH}')^2}{(\text{Fe}(\text{OH})_2)} = K_{10} \text{ ----- (10)}$$

As H' is removed from the solution in order that K_w remain constant more H' will be produced from the water, and more iron will pass into solution. The increase of (OH') in (10) will increase the (OH') in (5) with a reduction of the (H') : the solubility product

for $\text{Fe}(\text{OH})_2$ is very small,

$$(\text{Fe}^{2+}) (\text{OH}^-)^2 = 1.64 \times 10^{-14} \quad (2) \text{ at } 18^\circ \text{ -----} (7).$$

and at the temperature of soil water would probably be smaller than this figure. When this value has been reached for $\text{Fe}(\text{OH})_2$ (OH^-) will be removed from solution, and consequently (H^+) will be produced from the water in order that K_w remain constant. This then is the minimum value for (H^+) concentration, and the potential amount of H^+ would be determined by the total amount of water present. The Fe^{2+} might also be removed to form some undissociated FeSO_4 , but the degree of ionization of a saturated solution of CaSO_4 is in the neighborhood of .03, and it is probable that the concentration of Fe^{2+} and SO_4^{2-} is not sufficient to produce any undissociated FeSO_4 . Fe^{2+} may also be removed to form undissociated FeCO_3 , but again the concentration of the ions may not be sufficient to produce any undissociated FeCO_3 in solution. The effect however of the possibility of the production of FeSO_4 and FeCO_3 , and their effect on the (H^+) of such solutions can not be overlooked but sufficient data is not as yet available to discuss the effect of these on the (H^+) , and the self corrosion of cast iron in contact with such solutions.

If oxygen be present in the ground waters then the ferrous ion will be oxidized to the ferric ion, and still another equilibrium will be produced.

$$\frac{(\text{Fe}^{3+}) (\text{OH}^-)^3}{(\text{Fe}(\text{OH})_3)} = K_{11} \text{ -----} (11)$$

2

2.--Laidolt Bornstein Tabellen.

3.--Calculated from the equivalent conductivity of CaSO_4 obtained by Kohlrausch and Gruneisen, Laidolt Bornstein Tabellen.

The solubility product for $\text{Fe}(\text{OH})_3$ is very small,

$$(\text{Fe}^{++}) (\text{OH}^{\cdot})^3 = 1.1 \times 10^{-36} \text{ at } 18^\circ \text{ -----} (8)$$

and the concentration of Fe^{++} and $(\text{OH}^{\cdot})$ necessary to give this product would be reached much sooner than in the case of $\text{Fe}(\text{OH})_2$, consequently the $(\text{OH}^{\cdot})$ will be decreased and removed from solution as $\text{Fe}(\text{OH})_3$, and the (H^+) will be increased in order that $K_w(5)$ remain constant.

It is evident then that the (H^+) concentration is greater when oxygen is present in the solution, although the potential amount is still determined by the amount of water present. The (H^+) determines the rate of corrosion of the iron, and consequently oxygen although not combining directly with the iron stimulates the corrosion. CaSO_4 since it increases the (H^+) of solutions of CaCO_3 when added to them stimulates corrosion, as does also carbonic acid due to the ionization producing (H^+) . CaCO_3 alone in solution, since it undergoes basic hydrolysis, diminishes the (H^+) and would thus tend to inhibit the corrosion of iron.

The Carbonate bi-Carbonate Equilibrium from a Consideration of the Electrometric Titration Curves of Sodium Carbonate at Various Dilutions.

Electrometric titrations of solutions of Na_2CO_3 with HCl were made with $N/10, N/50, N/100, N/1000, N/1500, N/2000$ and $N/5000$, solutions of the Alkali. The results are shown graphically on Curves no. XIII.

The initial voltage reading for $N/10$ solution of Na_2CO_3 is the highest, and the readings decrease in the order of the increasing dilution. The acid used (HCl) in the titration was adjusted to four times the strength of the Na_2CO_3 solution, so that the titration would be completed within one filling of the burette, and in plotting the curves the cc. of acid added have been altered so that the curves do not cross each other more than once, i.e. near the end of the titration. This crossing is due to a decrease in the constant value of the (H^+) in the various titrations as the concentration of the acid is adjusted to to the concentration of the Na_2CO_3 solution.

Since in the discussion which follows we are concerned chiefly with the proportional amount rather than the actual amount of acid added, the alteration of the cc. of acid will not effect the calculations, nor will it alter the voltage readings at the end points for NaHCO_3 and H_2CO_3 .

The titration curves from $N/10$ to $N/1500$ inclusive show marked end points for both NaHCO_3 and H_2CO_3 , but the curves $N/2000$ and $N/5000$ show only one end point corresponding to that for H_2CO_3 .

That is at a normality equal to that of a saturated solution

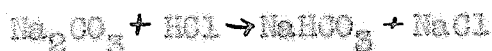
of CaCO_3 N/5000, and at a normality of twice this amount N/2000 solutions of Na_2CO_3 do not show an end point for NaHCO_3 .

Seyler and Lloyd(1) have pointed out that the secondary constant for ~~carbonate~~ carbonic acid given by the equation

$$\frac{(\text{H}^+) (\text{CO}_3'')}{(\text{HCO}_3')}$$

decreases with decreasing concentrations of the sodium carbonate solutions used in its determination by the McCoy(2) Method.

When a solution of Na_2CO_3 is titrated, say with HCl , from theoretical considerations the amount of acid necessary to complete the titration would be twice that necessary to convert all the CO_3'' present to HCO_3' . This follows directly from the equation.



Consequently in an electrometric titration the end point for NaHCO_3 should require one half the number of ccs. necessary to reach the end point for H_2CO_3 on the same curve. Consider the curve for N/10 Na_2CO_3 . The end point for H_2CO_3 required 34 ccs. of acid, while the end point for NaHCO_3 required the addition of 16.8 ccs of acid the theoretical amount is 17 ccs. Thus it is evident that all of the CO_3'' present at the beginning of the titration was not converted to HCO_3' before the reaction

1.--- "Seyler and Lloyd", (loc cit.)

2.--- "McCoy", (loc cit.)

$\text{H}^+ + \text{HCO}_3^- \rightarrow \text{H}_2\text{CO}_3$ began.

62.

This effect is more marked as the dilution increased, for N/1500 solution of Na_2CO_3 21.4 ccs. were required to attain the end point for H_2CO_3 , and only 6.4 ccs. to reach that for NaHCO_3 . The theoretical value would be 10.7 ccs.

The fact that all of the CO_3^{--} ion existing at the beginning of the titration was not converted to HCO_3^- seems to point to some relationship between the (H^+) and the (CO_3^{--}) . When the end point for NaHCO_3 has been reached. There may then be a minimum ionic product of $(\text{H}^+)(\text{CO}_3^{--})$ necessary in order that the HCO_3^- may exist. If this be true it is expected that this product would be a constant.

It is possible to calculate this product as well as that given by the equation

$$\frac{(\text{H}^+)(\text{CO}_3^{--})}{(\text{HCO}_3^-)}$$

from the electrometric titration curves.

Let us consider the curve produced by titrating a N/1500 solution of Na_2CO_3 . The end point for H_2CO_3 required 21.4 ccs. The theoretical end point for NaHCO_3 would require the addition of 10.7 ccs., but the actual amount used was 6.4 ccs. The ratio therefore of CO_3^{--} converted to HCO_3^- will be given by $\frac{6.4}{10.7} = .595$, and the ratio amount of CO_3^{--} at the commencement of the titration to the CO_3^{--} present at the end point for NaHCO_3 will be .405. The (CO_3^{--}) , assuming complete dissociation for the dissolved Na_2CO_3 will be equal to the normality of the solution divided by 2, since in all calculations the ionic concentrations are to be expressed in gram ions per liter.

The (CO_3'') is therefore equal to 3.85×10^{-4} gm. ions per liter.

It follows then that the concentration of HCO_3' at the end point for $NaHCO_3$ equals $.595 \times 3.85 \times 10^{-4}$ gm. ions per liter, and the concentration of CO_3'' ion remaining unchanged $.405 \times 3.85 \times 10^{-4}$. The

(H) is calculate from the voltage reading at the end point for $NaHCO_3$ (.870 volts.) and is equal to 5.62×10^{-8} gm. ions per liter.

The product (H) (CO_3'') will be given by

$$(5.62 \times 10^{-8})(.405 \times 3.85 \times 10^{-4}) = 8.76 \times 10^{-12},$$

and the value of

$$\frac{(H)(CO_3'')}{(HCO_3')} \text{ by } \frac{(5.62 \times 10^{-8})(.405 \times 3.85 \times 10^{-4})}{.595 \times 3.85 \times 10^{-4}} = \frac{8.76 \times 10^{-12}}{.595 \times 3.85 \times 10^{-4}} = 3.83 \times 10^{-8}$$

Similar calculations were made for the electrometric titrations of N/1500, N/1000, N/100, N/50 and N/10 solutions. It is not possible to calculate these values from the electrometric titration curves for N/2000 and N/5000 since there is no end point for $NaHCO_3$. The following table shows the data used in the calculations as well as the products calculated.

TABLE NO. 1.

Data obtained from the electrometric titration curves, and the products calculated therefrom.

Normality.	N/1500	N/1000	N/100	N/50	N/10
Initial (CO_3'')	3.85×10^{-4}	5×10^{-4}	5×10^{-3}	1×10^{-2}	5×10^{-2}
Converted to (HCO_3')	.595	.680	.912	.948	.988
ratio of (CO_3'') remaining	.405	.320	.088	.052	.012
(H) $\times 10^{-8}$	5.62	4.47	1.82	1.55	1.33
(H) $(CO_3'') \times 10^{-12}$	8.76	7.15	8.02	8.06	8.28
$\frac{(H)(CO_3'')}{(HCO_3')} \times 10^{-10}$	383.0	211.0	17.5	8.5	1.67
(HCO_3')					

The end points have all been carefully chosen as the center point of that portion of the curve approaching the vertical, and this choice is entirely a matter of judgment, but the values calculated from this data indicates that the product $(H)(CO_3'')$ is a constant. This product then defines the (H) , and (CO_3'') necessary in order that bicarbonate ion may exist in solution, and the product of the concentration of H and of CO_3'' could not in any solution exceed this value. This ionization product should be verified for K_2CO_3 and Li_2CO_3 .

The product given by the equation $\frac{(H)(CO_3'')}{(HCO_3')}$ decreases with increase of concentration of Na_2CO_3 used in the electrometric titration. This appears to be contrary to the results of Seyler and Lloyd, but a consideration of the method of McCoy will show that this decrease is in accordance with their results.

He ~~determined~~ determined the equilibrium between Na_2CO_3 , $NaHCO_3$ and CO_2 experimentally by examination of the liquid and the vapour phases in equilibrium with one another. The equilibrium is expressed in the form $2K^2C/kP(1-X)$ where X is the fraction of sodium in the form of carbonate, C the concentration of sodium in gram atoms per liter, k the solubility coefficient of CO_2 in water, and P the partial pressure of CO_2 .

By decreasing the concentration of Na_2CO_3 solutions used the value $1-X$ is decreased then the ratio $\frac{NaHCO_3}{Na_2CO_3}$ will increase or the ratio $\frac{X}{1-X}$ will increase.

In the titration by increasing the concentration of the Na_2CO_3

solutions, at the end point for NaHCO_3 the ratio $\frac{\text{NaHCO}_3}{\text{Na}_2\text{CO}_3}$ has been increased.

That is the same effect has been produced by decreasing the concentration of the Na_2CO_3 solution in the former, and increasing the concentration of the Na_2CO_3 solution in the latter; and in both cases as the ratio expressed by $\frac{x}{1-x}$ or $\frac{\text{NaHCO}_3}{\text{Na}_2\text{CO}_3}$ increases the secondary constant for Carbonic acid given by $\frac{(\text{H})(\text{CO}_3'')}{(\text{HCO}_3')}$ decreases.

The application of the product $(\text{H})(\text{CO}_3'')$ to the equilibrium between CaCO_3 , CaSO_4 and H_2CO_3 in water solution.

The constant value given by $(\text{H})(\text{CO}_3'')$ defines the conditions necessary to produce the HCO_3' .

The following equilibria are present in a solution of CaCO_3 when H_2CO_3 is present.

$$\frac{(\text{Ca})(\text{CO}_3'')}{(\text{H})^2(\text{CO}_3'')} K_1 \text{-----} (1)$$

$$\frac{(\text{H})^2(\text{CO}_3'')}{(\text{H}_2\text{CO}_3)} K_2 \text{-----} (2)$$

As carbonic acid is added the (H) and (CO_3'') tend to increase, now if any increase of (CO_3'') occurs in (1) in order that K_1 remain constant, (Ca) will decrease and may exist in the molecular condition or be precipitated as CaCO_3 thus removing some (CO_3'') from solution. It follows that the concentration of (CO_3'') should not increase.

The initial concentration of CO_3'' calculated from the solubility of CaCO_3 in pure water is 1×10^{-4} .

In order that HCO_3' be formed in the solution the product given by $(\text{H})(\text{CO}_3'') = 8 \times 10^{-12}$ must be satisfied. It is possible then

to calculate the (H) necessary for the production of HCO_3 this would be given by

$$(H) \times 1 \times 10^{-4} = 8 \times 10^{-12}$$

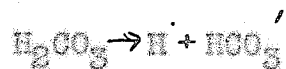
from which $(H) = 8 \times 10^{-8}$ or a pH. value of 7.1. That is in solution of $CaCO_3$ which have a pH. value of 7.1, due to the addition of acid, the HCO_3 may exist but in solutions having a higher pH. value the HCO_3 does not exist. This value agrees very well with that for the flexure on the Curves no. VI. They all tend to flatten out slightly above the neutral point. The point of flexure is at a voltage reading of .630 corresponding to a pH. value of 7.42. This value is slightly higher than the calculated value for in the calculation the (CO_3) concentration has been assumed constant, but the (CO_3) may increase on the addition of H_2CO_3 . The actual increase would be very small, and such an increase would account for the increased pH. value for the flexure of the curve over the calculated value. As we approach the lower flexure of Curves no. VI. we are also approaching the saturation point for H_2CO_3 in presence of $CaCO_3$, since no end point for HCO_3 ion is produced on the curves. Along the flat portion of the curve then there are two effects to be considered, the possible production of the HCO_3 , and the amount of H_2CO_3 present. Since H_2CO_3 is being bubbled through the solution the amount present would ^{not} be diminished, and along this portion of the curve the bicarbonate of Calcium may be produced. The addition of $CaSO_4$ to a solution containing $CaCO_3$ and H_2CO_3 will decrease the pH. value necessary to produce HCO_3 , since according to the discussion on this particular equili-

rium the (H) is increased by decreasing the (CO_3'') , consequently a larger concentration of (H) will be required in order to give the constant $(H)(CO_3')$ necessary for the production of HCO_3' .

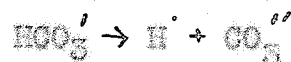
The actual pH. value of ground waters such as occur in the Winniped district is not as yet available, but is probably less or equal to that of pure water pH. 7.00, since the amount of CO_2 dissolved is governed by the partial pressure of CO_2 in the atmosphere, and the partial pressure is very small. Consequently the (H) will be conditioned by a very small amount of Carbonic Acid present, and by dissolved $CaCO_3$, and $CaSO_4$. Since the investigation does not deal with other salts present the effect of these must necessarily be omitted. The evidence is that HCO_3' does not exist in such solutions.

The Application of the product $(H)(CO_3'')$ to the ionization of Carbonic Acid.

Carbonic acid is assumed to ionize according to the following equations.



and



That is there should be two ionization constants for Carbonic Acid.

$$\frac{(H)(HCO_3')}{(H_2CO_3)} = K_a \text{-----(a)}$$

and

$$\frac{(H)(CO_3'')}{(HCO_3')} = K_b \text{-----(b)}$$

however

It has been shown, that the secondary constant K_b varies with increasing dilution, and this has been explained by showing that $(H)(CO_3'')$ equals a constant value while the (HCO_3') decreases with increasing dilution, and when the product $(H)(CO_3'')$

is less than its constant value (HCO_3') will cease to exist. Consequently when this value has been reached the constant K_a will be equal to 0. That is to say increasing the dilution increases the value of K_b , and decreases the value of K_a .

The product $(\text{H})(\text{CO}_3'')$ is then apparently the only constant value in the ionization of Carbonic Acid.

As CO_2 is bubbled into water H_2CO_3 will be produced, and will be completely ionized until the value $(\text{H})(\text{CO}_3'')$ has been attained then HCO_3' will be produced, and as we increase the amount of H_2CO_3 in solution it will ionize producing momentarily an excess of H ions, and these will unite to form HCO_3' until the product $(\text{H})(\text{CO}_3'')$ reaches its constant value.

In discussing carbonate bicarbonate equilibrium then it is this constant rather than that given by (a) or (b) that is the fundamental value. If this constant had been used in place of $(\text{H})(\text{CO}_3'')$ it would not alter in any way the consideration of

H_2CO_3
the equilibrium conditions under discussion.

The degree of hydrolysis of a saturated solution of CaCO_3 and the solubility product.

It is possible to calculate from the data obtained, by the electrometric titration of $\text{Ca}(\text{OH})_2$ with CO_2 , the degree of hydrolysis of a saturated solution of CaCO_3 . The normality of such a solution 2.4×10^{-4} , calculated from the solubility (1) of CaCO_3 in water at 20°C . Then if the salt were completely hydrolysed the amount of hydroxyl ion present would be 2.4×10^{-4} gm. ions per liter. The (H) corresponds to a voltage of the gas chain of .794
1.--"Holleman Kohlrousch and Rau", Z. physik. Chem. 12, 129, 241 (1893)

and is equal to 4.17×10^{-10} from the ionic product for water the $(OH)^{-}$ 2.4×10^{-5} the degree of hydrolysis is given by

$$\frac{2.4 \times 10^{-5}}{2.4 \times 10^{-5}} = 0.100 \text{ or } 10\%$$

This value is considerably smaller than that given by McCoy(1) who considered the hydrolysis to be 66% and that of Bodländer (2) 80-83.4% at 16° .

The product of the $(H)(CO_3^{--})$ in the saturated solution of $CaCO_3$ is given by $(4.17 \times 10^{-10})(1.2 \times 10^{-4}) = 5 \times 10^{-14}$,

this is much smaller than the product necessary for the formation of HCO_3^{-} . Consequently in such a solution the HCO_3^{-} does not exist, and the hydrolysis would be represented by the stoichiometric equation. $CaCO_3 + 2H_2O \rightarrow Ca(OH)_2 + H_2CO_3$.

The hydrolysis of $CaCO_3$ corresponds to a second stage hydrolysis, for which the equation giving the hydrolysis constant is

$$\frac{K_2^2}{(1-K)W^2} = K$$

and for $CaCO_3$ this value is found to be 1.11×10^{-11} .

The degree of hydrolysis can be calculated in a similar way from the initial reading of each of the Curves on no. XIII, and the following table shows the percentage hydrolysis so calculated.

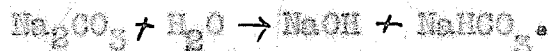
Percentage Hydrolysis of Na_2CO_3 solutions of Normalities.

N/10	N/50	N/100	N/1000	N/1500	N/2000	N/5000
.795%	1.62%	2.52%	4.17%	3.72%	3.32%	3.02%

1.---"McCoy", (loc cit).

2.---"Bodländer", ZS. ph. Ch. 35, 23/9. (1900).

A Na_2CO_3 solution is considered as undergoing hydrolysis according to the equation.



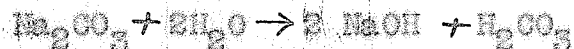
This corresponds to a first stage hydrolysis, and the equation from Ostwald's dilution law is

$$\frac{K^2}{(1-X)V} = K_h$$

where X is the degree of hydrolysis, V the number of liters containing 1 gm. mol. of the dissolved salt, and K_h the hydrolysis constant.

The value K_h has been calculated from the data obtained for solutions varying in dilution from $N/10$ to $N/5000$ these values are given in table No. II.

The value of K_h for dilutions at $N/1500$, $N/2000$ and $N/5000$, for the first stage hydrolysis is not constant, but diminishes from 3 to $.09 \times 10^{-6}$, and since the product given by $(H)(CO_3'')$ is not sufficient at dilution of $N/1500$, $N/2000$, $N/5000$. (The (H) is calculated from the voltage of the gas chain, the (CO_3') from the normality of the solution) to produce HCO_3' , the hydrolysis of Na_2CO_3 solutions at these dilutions may occur according to the equation



This corresponds to a second stage hydrolysis for which the equation is

$$\frac{K^3}{(1-X)V_2} = K_h$$

where X is the degree of hydrolysis, V the number of liters containing 1 gm. mol. and K_h the hydrolysis constant.

TABLE NO. II.

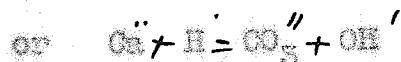
Normality	K	$K_h \cdot 10^6$	$K_H \cdot 10^{12}$
N/10	.00795	5.19	1270.0
N/50	.0162	2.67	432.0
N/100	.0252	3.26	411.0
N/1000	.0417	.907	18.4
N/1500	.0372	.479	5.94
N/2000	.0332	.285	2.37
N/5000	.0302	.094	.28

The values K_h agree very well including that for a N/1000 solution, but beyond this there is a gradual decrease in the value. For K_H the values up to N/1000 do not agree so well as those of K_h , and the remaining values show only a fair agreement. At dilutions represented by the last three normalities the dilution is approaching that value at which NaOH and H_2CO_3 produced by hydrolysis are completely dissociated, consequently the (H^+) and (OH^-) tend to become equal, and at infinite dilutions the ionic concentration H^+ and OH^- would be equal. This is evident by the increase in the degree of hydrolysis to a maximum (0.0417) followed by a gradual decrease. Since the hydrolysis effect is being overcome by the increased dilution, it is to be expected that the hydrolysis constant calculated at this dilution would vary.

Calculation of the Solubility product for CaCO_3 .

If calcium carbonate did not undergo hydrolysis the solubility product would be $(\text{Ca}^{++})^2$ since the (Ca^{++}) would equal the (CO_3^{--}) , but it is possible even when a salt undergoes hydrolysis to calculate the solubility product.

Since the solution is electrically neutral the sum of the positive ions present would equal the sum of the negative ions



If the salt be completely ionized the (Ca) will be one half the normality (1) 1.2×10^{-4} gm. ions per liter. The (H) has been measured, and is equal to 4.17×10^{-10} , and from the ionic product for water we can calculate the (OH) . This is equal to 2.4×10^{-5} . The (H) is so small that it may be neglected in the calculation. Therefore

$$\begin{aligned} (\text{CO}_3) &= (\text{Ca}) - (\text{OH}) \\ &= (1.2 \times 10^{-4}) - (2.4 \times 10^{-5}) \\ &= 1.04 \times 10^{-4} \end{aligned}$$

Then the solubility product

$$\begin{aligned} (\text{Ca})(\text{CO}_3'') &= (1.2 \times 10^{-4})(1.04 \times 10^{-4}) = 1.25 \times 10^{-8} \end{aligned}$$

This value is rather higher than that given by Bodländer (2) (2.8×10^{-9}) and that of Johnston (3) $.99 \times 10^{-8}$.

1.---The normality is calculated from the conductivity measurements of Kohlreusch (loc cit.)

2.---"Bodländer", ZS. ph. Ch. 35, 23, (1900)

3.---"Johnston", J. Am. Chem. Soc. 38, 975, (1916).

- 1.-- A Method of Making a Titration with Carbonic Acid is outlined.
- 2.-- The range of (H) for admixtures of $CaCO_3$, H_2CO_3 and $CaSO_4$ in water solution has been determined experimentally by means of the hydrogen electrode.
- 3.--x The addition of $CaSO_4$ to solutions of $CaCO_3$, and $CaCO_3$ and H_2CO_3 in water increases the (H) of these solutions.
- 4.-- $CaSO_4$ acts as an aggravator in the self corrosion of cast iron in contact with ground waters.
- 5.-- The ionization constant for carbonic acid given by the equation.

$$\frac{(H)(HCO_3)}{(H_2CO_3)} = K_1$$
 decreases with increasing dilution, and the secondary constant given by the equation.

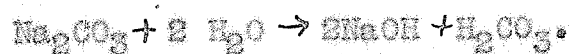
$$\frac{(H)(ZCO_3'')}{(HCO_3')} = K_2$$
 increases with increasing dilution.
- 6.-- The reaction represented by the equation

$$H' + CO_3'' \rightarrow HCO_3'$$
 does not go to completion and the product of the residual (H) and the residual (CO_3'') is a constant, and is 8×10^{-12} , for solutions of $MgCO_3$ from N/10 to N/1500 when titrated with HCl.
- 7.-- From the application of the product $(H)(CO_3'')$ to ground waters, and the results of the electrometric titrations it is evident that the HCO_3' does not exist in ground waters.
- 8.-- The degree of hydrolysis of a saturated solution of $CaCO_3$ in water is equal to 0.10, or expressed as percentage 10%. The hydrolysis occurs according to the equation

$$CaCO_3 + 2 H_2O \rightarrow Ca(OH)_2 + H_2CO_3.$$

or is a second stage hydrolysis and the hydrolysis constant is 1.1×10^{-11}

- 9.-- The percentage hydrolysis of solutions of N/10, N/50, N/100, N/1000, N/1500, N/2000 and N/5000 sodium carbonates were determined, and the hydrolysis constant is equal to 3.04×10^{-6} . For dilutions of N/1500, N/2000 and N/5000 the value decrease with increase of dilution and at these dilutions hydrolysis occurs according to the equation.



- 10.-- The solubility product for CaCO_3 from the electrometric titration of $\text{Ca}(\text{OH})_2$ with CO_2 is 1.25×10^{-8} .