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REPORT  
of  
COMMITTEE ON THESIS

THE undersigned, acting as a committee of  
the Graduate School, have read the accompanying  
thesis submitted by Adolph H. Nietz.  
for the degree of Master of Science.  
They approve it as a thesis meeting the require-  
ments of the Graduate School of the University of  
Minnesota, and recommend that it be accepted in  
partial fulfillment of the requirements for the  
degree of Master of Science.

Francis C. Frary  
Chairman

E. P. Harding  
Henry A. Erickson

May 22 1915

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Minneapolis, Minn.  
May 22, 1915

Dean G.S.Ford,  
Graduate School,  
University,

Sir,-

The undersigned, sitting as a Committee of the Graduate School, have this day conducted the oral examination of Mr. Adolph H. Nietz, candidate for the degree of Master of Science, and recommend him for this degree.

Alvin F. Kovant

Henry A. Erikson

J. H. Derby

E. Harsiee

Francis C. Tracy  
Chairman.

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THE SINGLE POTENTIALS OF DEVELOPERS  
AND THEIR MEANING.

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A Thesis submitted to the Faculty of the Graduate School  
of the University of Minnesota by Adolph H. Nietz, in partial  
Fulfillment of the Requirements for the Degree of Master of  
Science.

May 1915.

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Some attention has recently been drawn to the reducing power of photographic developers and the relation of their single potentials to the same. Up to the present time, so far as we know, no unit for the measurement of reducing power has been introduced, altho a chemical method of comparison has been suggested.<sup>1</sup> At any rate no clear explanation of the possible meaning of varying single potentials has been made, different writers reaching widely different conclusions. The object of this thesis is to standardize and systematize the technique of obtaining these potentials, and to draw only those conclusions which seem warranted by experience and experimental evidence.

The only known work on this subject at the present time is that of Mathews and Barmeier,<sup>2</sup> and that of Lidbury.<sup>3</sup> We are unable to agree with these authors on many points brought out by them, and have as a basis of argument much addi-

(Note: The numbers in the text refer to the bibliography at the end.)

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tional experimental work apparently not previously tried. The curves we obtained have the same shape and general characteristics as those given by Mathews and Barmerier, theirs being merely upside down with respect to ours, with more negative values at the top. According to the conception of single potentials given below, they have misused the value of the standard electrode, altho one finds a very loose use of this thruout work on electro-potentials. Accordingly, the initial potential of the developers investigated by them is given a value in the neighborhood of -1.0 volt while we have found this to be about + 0.25. The discrepancy is apparently due to the addition of the EMF of the couple to the value of the Calomel electrode, both assumed negative, instead of the more justified use stated below. (Pg. 29  $E_{\text{Pt-sol.}} = E_{\text{Hg-sol.}}^{-E}$ )

Summing up briefly the work done in the field of single potentials of developers, Mathews and Barmerier<sup>2</sup> obtained potentials which became more negative, rather rapidly at first and then more slowly. A number of developers were tried, but

no results beyond a period of a few hours were reported, in most cases eight hours was the time limit of observation. The fall of the potential (becoming more negative) they ascribed to oxidation, and concluded that it is the sulphite<sup>3</sup> in a developer that is oxidized. Lidbury obtained some results and reached certain conclusions which fit in fairly well with those of the present work, altho on account of his using  $-.56$  volt for the Normal Calomel Electrode (which would represent  $E_{\text{sol. -Hg}}$ ), his numerical values cannot be directly compared with those given later on. He concluded that the variation in potential at first exhibited by a developer was due to the "progress of reactions within the solution" (other than mere oxidation), and that this decreased with time. Also he found that it is necessary to wait some time before a constant value is obtained, and that there are irregularities shown in some determinations. No fixed technique was developed, and it is fairly certain that equilibrium was not reached with the solutions used, as Lidbury himself admits. This is the extent

of the work on the subject up to the present time. There is not enough evidence to prove anything definite about the comparative reducing power of different developers, nor to draw definite conclusions as to what happens in the developer.

In this work we shall attempt to show:

1. That the more or less rapid variation of potential observed during the first period (sometimes for weeks), whatsoever form the curve may take, shows absolutely nothing concerning the real single potential of the developer. Nearly all developers start at about the same point and closely parallel each other for some time. At any rate these beginning changes are valueless; it is the final point of equilibrium alone which can give us the desired information. The attainment of this presents many difficulties, as later experience shows.

2. That it is impossible to consider a fall of potential as being due to oxidation of any sort, much less that of the sulphite. Moreover, these changes cannot be due in any degree to the sul-

phite present; it is very probable that the sulphite plays an exceedingly minor role in the mechanism of the developer. But it seems borne out by experience and experimental evidence that the sodium carbonate is a very important factor. Our reasons for not agreeing with the sulphite-oxidation idea of the cause for falling potentials are presented in the following pages, which give a theory that has been based entirely on experimental facts.

In addition,

3. The fundamental theory of the production of a potential at the electrode by a developer, and the conditions preventing the immediate attainment of its true value will be discussed. The explanation of curves such as those obtained by Mathews and Barmerier would thus follow.

4. A method of comparing developers as to reducing power will be given.

5. The relation of the different parts of the developer to each other will be discussed.



It was <sup>that</sup> best for this purpose to confine attention to hydrochinon until as complete information as possible was obtained. Other developers would be likely to possess similar characteristics.

#### THEORETICAL.

It is first necessary to see why the production of a definite electrode potential on platinized platinum, by a developer, can give us any information. This electrode potential is brought about by the formation of gaseous hydrogen, in the developing solution, by the developing agent, and this hydrogen has of course the power of dissolving in the platinum. The hydrogen thus dissolved behaves like any metal dipping in an electrolyte and has a definite electrolytic solution tension. We can conceive of this gas formation as being brought about in the following manner. In any developer, acid or alkaline, there is a certain concentration of H-ion and of OH-ion, due to the electrolytic dissociation of  $H_2O$ , and added to or affected by, the H-ion content of

acid developers, and by the OH-ion concentration of an alkaline developer (from NaOH, KOH, or hydrolysis of  $\text{Na}_2\text{CO}_3$ ). In an alkaline developer of the common type, for instance, one containing  $\text{Na}_2\text{CO}_3$ , at a fixed temperature, there is a definite and fixed concentration of H-ions and of OH-ions which is conditioned solely by the alkalinity. The product of the H-ion concentration by the OH-ion concentration depends on the degree of dissociation of the water, and the introduction of either one of these ions by the addition of an acid or base would affect the equilibrium between the H- and the OH- ions in the usual manner. We have been able to show (pg. 95) that the hydrogen potential, and therefore the alkalinity, of a developer, is not changed to any measurable amount by the oxidation of the developer by air, however much prolonged. Hence it is evident that the oxidation of the developer (at least of Hydrochinon) probably does not produce either an acid or basic substance. And moreover, no error is introduced by taking the hydrogen potential of a developer at any stage of oxidation, altho in all of this

work we have obtained it within a comparatively short time after mixing.

The production of hydrogen probably takes place in a manner indicated by the following ionic reaction:



where R represents such a substance as hydrochinon. The extent of this reaction would depend directly on the reducing power of the developing agent. As has been seen, the actual concentration of the OH-ion or of the H-ion in the solution does not change. As soon as some of the ions are used up they are replaced, for the product concentrated  $\text{H}^+$  x concentrated  $\text{OH}^-$  must remain constant. The above reaction, however, cannot proceed indefinitely. It goes on until an equilibrium is established, and it is very likely that the gas equilibrium is here the important factor. When this stage is reached, the hydrogen gas is in equilibrium with the solution, the space above, and the platinum electrode. It must further be noted that this reaction takes place only on a small scale for the actual concentration of H and OH ions is

very small, and the developer can never evolve hydrogen at atmospheric pressure. Only a small partial pressure of hydrogen gas is produced, but this is measurable by a method given later. Moreover, the actual amount of the substance RO which is formed, is exceedingly small and negligible compared with the amount of R present. Also, as shown by the hydrogen potentials, the compound RO even in large quantities, produced by direct oxidation, does not affect the alkalinity of the solution.

Assuming for the time being, that this production of gaseous hydrogen is the cause of the electro-potential of a developer, we may discuss the character of such an electrode as exists in the solution. As is very well known, platinum black electrodes absorb hydrogen, and the latter, having a definite electrolytic solution pressure under fixed conditions, tends to enter the solution as H-ions. For every positive ion sent into the solution in this manner, the electrode acquires one negative charge, and the lowering of the electrode potential ensues. After a time, equili-

brium is established; the number of ions returning to the electrode equals the number entering the solution during the same period and the result is the formation of what has been termed the "electrical double layer". Aside from this ionic process, the production of hydrogen gas as described is also going on, - the developer is furnishing hydrogen to the electrode. The latter process may be referred to as a loading of the electrode with hydrogen, the mechanism of which will be discussed below. In accordance with Nernst's statement, and the above, the tendency of the gaseous hydrogen on the platinum to enter the solution as H-ions, and hence the potential, will depend on the concentration of the H-ions in the solution, and fundamentally on the pressure of hydrogen gas at the electrode. The production of hydrogen, and the change of the electrode potential, ceases when hydrogen gas is in equilibrium with the electrode, the solution, and any space above the solution. The ionic equilibrium depends on this; the double layer forms very

quickly and adjusts itself according to the pressure of gas at the electrode. This condition of complete equilibrium must be reached before the true potential of any developer can be found.

Further, as Nernst<sup>4</sup> states, ("Offenbar ist die oxydierende oder reduzierende Kraft umso grösser, mit je grösserem Drucke die Gasentwicklung sich vollziehen kann."), referring to oxidation and reduction cells, the reducing power is greater according as gas evolution takes place at a greater pressure. The actual reducing power of a developer conditions the partial pressure of hydrogen, which is the gas produced. This fact would be obvious from a reaction such as indicated. It has been seen that the pressure of hydrogen gas at the electrode, and the concentration of H-ions in solution determine the potential. Then, if we can compare developers quantitatively as to this gas formation, we may infer something as to their relative reducing powers. We fail to see any other method of drawing safe conclusions concerning the reducing power of a developer from a study of its electro-potential. Different

developers have different concentrations of H-ion,<sup>w</sup> which in part determines the potential but bears no relation to the reducing power, so that direct comparison of the initial potentials, or even those at equilibrium, is worthless.

However, it is possible to calculate the actual partial pressure of hydrogen developed at the electrode from the single potential of the developer, if we also obtain the potential of hydrogen at atmospheric pressure in this same developer. This will, in effect, give a hydrogen concentration cell in which the electrodes (hydrogen) have two different electrolytic solution pressures in the same solution, due to difference in gas pressure. The potential of EMF of such a concentration cell is made up of three parts, the single potential of each electrode, and the contact potential if the connection between the two is thru another liquid. As a matter of fact, it is not necessary to set up two electrodes against each other in the form of a true concentration cell; the single potential of each can be taken separate-

ly against the standard calomel cell, provided a solution is used which eliminates contact potentials. Saturated potassium chloride has this property, as noted on page 28, and when two hydrogen electrodes are thus measured, the difference between the two taken separately against the calomel half-cell is equal to the EMF of the two read as a complete cell, as we have been careful to ascertain by several direct experiments. One of the three terms, the contact potential, therefore need not enter into the formulation for the present case. Nernst's expression for the single potential at each electrode is

$$P = .0001983 \frac{T}{n} \log \frac{C}{c}$$

where T is the absolute temperature, n is the valence of the substance producing the electrical energy (hydrogen in this case), C is the gas pressure at the electrode, and c the osmotic pressure of the ions in the solution, both for the above mentioned substance. Since the osmotic pressure of the ions in solution depends directly



on their concentration, we may use ion concentration here in place of osmotic pressure.  $c$  will hereafter have this meaning (i. e.,  $c$  = ion concentration of hydrogen in solution). Applying this to our present use,  $n$ , the valence of hydrogen equals 1;  $C$  is the gas pressure of  $H_2$  at the electrode; and  $c$  is the concentration of H-ion in the solution. At temperature  $25^\circ$ ,  $.0001983 T$  becomes 0.05909. The EMF of the cell equals the difference between the single potentials of two such electrodes. Then we can write,

$$E = .05909 \log \frac{C}{c} - 0.05909 \log \frac{C'}{c}$$

in which case  $E$  is the EMF of the concentration cell,  $C$  the gas pressure at one electrode and  $C'$  the gas pressure at the other.  $c$ , the ion concentration of hydrogen in the solution, is the same in both cases. The above may be written

$$E = 0.05909 \log \left( \frac{C}{c} \cdot \frac{c}{c'} \right) = 0.05909 \log \frac{C}{C'}$$

This is the expression we desire, for if  $C$ , the hydrogen gas pressure at 1 electrode = 1 atmosphere,

we can calculate  $C'$ , since  $E$  can be observed.

It is obvious that if the gas pressure were the same in each case, the last equation could be changed so that it would now be possible to calculate the ion concentration of hydrogen in one of the solutions, the other ion concentration being known. The determination of hydrogen-ion by such a method has been frequently carried out. It should be noted that in all reference to this equation,  $E$  should logically be expressed on the hydrogen scale, an explanation of which follows.

Interpretation of  $E$ :

In the equation,  $E = 0.0001983 T \log \frac{C}{c}$

The zero point will be fixed by the conditions under which this equation reduces to zero. By inspection of the equation it will be seen that  $\log \frac{C}{c}$  must then equal zero. This expression may be resolved into  $\log C - \log c$ . Each term must vanish. According to the generally accepted interpretation  $C$  represents the pressure of the gas at the electrode, and  $c$ , the osmotic

pressure of the ions in solution. The latter is assumed a unit, equal to 1, if the solution contains 1 gram-ion per liter. The above conditions for the zero point are then obtained if we take the potential difference between a platinum electrode saturated with hydrogen at a pressure of 1 atmosphere and a solution containing 1 gram-ion of hydrogen per liter, in which case  $C = 1$  and  $c = 1$ , and the equation reduces to zero.

If these conditions are adopted, an electrode saturated with hydrogen at a pressure other than 1 atmosphere, dipping in a solution containing 1 gram-ion of hydrogen per liter; or an electrode with hydrogen at 1 atmosphere in a solution containing more or less than 1 gram-ion of hydrogen; or one with neither hydrogen at 1 atmosphere or a solution of 1 gram-ion of hydrogen; all will give real values for  $E$ , for at least one of the terms of the expression  $\log C - \log c$  will remain.

It is evident that the determination of the ionization of an acid, such as commonly used in setting up the hydrogen electrode, will

have much to do with fixing this zero point, for it is necessary to know the potential of platinum saturated with hydrogen, in a solution containing 1- gram-ion of hydrogen per liter.

For the basis of all of our work, employing the hydrogen scale, we will use the value for the 0.1 N calomel electrode, obtained by the use of data by Lewis and Rupert<sup>5</sup>; who state that there is abundant evidence that the dissociation of 0.1 N HCl is 0.86. Accordingly the 0.1 N calomel electrode has the value + 0.3355 volt on the hydrogen scale at 25°. Based on data by Noyes concerning the dissociation of the acid this value becomes +0.339 volt, but as Loomis and Acree also found,<sup>6</sup> the latter value does not give results, when applied to determinations of ionization constants and hydrolysis, quite so well in accord with other methods. To derive a conversion of absolute units to units on the hydrogen scale,

the following relations are used:

Value of 0.1 N Calomel electrode at 25° on absolute scale

$$= 0.6117^7 + .0008 (t-18) = 0.6173$$

1.0 N Calomel electrode at 25° on absolute scale difference	<u>0.5642</u> 0.0531
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Value on hydrogen scale:

0.1 N Calomel difference,	0.3355 <u>0.0531</u>
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1.0 N Calomel	0.2825
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We thus have 0.2825 volts as the difference in potential between the normal Calomel Electrode and the Pt-H<sub>2</sub> electrode in hydrogen-ion of unit concentration, the latter based on 0.86 as the dissociation of the HCl. The results are clearly shown in the accompanying figure, which gives the comparative values. To obtain the value of the potential on the hydrogen scale from the absolute scale, it is necessary to subtract 0.2815 (282) from the absolute value, as the figure will show.

## RELATION OF ABSOLUTE TO HYDROGEN SCALE

At 25°

	Abs.	Hydrogen
0.1 N calomel	.6173	+ .3355
1.0 N "	.5642	+ .2825

+ .2815 — 0.000

- .310 — -.4915

### THE DELAY OF THE EQUILIBRIUM.

Having considered in brief the fundamental theory of the value of the electro-potential of the developer, it remains to explain why this may not be reached instantaneously. It is at once obvious to the experimenter that the developer does not reach a state of equilibrium for some time, - when the potential is plotted against the time a curve is obtained which steadily drops, indicating, however, a tendency to approach some constant value. This equilibrium, which has previously been referred to, is delayed by two different types of causes: (1) Chemical, and (2) Physical.

(1) Of the first kind, the part played by the oxygen in the solution and the air above the solution, is one. The oxygen dissolves in the platinum, and reacts with the hydrogen, thus preventing the latter from exerting its full electrolytic solution pressure and consequently making the potential more positive. This effect

would persist until the oxygen was used up after which the developer would be able to load the electrode with hydrogen up to the equilibrium pressure. A secondary effect of the oxygen might be to oxidize some of the developer agent itself, thereby weakening its power to produce hydrogen. From these considerations it would seem plausible that the best way to obtain the electro-potential of the developer so as to eliminate errors as far as possible, would be to make it up from oxygen-free water in vacuo, allowing it to come to a constant value. Otherwise the uncertainty of the action of oxygen would still be involved.

Probably far more important than any possible action of oxygen is another chemical effect, - an inherent reaction resistance. In a latter series of determinations we succeeded in eliminating oxygen and other sources of error to a very large extent, but in spite of this the equilibrium is obtained in many cases only after a long period of time. It would seem reasonable to suppose, therefore, that in some manner, a factor within the developer opposes the forma-



tion of hydrogen gas and consequently retards the equilibrium. The exact nature of this is not known. Its effects are very evident, and developers differ considerably in showing them. Amidol has by far the lowest reaction resistance of the developers we have investigated. Hydrochinon has the highest, and metol-hydrochinon is intermediate. Of one thing only are we sure, something within the developer itself opposes the attainment of equilibrium, and is apparently beyond our control.

(2) Of the second type of causes, several may be mentioned. They all concern the removal of hydrogen from the active zone, that is the electrode and the space immediately surrounding it. This is brought about by mechanical means, and the result is a lower partial pressure of the gas than should otherwise be the case. The gas formation takes place in one of two ways. Either the hydrogen is produced by the developer thru the catalytic action of the platinum, in which

case it is formed right at the electrode, or it is formed thruout the solution and is extracted by the platinum of the electrode due to the greater solvent power of the latter for hydrogen. The effect of shaking the cell throws some light on this point, but it is not conclusive. In the first experiments described below, shaking the cell, or mechanically distributing the solution by bubbling a gas thru it near the electrode surface, causes the potential to rise suddenly (see curves 3, 4, 5, and 6), but this condition is accounted for by the fact that hydrogen gas is actually lost from the solution, diffusing into the air above, and being carried off by the gas passing thru the solution. If this were not the cause, the rise of potential under these conditions would indicate that the hydrogen was formed at the electrode, and shaking the cell would bring to the electrode surface developing solution less rich in dissolved hydrogen, resulting in a lower partial pressure of the gas at the electrode and a higher (less negative)

potential due to the removal of the gas from the electrode by the solution. According to the second idea the hydrogen is produced thruout the solution; in this case, shaking would bring to the electrode solution which is richer in hydrogen than that nearer the electrode, as the platinum has been extracting hydrogen from the latter. Then the amount of gas actually at the electrode would be increased and the potential should become more negative. As a matter of fact, this effect has been observed, when the cell is so arranged that no air or oxygen is present, and there is no space above the liquid, in other words, when there is no possibility of diffusion of the gas out of the system. The only effect that shaking ever has on such an electrode cell is to lower its potential, and we are inclined to favor this as the explanation of the phenomenon. Then we can conceive of the gas produced at all points of the solution slowly diffusing toward the electrode and being absorbed by the latter, and this slow diffusion alone would account for considerable delay in reaching an equilibrium. A slight diffusion of hydrogen into the interior of the platinum

no doubt takes place and is a factor in delaying the final adjustment. The effect of shaking an electrode has been observed in connection with certain oxygen electrodes by Kistiakowski<sup>8</sup>. He mentions the fact that in a solution containing oxidizing agents the potential of an electrode is changed by the electrode being moved or shaken. Little explanation was given and this may or may not have been a similar phenomenon.

We have, then, reached some conclusions as to the conditions existing within the developer, and the experimental results seem to bear them out. The potential will continue to change until the hydrogen gas is in equilibrium with the solution, the platinum of the electrode, and the space above the liquid surface. Any removal of gaseous hydrogen from the electrode itself will result in a rise of potential, since the electrolytic solution pressure is reduced by lowering the gas pressure.

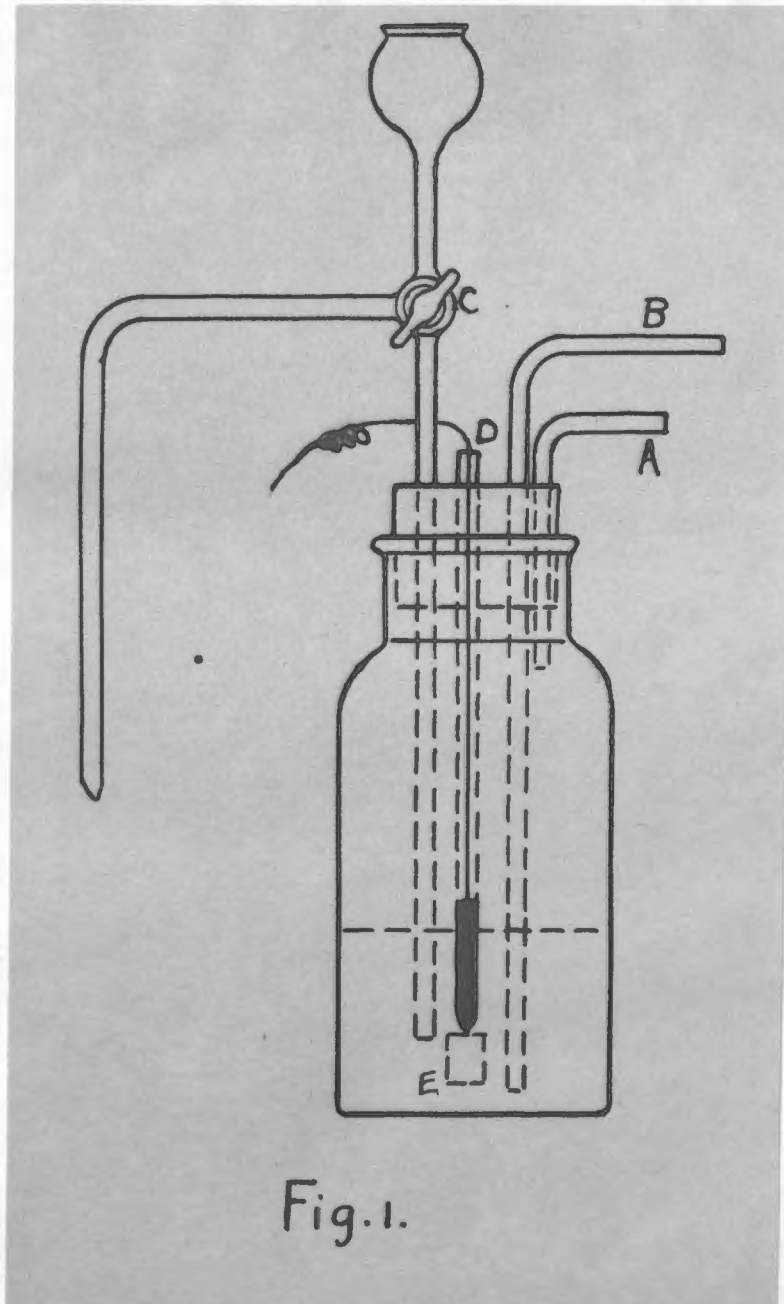
The true potential of the developer, then, is not immediately obtained because various factors are at work, especially during the early

stages of the process, which remove gaseous hydrogen from the system; the solution must become saturated with the gas at the given pressure, and this must be in equilibrium with the electrode and any space above the solution. Also the diffusion of hydrogen toward the electrode is slow, and this gives higher results at first, the potential gradually approaching its true value.

Some of the foregoing considerations will explain the shape of the curves obtained by Mathews and Barmeier, which they attribute to oxidation. All determinations made in connection with the present work showed similar characteristics, but were followed for a much longer period of time, after which the tendency toward a point of equilibrium became very evident.

#### EXPERIMENTAL.

The first electrode cells to be used in this work for the developer were of the kind shown in Figure 1. Such a cell will be satisfactory for preliminary experiments to illustrate



the theory given above. The bottle is of about 250 cc. capacity, and is fitted with a 4-hole rubber stopper thru which pass the tubes as shown. A and B are two tee-tubes, A passes just thru the stopper, while B reaches nearly to the bottom of the bottle. C is a 3-way stop-cock, one branch of which reaches to the bottom of the bottle, another serves as the side tube connecting with the central cell and is drawn out at its farther end, and third carries a thistle tube to serve as a filling funnel. D is the tube into which the platinum electrode is sealed.

The electrodes were coated with platinum black in the manner recommended by Ostwald-Luther<sup>9</sup>. For this purpose the following solution was used:

PtCl <sub>4</sub>	3 parts
Pb(C <sub>2</sub> H <sub>3</sub> O <sub>3</sub> ) <sub>2</sub>	.03 "
H <sub>2</sub> O	100 "

The electrode was alternately made the anode and cathode for about ten minutes. It was found advantageous to make it the cathode first, as this

prevented in most cases the formation of bubbles which made it difficult to get an even coat on the platinum. The electrode was then electrolyzed (as cathode) in 1:20 sulphuric acid for 15-20 minutes, after which it was treated with hot nitric acid for the removal of lead. The platinum electrodes thus made up were kept in weak sulphuric acid until ready for use.

The method of measurement of the single potential was the compensation method, using the normal calomel electrode and the Weston standard cell. This was carried out by means of a large potentiometer ("Kompensations-Apparat nach Franke")<sup>10</sup> with a very sensitive galvanometer. This apparatus gave a sensibility far in excess of that actually required for the third decimal place. The potentials are all given to the third decimal place; in many cases the fourth was determined for the purpose of checking, but on account of diffusion potentials and other factors this as an absolute value is rendered uncertain. The error in most cases is



about of the order  $\pm 0.001$ , usually no more.

The standard cell was compared with one certified by the Reichsanstalt of Berlin. The Calomel electrode was made up with care, and by its use the hydrogen potentials obtained for an exactly normal NaOH solution are in good agreement with those obtained by Lorenze and Mohn.<sup>11</sup>

A saturated solution of potassium chloride was used for the connecting cell between the calomel electrode and the cell in which the developer was placed. This almost completely eliminates contact potentials, the maximum contact potential due to the difference in migration velocities of the K- and Cl-ions being of the order of  $0.0007$  volt.<sup>12</sup> In most of the following work any larger contact potentials are eliminated, altho when they are not, the EMF of the given system will be stated.

There seems to be some confusion in the actual interpretation and use of the value of the calomel electrode, and the following

concerning its use in the present case should be noted. The value of the Normal Calomel Electrode is taken as

$$+0.5600 + 0.0006 (t-18) \text{ volt,}$$

the mercury being considered positive to the solution. Used thruout this work at 25° its value is +.5642 volt. All single potentials are given as Pt-solution. We will denote by E the EMF of a couple, one element of which is the calomel electrode and the other the developer cell,

$E_s$  is the potential of the calomel cell or  $E_{\text{Hg-sol.}}$

$E_x$  " " " " " developer  $E_{\text{Pt-sol.}}$

It will be seen that when  $E_{\text{Pt-sol.}} (=E_x)$  is a positive quantity, that is, when the Pt is positive to the solution, E will be less than  $E_s$  by an amount numerically equal to  $E_x$ , for the two halves of the cell are in opposition.

Then,

$$E = E_s - E_x \quad (\text{EMF} = E_{\text{Hg-sol.}} - E_{\text{Pt-sol.}})$$

When the platinum is negative to the solution, E will

will be greater than  $E_s$  by the numerical amount of  $E_x$ , as this time the two halves of the cell tend to send electricity in the same direction. But the above equation still holds, for  $E_x$  has itself now a negative sign.

Thus if  $E$  (=EMF) is  $+.400$  volt (the plus sign indicates the mercury positive)

$$E_x = E_s - E = .564 - .400 = +.164$$

Similarly if  $E = .760$  volt,  $E_x = .564 - .760 = -.196$ , or the value of Pt-solution is negative. This explanation is given so that there will be no doubt as to the meaning of the single potentials herein determined.

Some of the experimental work leading to the development of the theory previously stated will now be described.

The first solution to be tried was the one more widely used than any other, a metal-hydrochinon developer. The formula recommended

for many years for use with Seed plates was that used, and this is given in the table of developers and is listed as Developer No. 1-a. The formula is as follows:

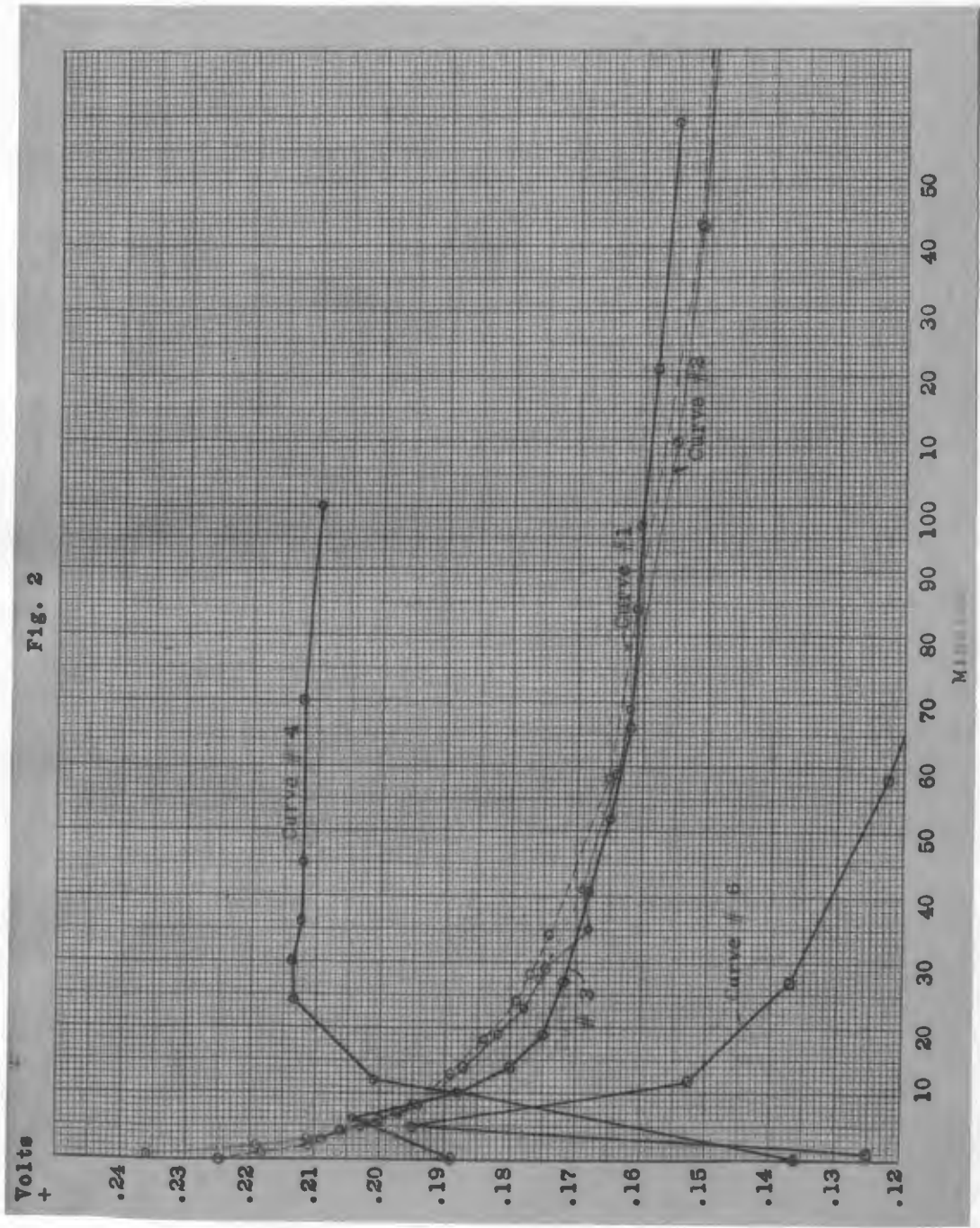
Developer #1-a.

H <sub>2</sub> O	1000 cc.
Metol	1.85 gm.
Hydrochinon	1.85
Na <sub>2</sub> SO <sub>3</sub>	13.9
Na <sub>2</sub> CO <sub>3</sub>	13.9

The Na<sub>2</sub>CO<sub>3</sub> used in Developer #1-a was Merck's dried, and on careful further drying at 270-300° the loss was 14.8 per cent.

The Na<sub>2</sub>SO<sub>3</sub> was Baker's analyzed which was that used thruout the work. 90 cc. of the developer thus made up were used in the cell already described (Fig. 1). The side tube of the cell was also filled, freed from bubbles, and plugged with filter paper. For the first experiment, the two tee tubes were closed by rubber tubes and pinch-cocks. On now making the proper connections and observing closely the changes in potential, as soon as possible

after mixing the developer and filling the cell, curves like the following are obtained when the results are plotted. (Fig. 2, Curves 1 and 2) After about three hours the changes are very slight, and the curve will eventually rise, in some cases this could be observed after a few hours. This rise may be ascribed to oxidation, as time after time it was seen to be accompanied by the yellow coloration of the developer. At this stage a word is necessary about the interpretation of the rise and fall of potentials. The more positive the potential Pt-sol., the more strongly oxidizing is the solution; the more negative it is, the more strongly reducing is the solution. <sup>13</sup> We therefore should expect a developer of stronger reducing power to produce a lower (i. e. more negative) electrode potential than one less powerfully reducing, but there is no simple numerical relationship between the observed potential and the reducing power. A relation exists, however, as already pointed out on page 11 .

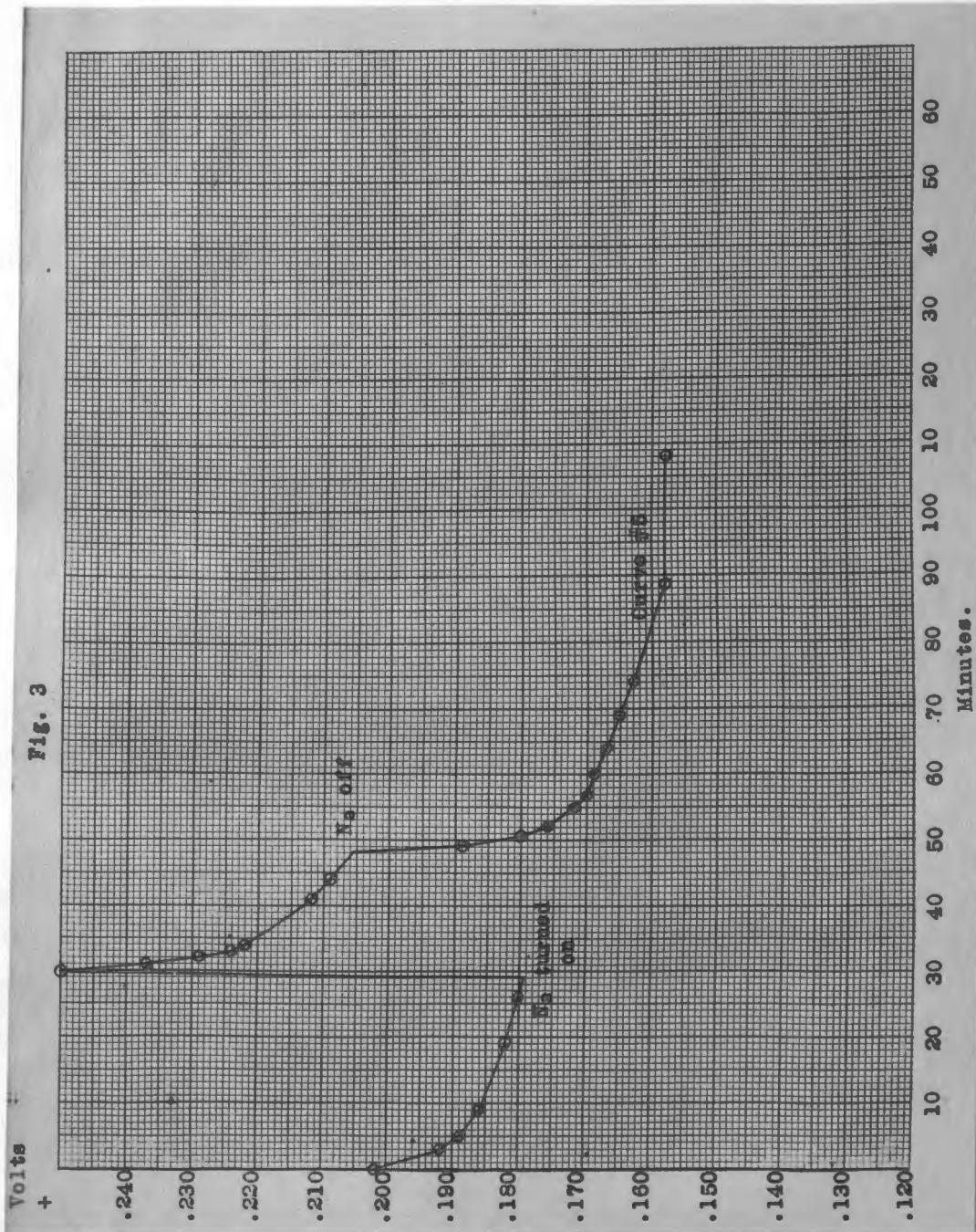


Applying the theory to the interpretation of the curves, we notice the tendency toward equilibrium, and can picture the process which is taking place. The developer is slowly producing hydrogen which is diffusing toward the electrode. As the electrode becomes more and more saturated with the gas, its potential is lowered accordingly. This lowering would take place much more rapidly, but the oxygen in the water is using up some of the hydrogen at the electrode, and the latter gas is also diffusing to some extent into the air above the solution and out of the apparatus. It must always be borne in mind that the actual amount of  $H_2$  is extremely small. An irregularity will be noticed in curve #2. Such points are likely to occur and they have not been shown to be anything else but irregularities due to unknown causes. These curves are like those given by Mathews and Barmeier, drawn reversed, showing more negative electro-potential with increasing time. So far the absolute value of the potential does not concern us, and these results are of

interest only as showing the changes described above. It is evident that the statement of Mathews and Barneier, that the fall of potential is due to oxidation, is erroneous. The only possible interpretation is that the potential becomes more positive on oxidation instead of more negative.

If nitrogen is bubbled thru the developer in one of the electrode cells, (thru the tube A), and air thru another, the potentials obtained give the curves #3 for nitrogen and #4 for air. Two cells were used which had been set up for sometime. This accounts for the low values at the start. The reading at zero time is the one taken at the instant of turning on the gas. The potential rises suddenly in either case. According to the conception above, this rise is due to the fact that the nitrogen, or air, is removing hydrogen from the cell, and more especially the electrode. The equilibrium already partially attained is upset, but after the momentary effect





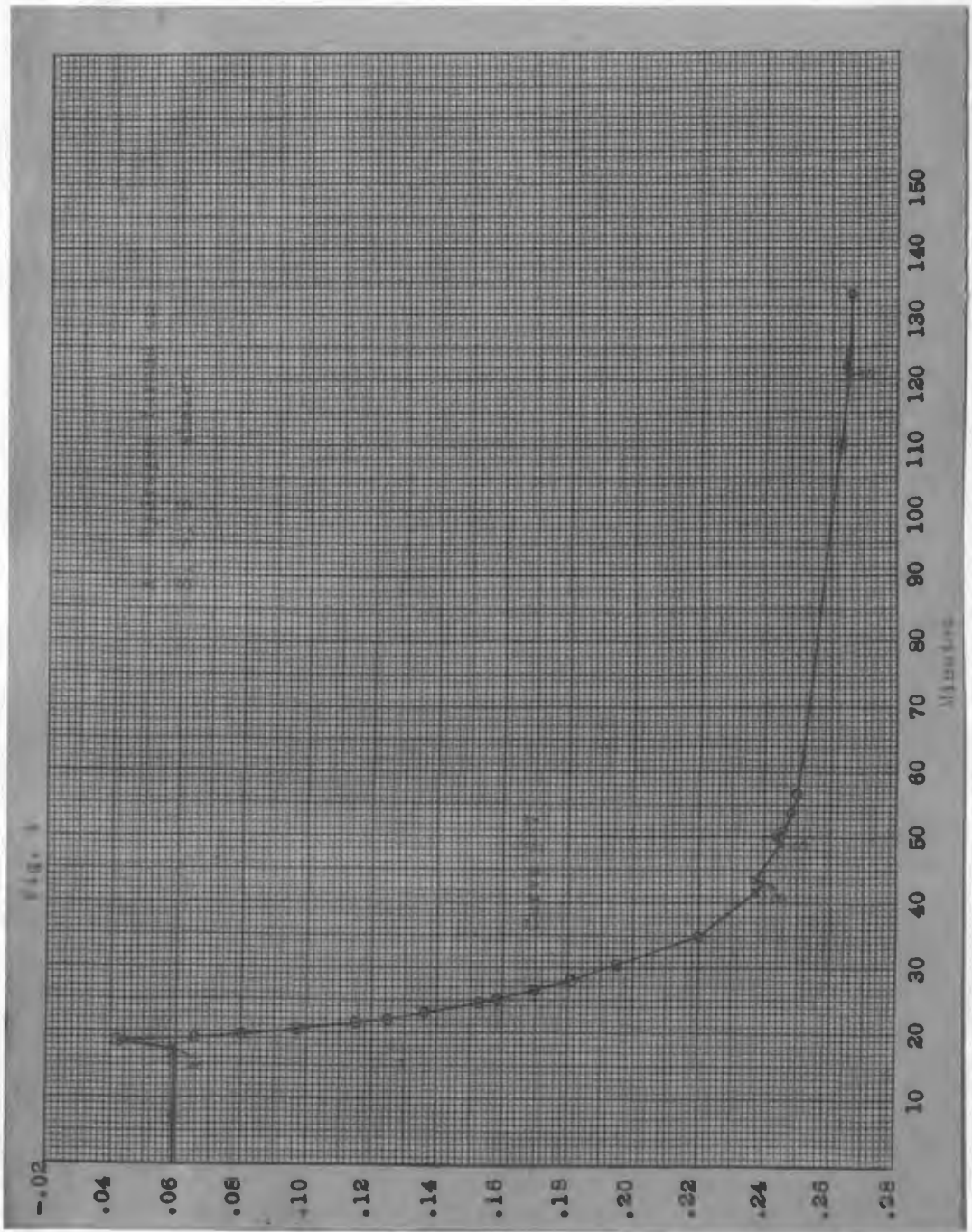
of stirring has passed, the solution again succeeds in giving up hydrogen to the electrode, and the potential gradually falls even while the nitrogen is still bubbling thru the solution. No doubt a new balance is established by the removal of some of the hydrogen. These effects are shown nicely by curve No. 5, Figure 3. It is seen that the nitrogen acts very decidedly as a retarding agent, for as soon as the nitrogen is turned off (at about time 50 minutes), the reaction proceeds more rapidly toward equilibrium. Curve # 4, showing the potentials obtained while air is passing thru the solution, differs from curve #3, as will readily be seen. The potential rises suddenly as before, but is maintained at a higher value than the corresponding one with nitrogen. This can be attributed to the fact that the oxygen of the air combines with the hydrogen under the catalytic influence of the platinum black, as mentioned in the discussion of chemical causes of the delay of the equilibrium.

In this way it is more effective in removing hydrogen from the system. Beginning oxidation of the developing agent also takes place. After the two cells had run in this manner for some time they were interchanged, the one fed nitrogen was now supplied with air, and vice versa. The second curve for nitrogen, from the other cell, and likewise the one for air, were almost identical with the first for nitrogen and air respectively. This showed that the developer was still subject to the same changes as before.

Shaking the cell vigorously for thirty seconds, and then taking the potential, gave curve #6, Fig. 2. The striking similarity of this curve to #3 for nitrogen should be noted. The effect is probably entirely mechanical as with nitrogen. If the potential is taken by means of an electrode dipping in an open dish, stirring will produce the same effect. The experiment was tried with cells in all stages, and qualitatively at least, the result was always the same.

The cell from which curve #6 was obtained had been set up seven hours previously. As might be expected, shaking is not so efficient in removing hydrogen as passing a gas thru the solution, hence the value drops at a slightly faster rate as soon as the first effect has passed.

Almost the best evidence in favor of the idea of hydrogen formation, as described, is given by an experiment in passing hydrogen gas thru the cell in the same manner as with the nitrogen or air. Curve #7 represents the potentials obtained. The cell had been set up for some hours in this particular case, and had attained the value  $-0.06$  volt, at which it was apparently constant during a short period. At time eighteen minutes, the hydrogen was turned on, and the potential rose as in the previous experiments, but a less amount, and immediately it began to drop at a rapid rate. At time forty-three minutes, the cell was shaken for 30 seconds, with only a slight rise. This was repeated at time 49 minutes, and again at 122 minutes, with decreased effect. In fact, in the latter, the rise was only a milli-



volt, and could only be detected because the readings were taken 30 seconds before and after shaking. The explanation of these phenomena is not difficult after the consideration of the production of gaseous hydrogen by the developer. At first the hydrogen has a slight mechanical effect like that of nitrogen, but the rise of the potential is not so great because the solution and the electrode are replenished with hydrogen from that bubbling thru the solution.

*As the electrode becomes more and more saturated with hydrogen,*  
(i. e. more negative), there being an atmosphere of hydrogen over the liquid, shaking has less effect, since it cannot remove hydrogen from the cell, or the electrode, to any extent, as did nitrogen, air or shaking. It was found that with any apparatus such as thus far used, where there was a possibility of the hydrogen diffusing outward thru rubber stoppers, etc., the potential would not remain at the low value attained, but would rise again when the active passage of hydrogen was stopped. There could be little doubt that this was due directly to loss of hydrogen from the electrode.

In the case of passing in air or nitrogen, a fact not mentioned above is that the larger the amount of liquid in the cell, the less the mechanical effect. Also the potential is

slightly affected at times by the rate of flow of the gas.

Summarizing the results of the foregoing experiments:

1. The first effect of all four is the same, - the potential rises suddenly.

2. The effect of shaking is much less in an atmosphere of hydrogen, becoming negligible when equilibrium is nearly attained.

3. The mechanical effect is less in larger quantities of solution, and the potential is sometimes affected by the rate at which the gas flows.

4. Air has the power of keeping the potential above its normal value. This effect must be attributed to a chemical combination of oxygen with hydrogen at the platinum electrode.

5. In all cases, after the first disturbance has passed, a tendency toward equilibrium is again apparent, altho the reaction

is retarded as long as the cause of the disturbance is not removed.

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With this evidence, we have at least a starting point on which to build the theory that the developer actually produces hydrogen, and that the production of hydrogen measures the reducing power of the developing agent. All succeeding experience with the electro-potentials of developing solutions supports rather than contradicts this idea, the main points of which are repeated below:

1. The single potential of a developer is dependent on the loading of the electrode with hydrogen.
2. The hydrogen is furnished by the developer in its attack on the OH ions.
3. The maximum partial pressure of hydrogen which the developer can produce measures the reducing power of the developing agent.
4. The loading process may be disturbed by mechanical means, such as shaking the solution, or by passing a gas thru it.



5. The process just mentioned may be disturbed by some chemical reaction at the electrode, such as the union of oxygen with some of the hydrogen, catalyzed by platinum black.

6. In the case of nearly all developers, there is a reaction resistance which delays the attainment of equilibrium, but which cannot be overcome by any known means.

7. The potential is a function of the concentration of H-ions in the solution, and of the pressure of hydrogen gas at the electrode.

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This brings us to the subject of the actual single-potentials of developers, and the method of obtaining them. If we attempt it in the manner in which curves numbers 1 and 2 were obtained, we succeed in obtaining a value which remains almost constant for a time, after which oxidation sets in and the curve rises. One could

not feel safe or justified in assuming that the lowest value thus obtained was the true potential of the developer in question. Such a curve consists of two portions, neither one of which represents the actual electrode potential. The first part shows the retardation of the equilibrium and the second part, if we took the trouble to determine it, would show the effect of oxidation. The combination of these two effects, during the middle period, gives a more or less constant electrode potential for a short time, but it is above the true potential.

It is necessary to reduce possible oxidation to a minimum, and also to wait for the equilibrium to be reached. Certain difficulties are met with in the determination, and a long time is required for the attainment of any satisfactory result. The diffusion of hydrogen toward the electrode is slow, and so far no method of hastening it to any extent has been discovered, altho it is sometimes possible to "shake down"

the cell more or less.

Various forms of apparatus were employed which need not be described, but no success was met with until the capacity of the cell was reduced and the form described below was used. Attempts were also made to set up a cell of the true oxidation-reduction type, with one oxidation electrode and the platinum black in the same solution in one single cell. Copper oxide and other substances were used, but as they were actually reduced by the developer, they were of course inconstant and useless. The form of apparatus shown in Figure 5, was then adopted. The total capacity to the stop-cock B is 4 cc. At B is a constriction so that, after filling, the apparatus may be evacuated and sealed off. The electrode E consists of only a small piece of sheet platinum, and is coated with platinum black by filling the cell with the platinizing solution, inserting a platinum wire down the tube for the other electrode, and proceeding in the manner previously given.

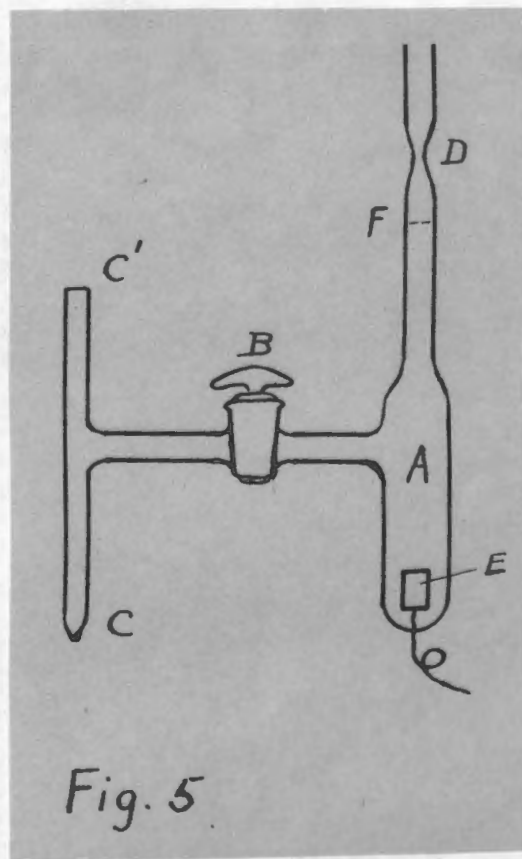


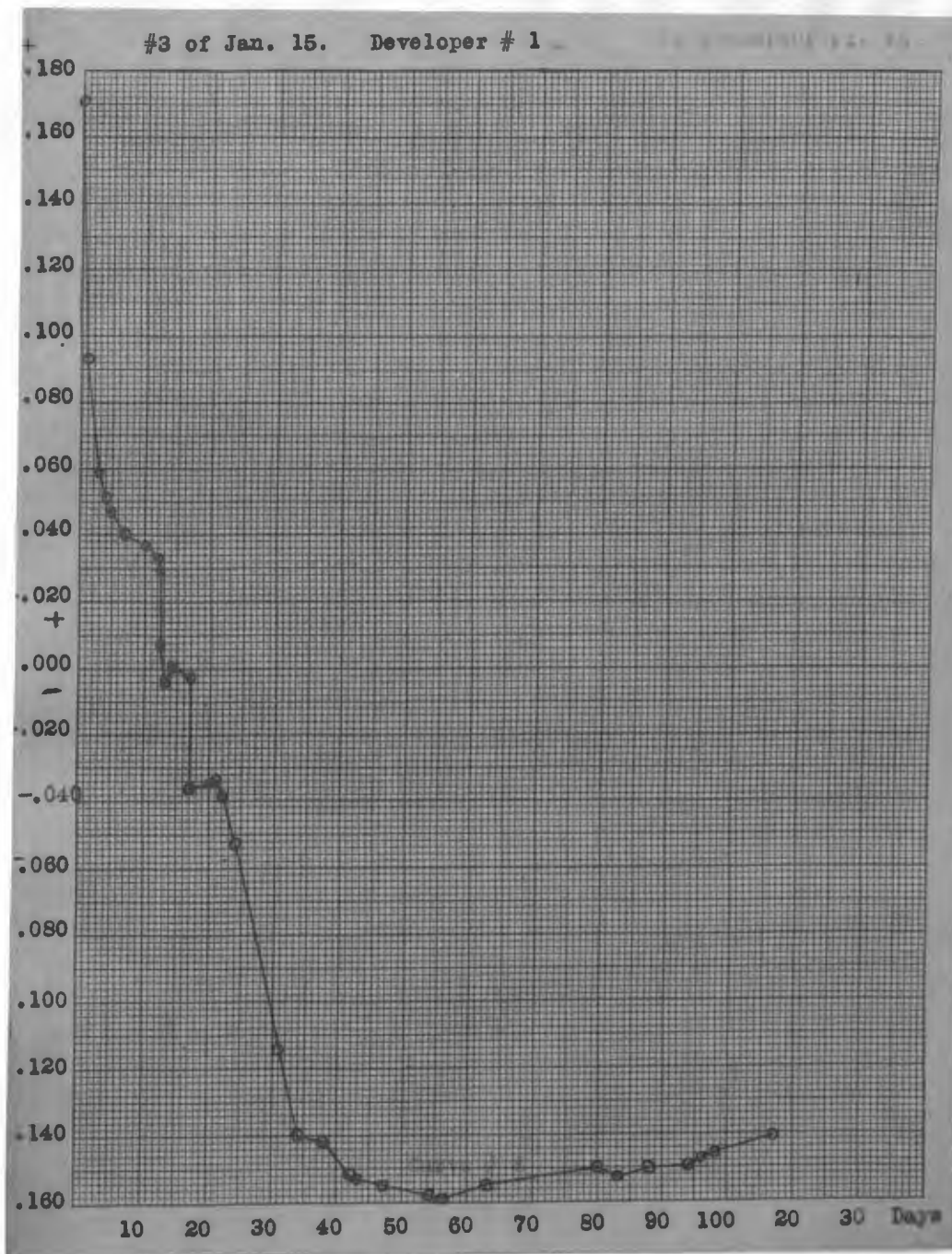
Fig. 5

The side tube is drawn to a fine opening at C which is plugged with filter-paper after the cell is filled.

As first used, these cells were filled as follows: The developer was quickly mixed and drawn up to the point F. The stop-cock was then closed, the cell evacuated as completely as possible, and sealed off. After cooling, the side tube was placed in a small amount of developer, and the stop-cock opened, upon which the cell filled almost completely, leaving only a minute bubble of air over the solution. The plug of filter paper was next inserted, and the apparatus was then set up with the calomel half-cell and was ready for the measurement of potentials.

With this cell, the potential of developer #1-a (Seed metal-hydrochinon developer) reached after five weeks the fairly constant value of -0.145 volt, and remained at this point for nearly two months. This value was also obtained from three other cells run simultaneously. The potentials obtained during this and a still more extended

period are plotted in curve #8 , which shows many unexplainable irregularities. But since four cells agreed on the final result and remained fairly constant, these irregularities are of minor importance. It is to be noted that the developer was made up in this case from Merck's sodium carbonate, which consists of approximately 85 per cent  $\text{Na}_2\text{CO}_3$ . As this substance is very important, later determinations were made with a more constant product. The importance of the value of the potential thus found will not be discussed until later. After discovering on certain occasions that disturbing the cells made the potential slightly more negative, small rods of glass were put in other cells to act as stirrers. With the aid of these the potential of one of the four cells used on developer #1a was very decidedly brought down by shaking, and the others were affected by the stirring process at times. But no uniformity could be traced in the results of shaking, altho it was observed that there was a certain stage, between +.35 and -.40 volt where the cell was more sensitive to shaking. Another very in-



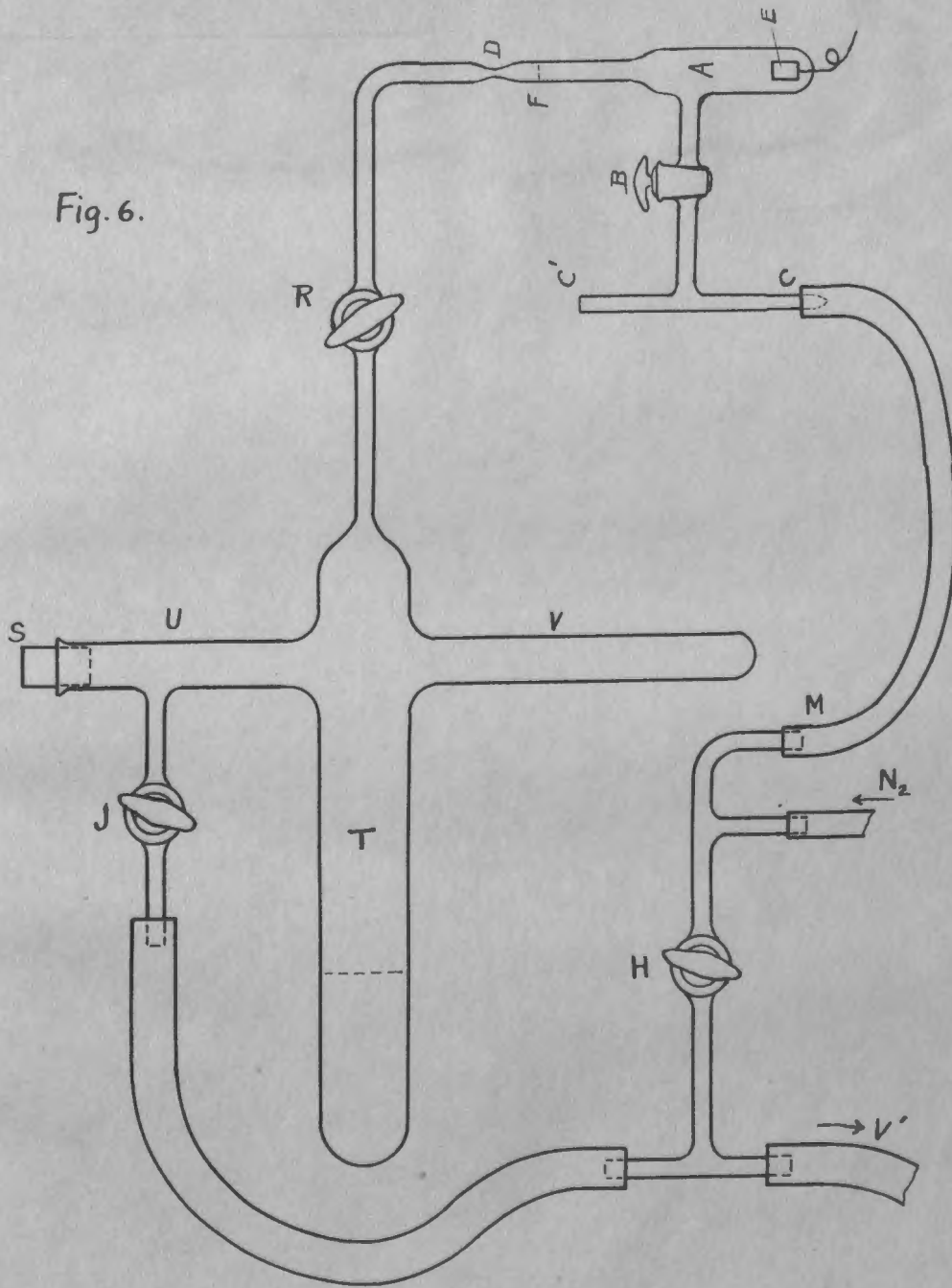
teresting phenomenon was noticed in this first set, and in later ones. They exhibit, more or less, a "sticking point", a temporary constant value which might prove misleading if at least two cells were not run simultaneously on the same developer. One of the cells on developer #1 remained at +0.35 volt for more than ten days, another at about zero for a period of days, and a third seemed constant or nearly so at -.036 for a week. It is thus seen that a long period of time is required to obtain the single-potential of a developer, and that one could draw no conclusions from a single determination unless the value remained unusually constant. The cell from which curve #8 was obtained, has been constant to within 5 millivolts for seven weeks, to the time of writing, and we feel safe in accepting this as the real single potential of the developer made up in the way described.

With a view to hastening, if possible, the attainment of the necessary point of equilibrium, and further eliminating sources of error, an apparatus was designed and made, whereby the developer



could be mixed in vacuo, with oxygen-free water, and then filled into the electrode cells of the same design as shown in Figure 5, the latter having also been evacuated and freed from air. The entire operation is accomplished in the absence of air in the apparatus as drawn in Figure 6. The apparatus and technique used will be described together. The tube V' is connected with the vacuum pump, N with the supply of Nitrogen, (which should be passed thru a potash bulb containing alkaline pyrogallic acid), and the tube M is connected with the tube C of the cell. All the glass parts are previously cleaned with chromic acid and thoroly washed with distilled water. The tight rubber stopper S is put in place and the tube is now evacuated. H is a stop-cock arrangement so that vacuum may be applied either at J or at C. A tight rubber tube and glass plug are placed over C. For the first part of the operation, the vacuum is applied at J, the stop-cock R being open, while the one, marked B, is closed. This removes most of the air in the mixing apparatus, and the electrode cell.

Fig. 6.



Nitrogen is now slowly admitted at C by manipulating the proper stop-cocks, and J is closed. The apparatus is filled with nitrogen, again evacuated, as before, and refilled with nitrogen. The contents of the tube T measure about 75 cc. or more, and this tube should be at least 20 cm. in length. It is graduated for 25 and 50 cc. About 100 cc. of distilled water are boiled for ten minutes in air. The stopper S is loosened and it is arranged that a rather brisk stream of nitrogen flows thru the apparatus from C when S is removed. The stopper is now removed for an instant, and 35 cc. of the boiling water quickly introduced into the apparatus by means of a pipette. The stopper S is inserted, the stop-cock R closed, and vacuum is again applied slowly at J, while a slight stream of nitrogen flows in from C. The water now boils in partial vacuum, and this operation must be conducted cautiously as the bumping may be very violent. The boiling in vacuo is continued for ten minutes more, after which the apparatus is gradually filled with nitrogen and cooled. The volume of the water must be adjusted accurately to either 25 or 50 cc. by drawing any excess out

thru the vacuum tube before filling with nitrogen. The developer, previously accurately weighed into small glass capsules, is now introduced thru the tube U, while nitrogen is flowing as before. The capsules are dropped into the tube V by inclining the apparatus, or carefully placed in the tube U, but are not allowed to come in contact with the water. The stopper S is now put in very tightly, and the apparatus up to the stop-cock B is evacuated, filled with nitrogen, and again evacuated and filled with nitrogen. The capsules of developer are then dropped into the water and quickly shaken until the contents are dissolved. Vacuum is applied, and the nitrogen dissolved in the developer boils off. Nitrogen is once more admitted and the whole is evacuated. By tipping up the apparatus, about 3 cc. of developer are allowed to flow over into the electrode cell A. R is closed. Vacuum is applied at C, drawing out the air up to the stop-cock B. A little  $N_2$  is admitted at J, and R is opened. On now opening B, the developer in A is drawn out and the cell rinsed. B is again closed, and another portion of 3 cc. allowed to flow over, which is again drawn out by means of the

vacuum tube at C as before. The highest attainable vacuum is next applied at the point C. The cell is now filled to a point about 2 cm. beyond the stop-cock B, leaving also a space of about a centimeter above the developer in the cell, to allow for sealing off. Some difficulty is experienced in getting all the adjustments right, but by frequent tapping and applications of vacuum at either J or C, the liquid can be adjusted to exactly the levels required. R is closed and nitrogen is admitted to tube T thru J. The cell is now sealed off at D. On cooling, the space above is almost completely filled when the stop-cock is opened. The outer part of the tube between B, and C and C' is not filled until after another cell has been sealed on and filled. As soon as the first cell is sealed off, another is put on in its place without in any way disturbing the contents of the tube T. The second cell is evacuated and filled with nitrogen, each twice, and is then rinsed and filled as the first one was. Air is now admitted thru the stop-cock R, the stopper S is removed, and the remainder of

the developer poured out to fill the tube CC' of each cell. After this is done, the tubes C in each case are plugged with filter paper, the cap and plug put on at C' and the cell placed in a rack and connected up for the taking of potentials. The main apparatus can be used as many times as required, other electrodes being sealed on and off.

With the use of the apparatus just described, 17 electrode cells were filled for investigation of the developers given below. Time did not permit of a complete study, even of these, as a long period is required in order to be certain of the equilibrium. Data obtained is given in part below, to give some idea of the rate of change. All the cells were placed in one rack, each was connected to a wire leading to a series of mercury contacts, the whole arrangement being such that the potential of any cell could be quickly read. Each was read soon after filling, several times during the first 48 hours, and was then followed at intervals of 1, 2, and later as much as 4 or 5 days. At the time of writing some of these have not reached equili-

brium.

Formulae of developers used:

The carbonate used in all the cases here was obtained by slowly heating Merck's C. P.  $\text{Na}_2\text{CO}_3$  to  $300^\circ \text{C}$ . This gives a uniform anhydrous product of high purity, sufficient for determinations of this kind. The sulphite was the same as that used thruout, - Baker's analyzed-anhydrous.

Developer # 1-b

Seed developer,

same as before, but using  $\text{Na}_2\text{CO}_3$  <sup>mentioned above</sup> (wt. given in formula for #1-a.) This is equivalent to a slightly larger quantity of carbonate than was used in the first case.

#6-a No. 1 - Hydrochinon.

$\text{H}_2\text{O}$	1000cc.
$\text{Na}_2\text{SO}_3$	50gm.
$\text{Na}_2\text{CO}_3$	150
Hydrochinon	7

#6-a	No. 2	Half the carbonate of the preceding.	
		H <sub>2</sub> O	1000 cc.
		Na <sub>2</sub> SO <sub>3</sub>	50 gm.
		Na <sub>2</sub> CO <sub>3</sub>	75
		Hydrochinon,	7
#6-a	No. 3	Twice the carbonate of No.1 (6a)	
		H <sub>2</sub> O	1000 cc.
		Na <sub>2</sub> SO <sub>3</sub>	50 gm.
		Na <sub>2</sub> CO <sub>3</sub>	300
		Hydrochinon,	7
#6-a	No. 8	6a No. 1 + KBr.	
		H <sub>2</sub> O	1000 cc.
		Na <sub>2</sub> SO <sub>3</sub>	50
		Na <sub>2</sub> CO <sub>3</sub>	150
		Hydrochinon,	7
		KBr	4.6
#7	Amidol.		
		H <sub>2</sub> O	1000cc.
		Na <sub>2</sub> SO <sub>3</sub>	100 gm.
		Amidol	20
#8	Metol		
		H <sub>2</sub> O	1000 cc.
		Na <sub>2</sub> SO <sub>3</sub>	25 gm.
		Na <sub>2</sub> CO <sub>3</sub>	25
		Metol	5
#9	Hydrochinon with tetrathiourea-ammonium-bromide		
		H <sub>2</sub> O	1000 cc.
		Na <sub>2</sub> SO <sub>3</sub>	63 gm.
		Na <sub>2</sub> CO <sub>3</sub>	126
		Hydrochinon	10.5
		Tetrathiourea-	0.5



Of these developers Numbers 1, 6a No. 8, 7, 8, and 9 are standard formulae as recommended for use.

The potential time data is given on the following sheet. Not all of the data obtained need be indicated, as the rate of change can easily be seen from a few representative readings.

All readings are positive unless with negative sign, and express the potential in volts. Thus 078 indicates +0.078 volt. Those values in parenthesis were obtained by shaking.

Dev. No.	Cell No.	Started.	First Read.	24 hrs.	48 hrs.	Mar. 27	Mar. 30	Apr. 6	Apr. 15	Apr. 21	Apr. 29	May 7	May 18
1-b	14	Mar. 22	166	092	053	014	(-006)	-006	004	-005	021	003	-035
	15	"	121	061	024	019	022	-034		004	-006	-005	-020
6-a No. 1	10	Mar. 22	128	078	-116		-190	-125	-025	-035	-037	-014	-086
	8	Apr. 6	118		033				-029	-038	-046	-062	-136
	9	"	106		051				001	000	-005	-003	-005
6-a No. 2	4	Apr. 6	112		077				(023)	031	052	017	-027
	7	"	105		057				009	-001	-007	-007	-015
6-a No. 3	1	Apr. 5		004	-061				-082	-060	-014	-039	-038
	2 <sub>m</sub>	"	122		060				000	-006	-007	001	-011
6-a No. 8	13	Apr. 7	139	100					048	029	012	000	-026
	15	"	122	078					057	026	039	016	027
7	11	Mar. 29	195	149				064	066	065	067	067	
	12	"	179	143				061	060	059	061	057	
8	17	Apr. 7	121	105					(010)	010	109	077	082
	18	"	-063	-050					-019	+035	+093	+049	088
9	19	Apr. 7	-026	-028					-046	-079	-020	-055	-115
	20	"	-083	-062					-255	-260	-162	-144	-148

Several significant facts are shown by this table. Mathews and Barmeier<sup>2</sup> stated that the potential did not change when the developer was made up from oxygen-free water in a vacuum. In these experiments, which were laboriously carried out, according to the technique given, we were sure of practically no oxygen in the entire apparatus, and still the potentials changed as before. There was no possibility of oxidation. It will be seen that oxygen in the water cannot be responsible for the changes in potential, as these authors state. On the other hand, the production of hydrogen and its slow diffusion toward the electrode, and the reaction resistance, explain why a constant potential is not reached at once.

It will be seen from the table that amidol (developer #7) has the lowest reaction resistance. It reached, with both cells, after five days, the value it has maintained for six weeks. Several of the other developers have a very high resistance apparently, for we are not as yet sure of equilibrium. In some cases, it might almost seem that the electrode itself is

a factor in determining this reaction resistance, for in developers 6-a No. 1, No. 2 and No. 3, one cell has apparently developed a "sticking point" while its mate seems not to have done so. From various considerations, it is more than likely that cells numbers 14, 16, 9, 7, and 2 have not passed this point of apparent equilibrium, and the others, with the exception of amidol, are still in such a state of uncertainty that we can draw no conclusions from them at the present time. Altho almost two months ~~has~~ already elapsed two more may be required in some cases before one could be positive of equilibrium.

Amidol (#7) and hydrochinon with tetra-thiourea-ammonium bromide (#9) are the only developers which differ to a certainty from the mean starting value (approximately +.125 volt). The initial reading depends on the length of time the developer has been in contact with the electrode. This is to be expected from previous considerations of the process which takes place. When the developer is mixed in the vacuum apparatus, and

the second cell is not filled until some time after the first, there is far less difference between the initial readings than when both are filled at nearly the same time, one read at once and the other after a few hours.

No conclusions can be drawn at this time concerning the effect of carbonate or of bromide from the series 6a. When these cells have reached constant and concordant values, we hope to determine the relative reducing power of all the developers in question. Up to the present time, however, we are certain of the single potential of developers #1a and #7. According to the method previously outlined (on pg. 11-18 inclusive), we will now adopt the use of the hydrogen electrode and attack the problem of relative reducing power for these two developers.

For all work on hydrogen potentials, the form of apparatus shown in Fig. 7 was employed. This gives an electrode of simple construc-

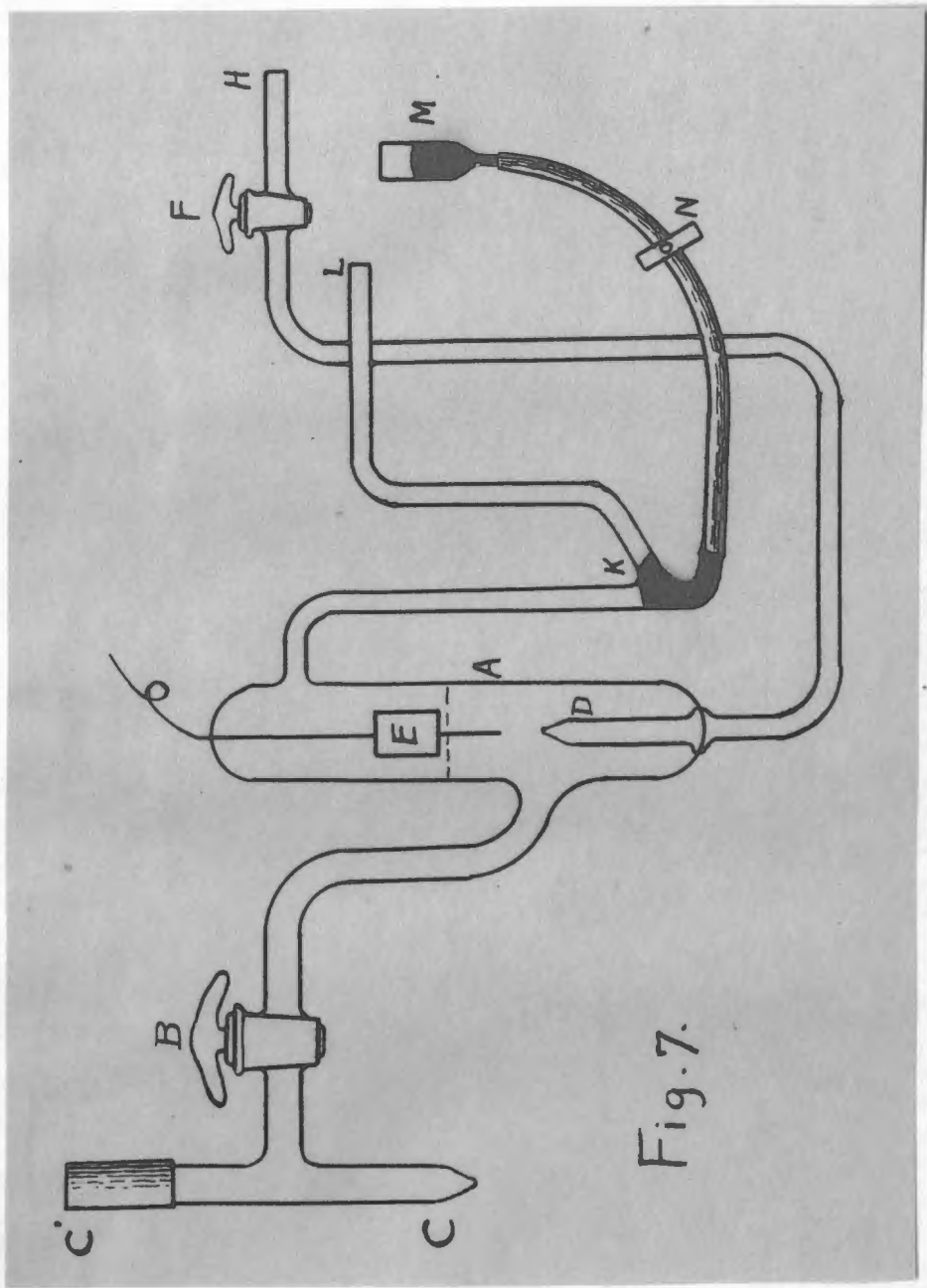


Fig. 7.

tion, and one with which reliable results to an accuracy of 0.0001 volt can be obtained. For a discussion of the hydrogen electrode, the reader is referred to the work of Loomis and Acree<sup>12</sup>, and the very extensive bibliography<sup>14</sup> on the subject given by the same authors.

It was our experience that no form of hydrogen electrode cell was reliable in which rubber stoppers were used above the electrode chamber, especially if the passage of gas was stopped. By the use of the apparatus illustrated in Fig. 7, it is very often possible to maintain at a constant temperature, a potential constant to 0.1 millivolt with the hydrogen turned off, provided that equilibrium had been previously reached.

A is the main electrode chamber, and E is the electrode consisting of a rectangular *piece* of platinum with a short length of platinum wire extended down from it as shown. The

electrode is platinized as usual. The hydrogen enters at H and bubbles up thru the solution to be investigated, at D. The gas is first passed thru two small wash bottles, containing acid potassium permanganate, and a third containing weak NaOH. The hydrogen leaves the apparatus thru the trap K, which contains mercury, the height of which is regulated by the reservoir M and the pinch-cock N. The meniscus of mercury is so adjusted at the angle K that the gas pushes it aside when a slight pressure acts upon it, allowing the gas to escape, but preventing the inward flow of the air. A small trap of liquid might be inserted in the exit tube if desired, but the arrangement just described was found entirely satisfactory for our purpose. Connection with the central cell and calomel electrode is made thru the side tube CC' as in previous cases, the tube being filled with the same solution as that in A, and plugged with filter paper at C. The height of liquid in the cell should be about that indicated by the dotted line. It was found that if the electrode



was first well rinsed, and wet with the solution, equilibrium could be more quickly obtained if the liquid only covered the short wire, or at most the lower edge of the electrode. The time required to reach equilibrium, in the case of an electrode in good working condition varied from four to fifteen minutes with most solutions. Very dilute alkalies gave much trouble as to time required. As soon as one determination was completed, the cell was washed with hot water and filled with weak sulphuric acid (1:20) as this was found to aid greatly in keeping the electrode in suitable condition and reduced the time required for equilibrium.

The temperature at which the hydrogen potential is determined is important. The standard temperature of 25°, used thruout this work, was maintained by immersing the electrode in water kept at 25°. The calomel electrode was also kept in a water bath so that its temperature could be accurately known. Much of the earlier work on single potentials is rendered uncertain by the failure to correct for temperature, the

value 0.56<sup>v.</sup> being used for the calomel electrode regardless of the temperature at which the measurements were carried out. The corrections for differences in barometric pressure from time to time are extremely small as a rule, and may be entirely neglected.

In applying the hydrogen electrode to the problem of reducing power of the developer, it must be remembered that the accuracy of the final result is no greater than that with which the normal single potential of the given developer can be determined. By the last expression we designate the potential obtained in the manner just described (ppg. 43-55). Since the greatest accuracy we can hope to attain in finding this single potential is 1 millivolt, the hydrogen potential constant to the same amount will be sufficient for this determination. No trouble was found in obtaining such a constant result, either from separate portions of the same developing solution, or from several solu-

tions made according to the same formula.

The Partial Pressure of Hydrogen Produced  
by Developer 1-a.

The hydrogen potential of this developer (#1-a Seed formula) was originally determined at 23.5°, but the temperature coefficient has been carefully studied, so that we may use the hydrogen potential (hereafter designated by  $E_{H_2}$ ) for 25°. Several determinations were made on this solution, of which the following is the best, altho the others agreed well with it. The first reading was taken after equilibrium had been established, and the first two were taken while hydrogen was passing thru the cell. The gas was then turned off, the mercury seal closed, and the cell left standing for two days, after which it was again read, but without turning on the hydrogen. At temperature 23.5° for the hydrogen electrode; 25° for the normal calomel electrode.

Time.	EMF	$E_s$	$E_{H_2}$
2/4 11:50 A.M.	+ .8738	+ .5642	- .3096
1:45 P.M.	+ .8739		- .3097
-----			
2/6 10:15 A.M.	+ .8750	+ .5642	- .3108

One would scarcely expect the cell to remain even as constant as the last reading indicates, considering the fact that the hydrogen had been turned off two days previously. The value  $-.3096$  at  $23.5^\circ$  is without doubt correct, within a small error.

#### Temperature Coefficient:

This was determined by immersing one of the hydrogen electrodes, containing the developing solution, in water thru a range of temperature and observing the changes in potential. It was found that the hydrogen electrode responds very quickly to changes of temperature, in developers as well as in solutions of alkalies, etc. The following are some results on the

## Developer #1-a:

Temperature.	$E_{H_2}$
25.3°	-.3103
42.0	-.3166
69.0	-.3267
7.0	-.3040

Change per degree between 25.3 and 42°	.000377
42 69	.000374
7 25.3	.000345
7 69	.000366
average,	<u>.000387</u>

We may thus take the temperature coefficient of this developer as  $-.0004$ , that is, for every degree rise in temperature, its potential becomes more negative by  $-.004$  volt. This is about the value of the temperature coefficients for the hydrogen electrode in other developers and also in carbonate solutions. The hydrogen potential of this developer may then be calculated to  $25^\circ$ , which gives

$$E_{H_2} = -.3096 - .0004 (25-23.5) = -.3102$$

and we may state

$$E_{H_2} = -0.3102 - 0.0004 (t-25).$$

Normal single potential of Developer 1-a.

It was previously stated (pg. 44) that the average value obtained for this potential from

the cell # 3 was -0.145 volt. But since it is necessary to determine this as accurately as possible, we will take the average of several cells and a large number of readings.

Average of 14 readings from  
Cell #3 over a period of 80 days,      -0.151 volt

Other readings which did not  
remain constant for so long

Cell #5	- .155	
	- .149	
	- .150	
Cell #6	- .141	
" #1	- .141	
av.	<u>- .148</u>	<u>-0.148</u>

Value used      -0.149

The above paragraphs give rather a complete idea of the determinations necessary and the general method of procedure. It now only remains to see what information these values give us.

On pages 11-15, we discussed the manner in which <sup>the</sup> partial pressure of hydrogen, which the developer can produce, may be calculated. We may now consider our concentration cell made up of the cell in which we measured the normal single potential of the developer, and the hydrogen electrode in the same

developer. The first measures the potential of hydrogen at the pressure at which the developer can produce it, and the second gives the potential of hydrogen at atmospheric pressure, both in the same solution, and hence the same hydrogen-ion concentration. The formula of page 14 now applies i. e.,

$$E = 0.05909 \log \frac{C}{C'} \quad \text{where } C \text{ and } C' \text{ represent gas pressures at the two electrodes.}$$

Since, for the hydrogen electrode,  $C = 1$  (1 atmosphere) the equation becomes

$$E = 0.05909 \log \frac{1}{C'}$$

in which  $C'$  gives us the partial pressure of the hydrogen,  $E$  is the difference between the potentials of the two electrodes. It is not necessary in this case to express the potentials of the two electrodes on the hydrogen scale, as will be seen, but it is better to do so for the sake of uniformity.  $E$ , in this connection, is independent of whatever may be chosen for the value of the calomel electrode on the hydrogen scale.

Applying the equation above to Developer

#1-a:

	Abs.	Hydrogen scale.
Normal single potential	-.149	-.431
Hydrogen potential	-.310	<u>-.592</u>
	Difference = E	.161 volt

Substituting these values in the equation,

we have

$$0.161 = 0.05909 \log \frac{1}{C'}$$

$$\log \frac{1}{C'} = \frac{.161}{.05909} \quad \text{From which } C' = .00188$$

This developer can therefore produce hydrogen at a pressure of 0.00188 atmosphere.

If we can obtain  $C'$  for any other developer, we may compare the developers as to reducing power, as already explained. We are fairly certain of the single potential of Amidol (#7) and will carry out this comparison as an example of what may be done.

Hydrogen potential of Dev. #7 at 25°	- 0.031
Normal single potential, from an average of 10 readings from two cells, over a period of 6 weeks,	+ 0.063

---


$$\text{Difference} = E \quad 0.094 \text{ volt}$$

Substituting in equation as before, we get,

$$C' = 0.0257 \text{ atmosphere}$$



It is at once evident that Amidol made up according to formula 7 has a greater reducing power than the Seed developer, #1-a, for it can produce hydrogen at a greater partial pressure.

(See statement of Nernst, pg. 11).

Ratio of the reducing power of Amidol to that of Metol-Hydrochinon.

$$\frac{C' \text{ Amidol}}{C' \text{ Metol-Hydrochinon}} = \frac{.0257}{.00188} = 13.6$$

Hence we may say that Developer #7 has about 14 times the reducing power of Developer #1-a. This seems according to experience and agrees with other facts concerning the two developers in question. Amidol does not require the use of alkali to assist in opening the pores of the gelatin and in that way to facilitate the action of the developer on the silver bromide. It has a rather greater fogging power than the metol-hydrochinon developer, and is often used with bromide as a restrainer. Amidol develops images to a greater density, and is useful for cases of under-exposure. All these facts would tend to indicate that

it has a greater reducing power, as the figures just obtained show.

It is to be noted in this connection that an error of  $\frac{4}{\lambda}$  millivolts in E changes the value of the hydrogen partial pressure about 0.0092 atmosphere and changes the value of the ratio approximately 2.0, altho since a logarithmic function is involved, this cannot be taken as the rule. However, even a maximum error of 4 or 5 millivolts, which is much greater than would ordinarily occur, would not change the results enough to interfere with their value.

Time has not permitted us to carry this comparison to completion for other developers, but there is little doubt that some interesting facts would be brought out if such determinations were made.

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(See next page.)

The last portion of our work deals with the relation of the different parts of the developer to each other. We had occasion to make use of this developer, which will be designated as #5:

H <sub>2</sub> O	900 cc.
Na <sub>2</sub> SO <sub>3</sub>	7 gm.
Hydrochinon	10
Na <sub>2</sub> CO <sub>3</sub>	150

The carbonate used was Merck's, which is very closely 85 per cent Na<sub>2</sub>CO<sub>3</sub>. Figuring this to pure anhydrous Na<sub>2</sub>CO<sub>3</sub>, and reducing the formula to a liter basis, it reads,

H <sub>2</sub> O	1000 cc.
Na <sub>2</sub> SO <sub>3</sub>	7.8 gm.
Hydrochinon	11.1
Pure Na <sub>2</sub> CO <sub>3</sub>	141.7

If the hydrogen potential is taken on this solution before the hydrochinon is added, (i. e. on the same <sup>conc. of</sup> Na<sub>2</sub>SO<sub>3</sub> + Na<sub>2</sub>CO<sub>3</sub>) at 25°, the result is -0.355. On now adding the hydrochinon, and again taking the hydrogen potential, the value -0.325 is obtained, there being a difference of 30 millivolts from the previous reading. Very evidently the addition of hydrochinon has changed the alkalinity to quite an extent, since the alkalinity alone determines the hydrogen potential. This is a rather surprising fact, since

it has long been supposed that the sodium carbonate played no part in the developer except a mechanical one, in opening the pores of the gelatine and thereby promoting development, or possibly a minor chemical role in reactions with the oxidation products of the developer during the process of development. But here we are confronted with the fact that there is a definite reaction between the carbonate and the hydrochinon before any development takes place.

The same relation is observed in connection with other developers containing carbonate. This prompted us to a study of this reaction, with a view toward determining its exact nature. But such a great deal of experimental work is involved, that we at this time can give only approximate results in one or two cases, and suggest a few lines of study in which further work would be of value. Recalling what was said concerning the electro-chemical equation on pg. 15-16, we can use it for the determination of H-ion, when

the pressures of the hydrogen at the two electrodes are identical, as they are when the hydrogen potentials are obtained for two different solutions. In this form we use  $c$  and  $c'$  for the hydrogen concentrations at two electrodes respectively, giving,

$$E = 0.05909 \log \frac{c}{c'}$$

Now, if  $E$ , the hydrogen potential of any solution with hydrogen-ion concentration  $c'$ , is expressed on the hydrogen scale, it becomes equal to the EMF of a concentration cell where the cell containing the given solution forms one electrode, and the standard hydrogen electrode in hydrogen-ion of unit concentration forms the other. Then  $c = 1$  and the equation has a form like the one used for gas pressures, except that  $c'$ , the unknown H-ion concentration, replaces  $C'$ , the unknown gas pressure, and

$$E = 0.05909 \log \frac{1}{c'}$$

Before proceeding farther on this problem, it will be necessary to study the relation of the hydrogen-ion concentration, as indicated by the hydrogen potential, to the various factors entering into the probable reaction involved. It is a matter of everyday experience and importance that sodium carbonate in the presence of water hydrolyzes into  $\text{NaOH} + \text{NaHCO}_3$  and this hydrolysis is conditioned by the electrolytic dissociation of water. At the very start, therefore, it is desirable to know the degree of this hydrolysis under the conditions which will be met with. As the first step toward this end, we thought it worth while to determine the dissociation of water in the presence of sodium hydroxide, by the same method as that used in studying the reaction mentioned. Then any error or correction inherent in the method would be involved in the constant thus obtained, and the actual value applied to the developing solutions would be free from that error. It did not seem quite rational to accept the dissociation constant of water, as determined by the saponification of esters and the like, for calculation under the conditions here involved. The result we ob-

tained for the constant may include some such error, for it is higher than that resulting from the application of other methods, but the values over a wide range of dilutions of NaOH (from 1.0 to 0.0008 N) are in such good agreement comparatively, that we are reasonably sure that the constant so determined represents the dissociation of water in the presence of sodium hydroxide at least. The results of Lorenze and Mohn<sup>11</sup> on the hydrogen potentials of sodium hydroxide solutions, while not as concordant as those we obtained would also indicate the correctness of the experimental work.

Considerable work has been done on the dissociation of water, but the only method at all like the one employed here is the use of the acid-alkali cell. A brief resume' of such results are given, together with two which represent the extreme values assigned to the constant. Ostwald<sup>17</sup> made use of the acid-alkali cell as early as 1893, but his results have since been superceded by other determinations. Lorenz

and Böhi<sup>18</sup> in 1909 obtained for  $k$ , at 18°  
 $0.72 \times 10^{-14}$ , at 25°,  $k = 1.21 \times 10^{-14}$ .

Löwenherz<sup>19</sup>, somewhat earlier, (1896) had  
 used the acid-alkali cell with the following  
 results:

From 0.1 N. HCl            at 25°  $k = 1.42 \times 10^{-14}$   
           0.1 N. NaOH

          0.01 N. HCl            25°  $k = 1.16 \times 10^{-14}$   
           0.01 N. NaOH

The lowest value recorded in available literature  
 is given by Kanolt<sup>20</sup> (1907), whose result by  
 the hydrolysis of a complex organic salt is  
 $0.82 \times 10^{-14}$ . The highest is the one by  
 Löwenherz, given above, and another close to  
 this is by Wijs<sup>21</sup> (1894) who obtained  $1.4 \times 10^{-14}$   
 by the catalysis of an ester by water.

The method employed in the present  
 case is based on the hydrogen potentials of NaOH  
 solutions thru a range of dilutions, the equation  
 last given being the one used for the calculations.  
 It will only be necessary to put it in the proper  
 form. If  $k$  = the dissociation constant of water,  
 then  $k = \text{conc. H}^+ \times \text{conc. OH}^-$ . In the equation



conc.  $\overset{+}{\text{H}} = c$ . Hence  $c = \frac{k}{\text{conc. OH-ion.}}$  Substituting

$$E = 0.05909 \log \frac{\text{conc. OH}^-}{k}$$

$$= .05909 (\log \text{conc. OH}^- - \log k)$$

from which

$$\log k = \log \text{conc. OH}^- - \frac{E}{.05909}$$

The very best obtainable conductivity data was used for the calculation of the dissociation of the NaOH, and the data, with the source, follows.

Conductivity of NaOH solutions at 18°.

v (=dilution in liters per gram-equivalent)	$\lambda_v$ at 18°	Determined by
v = 1.0 liters	157.0	Foster <sup>22</sup>
2.0 liters	174.1	"
10	195.4	"
50	197	Kohlrausch <sup>23</sup>
100	200	"
200	203	"
500	204.5	Foster
1000	208	Kohlrausch
-----		
At 25° 5	210.3	Goldsmith and Larsen <sup>24</sup>

The temperature coefficients of  
 25  
 Arrhenius are given as

$$v = \begin{array}{r} 2 \\ 10 \\ 100 \end{array} \text{ temp. coefficient} = \begin{array}{r} 0.0202 \\ 0.0202 \\ 0.0213 \end{array} = c$$

for temperatures between 18° and 40°.

No data can be found giving more complete information concerning temperature coefficients, and most of the work on the conductivity of the alkali has been done at 18°. However, we have calculated the conductivity from the above values, and also the degree of ionization. The results so calculated are a very close approximation, and when the dissociation is plotted against the dilution (See Fig. 8), a smooth curve is obtained.

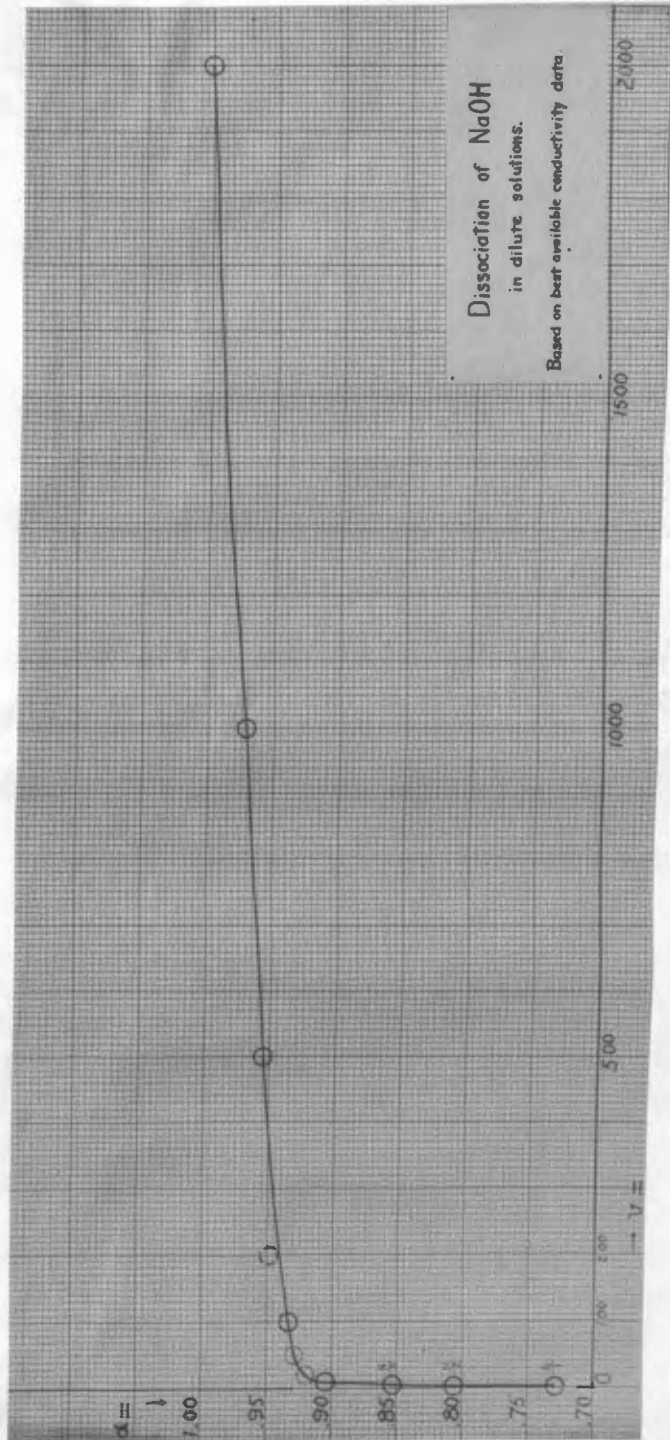
Recent determinations of the conductivity of the ions give, for 25°

$$\begin{array}{r} \text{Na} \\ \text{OH} \end{array} \begin{array}{r} 50.5 \\ \frac{196}{246.5} \end{array} = \lambda_{\infty}$$

from which the equivalent conductivity of NaOH at infinite dilution is 246.5. In the following table, the previous values are used, with the coefficients mentioned here, to calculate the degree of ionization, Temperature coefficient = c.

v =	$\lambda_v$ at 18°	c	$\lambda_v$ at 25°	$\alpha = \frac{\lambda_v}{\lambda_{\infty}}$
1	157.0	.0202	179.2	0.727
2	174.1	.0202	198.7	0.806
5			210.3	0.853
10	195.4	.0202	223.0	0.905
100	200	.0213	230	0.933

Fig. 8.



$v =$	$\lambda_v$ at 18°	$c$	$\lambda_v$ at 25°	$\alpha = \frac{\lambda_v}{\lambda_\infty}$
200	203	.0215	233.6	0.948
500	204.5	.0215	235.3	0.955
1000	208	.0215	239.3	0.971

$\alpha$  expresses the fraction ionized. These results were plotted carefully, on a large scale, so that interpolation from the curve would be as close as the values above would warrant. We assume complete ionization at  $v = 2000$ . The curve also indicates this. The two dotted circles are interpolated from an enlarged curve made for dilutions from 0 to 100. The point indicated by a circle in dashes is one based on the older data of Kohlrausch. As it is very evidently not in agreement with the others, it is omitted in drawing the curve. The curve is shown reduced in Fig. 8.

#### EXPERIMENTAL.

For all the solutions necessary in the determinations water of low known conductivity ( $0.85$  to  $1.6 \times 10^{-6}$ ) was employed. The NaOH was prepared by electrolysis of pure  $\text{Na}_2\text{CO}_3$  over mercury, the mercury having been previously purified. The amalgam obtained was washed several times by

shaking with water. It was then placed in a seasoned Jena glass flask of liter capacity, fitted with a rubber stopper, and exit tube, which ended in a seal to prevent the entrance of  $\text{CO}_2$ .  $\text{CO}_2$ -free air was now blown thru the apparatus and conductivity water was run in after this treatment. The amalgam was allowed to react several days with the water. It was aimed to conduct all the operations in the making of the solutions in the absence of  $\text{CO}_2$  as far as possible. To this end, all flasks (of seasoned Jena glass) were first filled with  $\text{CO}_2$ -free air and dilutions were made very quickly. The first solution was standardized once by means of a standard acid solution, and then gravimetrically. (Addition of  $\text{HCl}$  to a few cc. in platinum dish, evaporation to dryness, and weighing as  $\text{NaCl}$ ). The dilution required to bring it exactly normal was then made with conductivity water. All solutions were made directly or indirectly by dilution from the 1. 0. N. The strength of each solution was

carefully determined just after the determination of the hydrogen potential.

All hydrogen potentials were taken in two cells of the type shown in Fig. 7. Every reading given below is the average of at least two (in some cases 4-5) results differing by less than a millivolt. While this would not be a high degree of accuracy if one were working with acids or salts for an exact determination of H-ion, alkalies will be found to present greater difficulties. The adsorption of the alkali by the platinum black seems to be responsible for much of the trouble experienced, and either frequent electrolysis with the electrode in weak sulphuric acid or replatinizing was necessary to keep the cells in good working condition. The electrode cells were immersed in water at 25° as before. The method of calculating the dissociation constant of water has been given (pg. 77)

$$\log k = \log \text{conc. OH}^- - \frac{E}{.05909}$$

The concentration of OH-ion was obtained by interpolation from the curve on Fig. 8, and applying the value of  $\alpha$  to the known strength of the solution. The complete results are summed up in the table. E must be expressed on the hydrogen scale. This we will designate as  $E_h$ , which is to be distinguished from  $E_{H_2}$  the hydrogen potential on the absolute scale.

Ionization constant of water in the presence of NaOH.

Approx. Strength.	Exact Strength.	$\alpha$	Conc. OH	$E_{H_2}$	$E_h$ (= $E_{H_2} - .282$ )	k
1.0 N.	1.000	.727	.727	-.525	-.807	$1.60 \times 10^{-14}$
0.5	0.507	.805	.408	-.506	-.788	1.88
0.2	0.2039	.852	.1737	-.484	-.766	1.89
0.1	0.102	.9025	.0920	-.470	-.752	1.73
0.01	0.01057	.933	.00986	-.413	-.695	1.71
0.001	0.00078	.983	.0007667	-.344	-.626	1.95

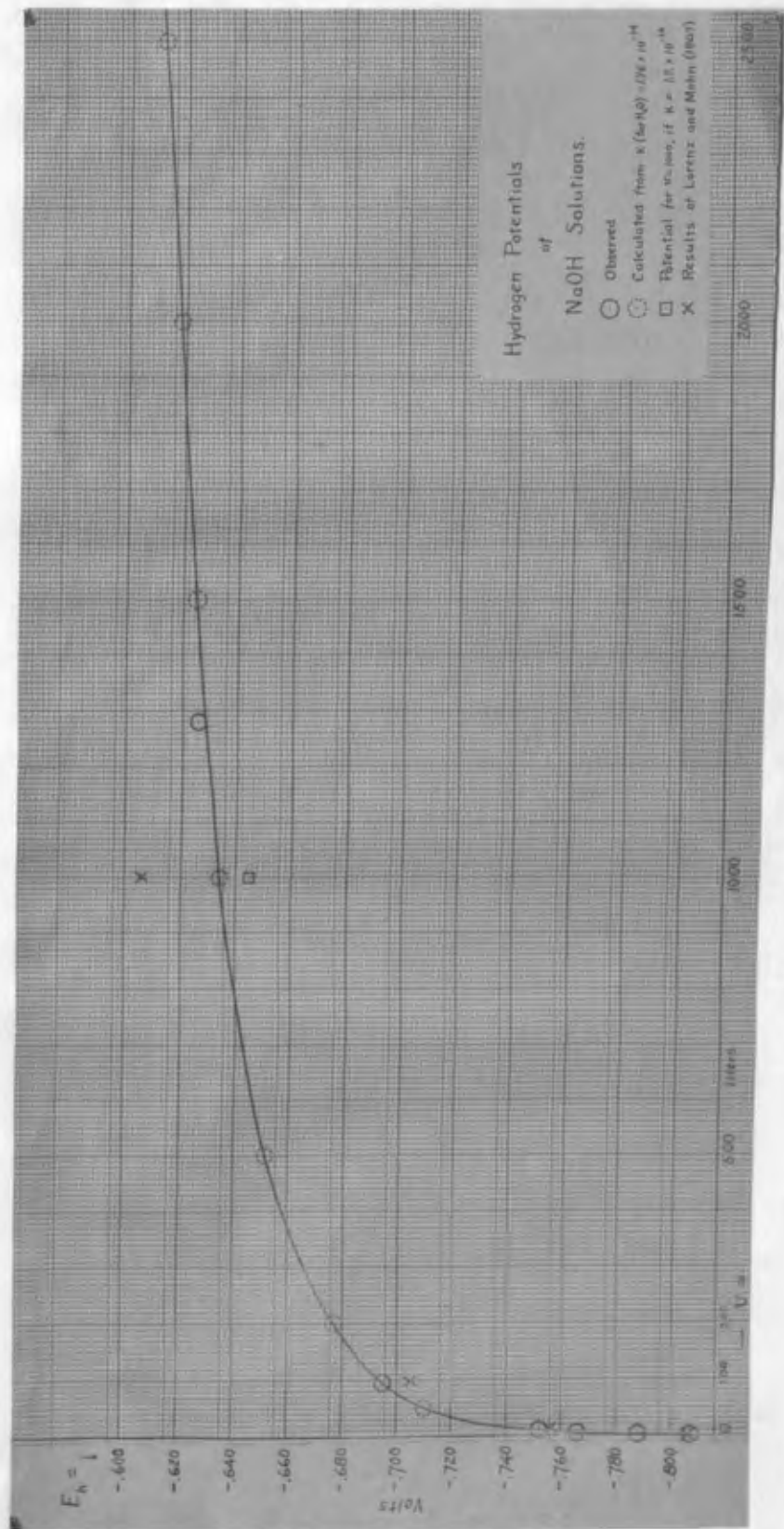
We feel justified in omitting the last from the average, since in sodium hydroxide of such a dilution, any small error due to adsorption or other effect of glass or CO<sub>2</sub> would make a large difference, and the last reading was no doubt influenced by this fact.

The average of the first five values gives  $1.76 \times 10^{-14}$  for k at 25°. It will be seen that the above results are in better agreement with each other than the results of Löwenherz with the acid-alkali cell at two different concentrations. (pg. 76)

The hydrogen potentials of sodium hydroxide solutions are plotted against the dilutions in Fig. 9 which is a reduced copy of a large curve such as will be found extremely useful in the study of carbonate solutions and developers.



Fig. 9.



In connection with the curve (Fig. 9) we wish to point out the relation of our results to others. At  $v = 1000$  will be seen a point enclosed by a square. This represents the hydrogen potential for the given dilution, calculated back on the assumption that  $k$  for water, at  $25^\circ$ ,  $= 1.2 \times 10^{-14}$ , the usually accepted value. It will then be seen that if the constant is less than the value we obtain, and if the hydrogen potentials could be obtained which correspond to this fact, then the curve would lie below the one we have drawn. The results of Lorenz and Mohn<sup>11</sup> are shown by crosses. At  $v = 1000$  their value is entirely erroneous as can be readily seen. At  $v = 1$ , our value agrees with theirs to 1 millivolt. The points indicated by dotted circles represent the potentials obtained by calculating back from our average for  $k$  ( $= 1.76 \times 10^{-14}$ ). The observed value at  $v = 1282$  lies close to the curve, as calculated for its outer portion.

It has been suggested that in the presence of a strong electrolyte, such as NaOH, the H- and OH-ion equilibrium for water differs from that which holds for pure H<sub>2</sub>O in the absence of the solute. Such a statement cannot, however,

be made on the basis of only a few determinations. It has been found that in the case of some organic acids, the degree of dissociation is affected by the presence of certain salts, other than those containing an ion in common with the acid. If the hydrogen electrode were employed to the extent it undoubtedly deserves, and other methods were applied to the same study, careful work might clear up this point in connection with aqueous solutions of the type here used.

#### The hydrolysis of $\text{Na}_2\text{CO}_3$ .

It was thought that with the information concerning sodium hydroxide just derived, it would be possible to study the hydrolysis of sodium carbonate in a similar manner. Here a far more complex problem is met, for there are several facts influencing the amount of NaOH apparent from the hydrogen potential of the carbonate solution. The apparent amount of NaOH, which is easily determined now by reference to

the curve (Fig. 9) represents some larger amount not completely dissociated, due to the fact that sodium hydroxide is not completely ionized, and even the normal dissociation is repressed by the sodium carbonate. Since strong electrolytes show a departure from the simple mass-action formulation, the difficulty is increased. The dissociation of  $\text{Na}_2\text{CO}_3$  from conductivity data, is closely as follows, at  $25^\circ$ ,

2.0 molar	20	per cent
1.0	31	
0.5	39	
0.2	47	
0.1	54	

(Graphically interpolated, from data by Jones and West<sup>26</sup>, and Kohlrausch<sup>27</sup>)

These values represent the resultant of all primary and secondary dissociations, and consequently several equilibria within the solution. It will thus be seen that this effect of the carbonate on the equilibrium might be considerable. The hydrolysis constant for  $\text{Na}_2\text{CO}_3$  represents

the value of the expression

$$\frac{\text{NaHCO}_3 (\text{NaOH})}{\text{Na}_2\text{CO}_3}$$

Auerbach and Pick<sup>28</sup> have recalculated data by Koelichen<sup>29</sup> and obtain for the value of the hydrolysis constant

$$k = 1.9 \times 10^{-4} \text{ at } 25^\circ$$

Using the same data and calculating without correction according to the formula just given, we obtain

$$\text{for a dilution of } 10.61 \text{ liters/mole } 7.12 \times 10^{-5}$$

5.31	7.33
------	------

Evidently Auerbach and Pick have applied some correction to the method of calculation, but since at the present writing, we have not been able to secure the journal in which the calculations were published, we are at a loss to understand how such a high result was obtained. We have applied a correction for the dissociation of  $\text{Na}_2\text{CO}_3$  (primary and secondary), and obtain a lower result, not constant thru a range of dilutions. It would seem that the effect of  $\text{Na}_2\text{CO}_3$  is by far the largest factor to be considered.

Below are given the hydrogen potentials over the range of dilutions employed, and a brief outline of the experimental work.

The carbonate was prepared from Kahlbaum's  $\text{NaHCO}_3$  #1. This was slowly heated in an electric oven to a temperature of  $300^\circ$ , and maintained at this temperature for one hour, insuring the removal of moisture and conversion to the normal carbonate. From this product a 2.0 molar solution was made, and the other dilutions were obtained with this as a starting point. The hydrogen electrodes were used as before, immersed in water for temperature control, and several concordant readings were obtained for each solution. Following are the results:

Strength of $\text{Na}_2\text{CO}_3$ sol.	E $\text{H}_2$	E h	Apparent conc. of NaOH (from curve)			Apparent OH conc.
			v= =	conc= =		
0.1 molar	-.376	-.658	405	.95	.00247	N .00236
0.2	-.382	-.664	323	.948	.00310	.00294
0.5	-.390	-.672	240	.943	.00417	.00393
1.0	-.396	-.678	190	.94	.00526	.00494
2.0	-.405	-.687	133	.936	.00752	.00704

The correction we make is explained as follows. According to recent work, chiefly by Bray and Hunt<sup>30</sup>, there seems to be good evidence that if two salts in the same solution have a common ion, each is dissociated to the same extent that it would be in a solution having the same total concentration of the common ion. From the dissociation values of  $\text{Na}_2\text{CO}_3$  stated on page 86, we can determine approximately the total sodium-ion concentration in the given carbonate solution. The degree of dissociation of the  $\text{NaOH}$  in the presence of the carbonate can then be calculated. Let  $x$  = the normality of the solution of  $\text{NaOH}$  which would yield the same total conc. of  $\text{Na}$ -ion as is present in the  $\text{Na}_2\text{CO}_3$  solution.  $\alpha$  = the degree of dissociation of this  $\text{NaOH}$  solution. It is required to find  $x$ , and apply its degree of dissociation to the concentration of  $\text{OH}^-$  apparent from the hydrogen potential. Take as an example the 2.0 molar solution of  $\text{Na}_2\text{CO}_3$ . It is 20 per cent dissociated. The total

concentration of Na-ion is then 0.20 (2.0) (2) since each molecule furnishes two Na-ions. This amounts to a normality of 0.8 in Na-ion. We now refer to a carefully drawn curve for the dissociation of sodium hydroxide and by trial find such a point on the curve that the product of the concentration of NaOH by the degree of dissociation equals 0.8, or in other words, determine the normality of the solution of NaOH which on dissociation yields a solution 0.8 normal in Na-ion. This point is found to be at conc. of NaOH = 1.13 N. ( $=x$ ) and  $\alpha$  for this strength is .708. According to the assumption made above, this degree of dissociation is the same as that of the actual NaOH present in the  $\text{Na}_2\text{CO}_3$  solution, and having the degree of dissociation and the apparent amount of NaOH, we can calculate the actual amount of NaOH present and thus the hydrolysis constant. The apparent  $\text{OH}^-$  concentration for



the 2.0 molar solution was seen to be .00704.  
 $\frac{.00704}{.708} = 0.0995$ , the real concentration  
of NaOH. This is also equal to the concentra-  
tion of  $\text{NaHCO}_3$ , since for every molecule of  
one there is one molecule of the other pre-  
sent. Hence the hydrolysis constant  $k$  becomes

$$\frac{(.0995)^2}{1.9005} = 5.21 \times 10^{-5}$$

(The concentration of the  $\text{Na}_2\text{CO}_3 = 2.0 - .0995$ )

Applying the same reasoning to the other  
concentrations of  $\text{Na}_2\text{CO}_3$  we obtain the results  
summarized in the following table.

Strength of $\text{Na}_2\text{CO}_3$	Fraction of $\text{Na}_2\text{CO}_3$ dissociated.	Corresponding Na-ion conc.	Conc. of NaOH at same Na-ion conc.	$\alpha$ for the latter	Observed - OH conc.	Corrected NaOH conc.	k
2.0 M.	.18*	.72	0.988 N.	.728	.00704	.0966	4.92 x10
1.0	.31	0.62	0.81	.758	.00494	.00652	4.28
0.5	.39	0.39	0.49	.807	.00393	.00487	4.78
0.2	.47	0.184	0.22	.849	.00294	.00347	6.15
0.1	.54	0.108	0.12	.889	.00236	.00266	7.28

\* (Graphically ~~inter~~<sup>extra</sup>polated. Uncertain and probably too high)

This yields a value for k which increases with decreasing concentration of  $\text{Na}_2\text{CO}_3$ , but which must very nearly represent the hydrolysis constant at the given dilution.

The hydrogen electrode method has been applied by Denham <sup>16</sup> to the hydrolysis of aniline hydrochloride with success, but in that case the hydrolysis of the hydrochloride was not complicated to any great extent by the original salt or its products.

In beginning this section of the work on the relation of the different parts of the developer to each other, the extent of the change of hydrogen potential in Developer #5, on addition of the hydrochinon was mentioned. We will make a calculation for this developer to show the method that may be employed. Taking the hydrogen potentials for the three solutions,  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_3$ , and the complete developer, reference to the NaOH-hydrogen potential curve will give the concentration of NaOH directly. All of the factors influencing the apparent amount of NaOH in the hydrolysis of  $\text{Na}_2\text{CO}_3$  are also at work in this case, but their effect is not great enough to render the present method of calculation very far from correct. The actual application to a developer such as #5 will best illustrate the theory involved.

The experimental results are as follows:

Hydrogen potential at 25° for

			$E_{H_2}$	$E_h$
Sol. 1	H <sub>2</sub> O	1000 cc	-.353	-.635
	Na <sub>2</sub> CO <sub>3</sub>	141.7 gm.		
Sol. 2	H <sub>2</sub> O	1000 cc.	-.355	-.637
	Na <sub>2</sub> CO <sub>3</sub>	141.7 gm.		
	Na <sub>2</sub> SO <sub>3</sub>	7.8		
Sol. 3				
(Dev.#5)	H <sub>2</sub> O	1000 cc.	-.325	-.607
	Na <sub>2</sub> CO <sub>3</sub>	141.7 gm.		
	Na <sub>2</sub> SO <sub>3</sub>	7.8		
	Hydrochinon,	11.1		

First of all, it should be noticed that the addition of Na<sub>2</sub>SO<sub>3</sub> scarcely affects the hydrogen potential of the carbonate. With various concentrations of Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> the effect of the sulphite may be either to raise or to lower the potential a slight amount, depending on the ratio of the sulphite to the carbonate. At any rate, it is certain that the changes involved occur between the carbonate and the hydrochinon. We hope later to make a series of determinations on various concentrations of these two substances together, but in the absence of Na<sub>2</sub>SO<sub>3</sub>. As stated in the first pages of this work, the hydrogen potential of Developer #5 was found to be absolutely independent of the state of oxidation. Four determinations

were made; one on the normal developer freshly made, a second on a sample which had stood in the air for one hour, a third on a portion oxidized by blowing air thru the solution for two hours, and a fourth on a solution treated in the same manner for ten hours. No difference could be detected in the potentials obtained, except that in the latter cases a much longer time was required to reach equilibrium, probably because the solution was saturated with oxygen. This brings out very clearly the fact that the oxidation of hydrochinon under these conditions does not produce an acid or a basic substance.

Having now obtained the hydrogen potentials, reference to the curve gives for the NaOH concentrations,

Sol. 1	0.001031 (reciprocal of v)
Sol. 2	0.001124

The value for Sol. 3 lies beyond the range of the curve and must be calculated from the relation

$$\log \text{conc. OH}^- = \log k + \frac{E}{.05909}$$

where  $k$  is the dissociation constant of water in the presence of NaOH ( $1.76 \times 10^{-14}$ ) and  $E$  has its usual meaning. This will give for the conc. of NaOH, 0.000330

Putting the three values before us for convenience

Sol. 1	conc. of NaOH	.001031
Sol. 2		.001124
Sol. 3		.000330

It will be seen that in the latter the apparent concentration of NaOH has only one third the value that it has without hydrochinon. But this is not the end of the matter. Referring again to the hydrolysis equilibrium expression, and using the constant we have obtained for the same dilution of  $\text{Na}_2\text{CO}_3$  ( $\text{Na}_2\text{CO}_3 = 1.337$  molar.  $K =$  approximately  $4.5 \times 10^{-6}$ )

$$k = 0.000045 = \frac{x}{y} \frac{(\text{NaHCO}_3)(\text{NaOH})}{\text{Na}_2\text{CO}_3}$$

If we now designate the concentration of the  $\text{NaHCO}_3$  by  $x$ , and the concentration of the  $\text{Na}_2\text{CO}_3$  by  $y$ , it will be possible to calculate the ratio between  $x$  and  $y$ , and from the total

known concentration of  $\text{Na}_2\text{CO}_3$  originally present, to determine the actual concentration of  $x$  ( $\text{NaHCO}_3$ ) in the three solutions, for that of  $\text{NaOH}$  is known. Applying this reasoning to Sol. 1 for example,

$$.000045 = \frac{.001031}{y} x \quad \text{from which } y = 23 x$$

But since each molecule of  $\text{Na}_2\text{CO}_3$  yields two molecules on hydrolysis,  $x + y =$  the concentration of  $\text{Na}_2\text{CO}_3$  originally present. If  $y = 23 x$ , then  $x + y = 24$  parts and  $x = \frac{1}{24}$  part of the  $\text{Na}_2\text{CO}_3$  originally present. The strength of  $\text{Na}_2\text{CO}_3$  is 141.7 gm./liter representing a molar strength of 1.337. Hence the concentration of the  $\text{NaHCO}_3$  is  $\frac{1}{24}$  of 1.337 or 0.058 molar. Carrying out the same calculation for each of the three solutions

we have:

	Conc. of $\text{NaHCO}_3$	
Sol. 1 (carbonate)		.058
Sol. 2 (carbonate + sulphite)	.045	..051
Sol. 3 (Developer complete)	.180	..154

Now we have the necessary data. Due to the removal of  $\text{NaOH}$  by the hydrochinon, which seems to be the only explanation of the loss of alkalinity, a progressive hydrolysis of the carbonate takes place, yielding an ever increasing concentration of  $\text{NaHCO}_3$  as the  $\text{NaOH}$  is removed. It is thus

evident that the apparent decrease of NaOH would not give us a true measure of the reaction. But from the increase of NaHCO<sub>3</sub> we can easily determine the amount of NaOH used up.

For every molecule of NaHCO<sub>3</sub> formed in addition to what was originally present, one molecule of NaOH has disappeared as such. Hence the increase in NaHCO<sub>3</sub> measures the decrease in NaOH and gives the quantity of the latter which has combined with the hydrochinon. The increase on adding the hydrochinon to the Na<sub>2</sub>CO<sub>3</sub> + Na<sub>2</sub>SO<sub>3</sub> mixture is

$$\begin{array}{r} \text{Developer,} \quad .154 \\ \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_3 \quad .05 \text{ l} \\ \hline \quad \quad \quad .103 \end{array}$$

From what has just been said then, the NaOH used up represents 1 liter of a .103 molar solution. (Considering one liter of the developer as a basis). This in actual quantity is about 4.12 grams of NaOH, which has been combined with 11.1 grams of hydrochinon. To form the mono-phenolate, C<sub>6</sub>H<sub>4</sub>(OH)(ONa), 110 gm. of hydrochinon combine with



40 gm. of NaOH. The figures above are very close to these proportions, considering the possibilities of error in the constant. We are inclined to believe that the formation of the mono-phenolate takes place. For the present, we cannot discuss its relation to development.

If we use the constant of Auerbach and Pick in making the above calculations, we obtain, as the amount of NaOH reacting with 11.1 grams of hydrochinon, 11.6 grams. This would correspond closely to the consumption of three molecules of NaOH for one molecule of hydrochinon. From the chemical point of view, it seems hardly reasonable to expect hydrochinon to act as more than a mono-basic acid in such weak alkaline solution.

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#### CONCLUSIONS.

1.0 The single potential of a developer is due to the formation of gaseous hydrogen by the developing agent. This is produced thru a reaction between the latter and the H- and OH-ions present in the solution.

2. The reducing power of the developer is measured by the power of the developing agent to produce hydrogen, i. e., by the partial pressure of hydrogen which is formed.

3. The partial pressure of hydrogen which a developer can produce can be calculated if its normal single potential is obtained, and also the hydrogen potential of the same solution.

4. Various factors delay the equilibrium necessary for the normal single potential, chief of which are: the action of oxygen in the solution and the space above, slight oxidation of the developing agent, an inherent reaction resistance, mechanical removal of hydrogen from the electrode, and diffusion of the hydrogen into the electrode.

5. The statement of Mathews and Barmerier that the potential becomes more negative with increasing time due to an oxidation is erroneous, as oxidation of any of the constituents of any developer would tend to make the potential more positive.

6. The normal single potentials of developers can be obtained in most cases only after a long period, due to the delay of the equilibrium by causes already mentioned.

7. If a developer be mixed in vacuo, with oxygen-free water, its potential changes as much as it otherwise would, contrary to the statement of Mathews and Barmer.

8. By the method suggested by (2) and (3) the reducing power of amidol was found to be 14 times that of metol-hydrochinon, (Seed formula), the actual partial pressure of  $H_2$  being for Amidol 0.0257, for Metol-hydrochinon, 0.00188 atmosphere.

9. In connection with work on  $Na_2CO_3$ , the dissociation constant of water, in the presence of NaOH was found to be  $1.76 \times 10^{-14}$ .

10. The hydrolysis of  $Na_2CO_3$  studied by the hydrogen electrode method gave about  $4.5 \times 10^{-5}$  for the value of the expression

$\frac{(NaHCO_3)(NaOH)}{Na_2CO_3}$  The results vary somewhat, increasing with decreasing concentration of  $Na_2CO_3$ .

11. By means of the hydrogen electrode, it was found that there is a definite reaction between hydrochinon and sodium carbonate upon mixing the developer.

12. Applying preceding data on the dissociation constant of water and the hydrolysis constant of  $\text{Na}_2\text{CO}_3$ , this reaction was found to be the formation of the mono-phenolate  $\text{C}_6\text{H}_4(\text{OH})(\text{ONa})$ .

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A. H. N.

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