demonstrated during the past thirty years that the present tariff rate of 30 per cent. on dyestuffs is not sufficient to induce the domestic dyestuff industry to expand at a rate comparable with the consumption of dyestuffs in this country and that, therefore, all dyestuffs made from coal tar, whether they be aniline dyes or alizarin, or alizarin dyes, or anthracene dyes or indigo, so long as they are made in whole or in part from products of or obtainable from coal tar, should all be assessed alike, namely, 30 per cent. *ad valorem* plus $7^1/_2$ cents per pound specific, and that all manufactured products of or obtainable from coal tar, themselves not dyes or colors and not medicinal, should be taxed 15 per cent. *ad valorem* and $3^3/_4$ cents per pound specific."

Are the people of this country ready to coöperate with the chemists by authorizing the prompt enactment of such legislation? If so, there need be no fear that active capital will be longer withheld, and thus we can feel confident of a synthetic dyestuff industry commensurate with our needs.

As I think of the possibility of such an industry, I recall the words of the Swiss professor, Gnehm, who, in 1900, after one of his lectures on coal-tar dyes, said to me: "The natural home of the dyestuff industry is in your country and some day it will flourish there."

The creation of such a self-contained industry, however, has far deeper meaning for our national welfare than the supplying of needed dyestuffs, for such plants would constitute an easily convertible reserve for the manufacture of coal-tar explosives in times of war.

Through its stimulative effect on research, on technique and in supply of material the dyestuff industry has furthered the development of both the explosives and the medicinal industries. Its firm establishment here would foretell the complete development of each of this great trio of industries, which, as a whole, furnish the rational and economic utilization of that great mass of coal tar which now wastes itself in useless flames above the coke ovens throughout the land.

Coöperation—it is a good word, and carries with it a wonderful power of accomplishment!

CHAPEL HILL, N. C.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

THE REDUCING POWER OF PHOTOGRAPHIC DEVELOPERS AS MEASURED BY THEIR SINGLE POTENTIALS.

BY FRANCIS C. FRARY AND ADOLPH H. NIETZ.

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One of the most important properties of a developer is its reducing power, as measured by the free energy of the reaction when it is oxidized. It is evident that this must be adjusted to lie within certain limits; to insure proper development of the image on the one hand, and on the other to avoid the production of chemical fog, due to the development of unexposed silver bromide. No direct determinations of this property have hitherto been made. Sheppard and Mees,[1] by an indirect method depending on the restraining power of potassium bromide, have obtained values representing the relative reducing power of *p*-aminophenol, hydrochinon, hydroxylamine and ferrous oxalate developers. Assigning a value of 1.00 to ferrous oxalate, they find the following numbers for the other developers: *p*-Aminophenol, 3.4; hydrochinon, 0.6; hydroxylamine, 1.13.

Mathews and Barmeier,[2] and Lidbury,[3] have recently published some work on the single potentials of various developers, but have neither given data nor suggested a method by which either absolute or relative reducing powers of these developers could be determined. It is to be noted that the observations of Mathews and Barmeier extended over periods of only six to twenty hours, in which time it is impossible to even approach equilibrium values for the single potentials. Lidbury extended his observations over a longer period of time, but frankly states that he did not consider that he obtained equilibrium values. The determinations of Mathews and Barmeier are also obscured by an error in calculation, apparently due to a false conception of the sign and use of the normal calomel electrode. They drew certain conclusions from the shape of the curves representing the value of the single potential as a function of the time; but, as will be shown later, the shape of these curves is incidental to the approach of the equilibrium, and in no way a basis for the conclusions which they draw.

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), shows absolutely nothing concerning the real single potential of the developer, no matter what form the curve may take. Nearly all developers start at about the same point and closely parallel each other for some time. At any rate, these initial changes are unimportant and incidental; 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 sulfite, as suggested by Mathews

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[1] Sheppard and Mees, "Investigations of the Theory of the Photographic Process," pp. 188–196 (Longmans, Green & Co.).

[2] Mathews and Barmeier, *Proc. 8th Intern. Congr. Appl. Chem.*, **20**, 201.

[3] Lidbury, *Ibid.*, **20**, 189, 193, 197.

and Barmeier. Moreover, these changes can not be due in any degree to the sulfite present; it is probable that the sulfite plays a minor role in the mechanism of the developer.[1] But it seems to be established by experience and experimental evidence that the carbonate is a very important factor. Our reasons for not agreeing with the sulfite-oxidation theory 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, the fundamental theory of the production of a difference of potential between the electrode and the 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 Barmeier will be obvious. A method of determining both the absolute and relative reducing power of a developer will be discussed and employed.

Theoretical.

The cause of a difference of potential between a platinized platinum electrode and a developer must be the gaseous hydrogen formed in the developer and deposited on the electrode. The electrode potential will then be a function of the partial pressure of the hydrogen on the electrode and the hydrogen-ion concentration of the developer. The production of hydrogen probably takes place in the manner indicated in the following ionic reaction:

$$H^+ + OH^- + R = RO + H_2,$$

where R represents the active portion of the reducing agent in the developer, and no assumptions are made as to the way in which it combines with the oxygen. It is evident that the concentration (and therefore the partial pressure on the electrode) of the hydrogen produced depends on the temperature, the concentration of the reducing agent, and the nature of the latter. Since the product of the hydroxyl-ion and hydrogen-ion concentrations is constant at any given temperature, the only way in which the alkalinity of a developer can affect its reducing power is by changing the concentration or nature of the active portion of the reducing agent. It is probable that the reducing agent is present in the form of a sodium salt, more or less hydrolyzed and dissociated, and that the active portion consists of the anion formed in the dissociation. It is probable that the greater part of the effect of the carbonate in conditioning the velocity and density attained in development is due to its action in swelling the gelatin and thus facilitating the action of the developer on the silver salt.

Since the single potential of a developer depends both on the alkalinity

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[1] Sheppard and Mees, *Loc. cit.*, p. 179.

of the solution and the concentration or pressure of the hydrogen on the electrode, and the latter alone is the measure of the reducing power of the developer, it is obvious that a direct comparison of the single potentials of developers would give us no information as to their relative reducing powers. Nernst[1] states that the reducing power is greater according as the gas evolution (hydrogen) takes place at a higher pressure. In order to determine the absolute pressure of hydrogen represented by a given single potential E_x of a developer, it is only necessary to also determine, in the same solution, the potential E_{H_2} of a platinized electrode saturated with hydrogen at atmospheric pressure. For two hydrogen electrodes in the same solution, but saturated with hydrogen at different pressures, the difference of potential is represented by the formula

$$E = 0.0001983\ T \log C/C',$$

where C and C′ represent the hydrogen pressures. Since the pressure in one case is known to be one atmosphere, C = 1, and at 25° the equation becomes

$$E = 0.05909 \log 1/C',$$

E being the difference between the hydrogen potential of the developer and its single potential ($E = E_{H_2} - E_x$). This partial pressure of hydrogen (C′) seems to be the only absolute standard to which the reducing power of the developer can be referred.

By determining the hydrogen potential (E_{H_2}) of the same developer in several stages of oxidation, it was shown that, in the case of hydrochinon at least, the alkalinity of a developer was not affected by its oxidation, and no error is therefore introduced by any such change during the determination.

In such a complex system it should not be expected that equilibrium would be at once obtained. When it is finally reached, it is obvious that the electrode, the solution, and any space above the solution, must all be saturated with hydrogen at the same partial pressure. The attainment of this condition is delayed by two different types of causes: chemical and physical.

Of the chemical causes, the presence of oxygen in the solution is at first very important. This continually dissolves in the platinum and acts as a depolarizer, until it is all consumed. The extent of this delay is determined by the quantity of the oxygen and by the difficulty with which the last traces of it may reach the electrode. Another chemical cause, which seems to be particularly important in the case of hydrochinon, is a sort of reaction-resistance, apparently inherent in the substance itself, and probably allied with the initially low chemical velocity found

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[1] Nernst, "Theoretische Chemie," 5th ed., p. 740.

in the hydrochinon developer by Sheppard and Mees.[1] We were able to eliminate the errors due to the presence of oxygen by making up the developer *in vacuo* with special precautions, and by this means obtained equilibrium within a week for amidol, but were unable to approach it with pure hydrochinon developers in three months. A hydrochinon developer made up with 0.5 g. tetrathiourea ammonium bromide per liter, seemed to come to an equilibrium very quickly at a potential indicating much higher hydrogen pressure than would be expected for hydrochinon. After maintaining this potential for a week, the very small quantity of the thiourea salt seemed to have been decomposed by the alkali, and the potential very quickly rose to approximately the value previously obtained for metol-hydrochinon, and probably nearly correct for hydrochinon alone. This value was maintained for six weeks. Apparently the thiourea salt either lowered the reaction resistance or aided in bringing about a condition which the hydrochinon was able to maintain after the thiourea salt was decomposed.

The physical causes all concern the problem of getting the hydrogen to the electrode, and the mechanical removal of the hydrogen. In order to study these it will first be necessary to consider the manner in which the hydrogen gas is produced. Either it is produced by the developer through the catalytic action of the platinum black, and therefore directly on the electrode, or it is formed throughout the solution and is extracted by the platinum electrode on account of its solubility in platinum black. Bubbling an inert gas through the solution at the electrode causes an immediate rise in the potential, which might be due to the mechanical removal of the hydrogen from the electrode by the gas. If the hydrogen were formed at the electrode only, on account of the catalytic action of the latter, stirring the solution in a closed cell completely filled with liquid should have the same effect, to a smaller extent, as bubbling an inert gas through the solution. The fresh solution should dissolve hydrogen out of the electrode and cause its potential to rise (become more positive). As a matter of fact, many experiments along this line, when they have given any results at all, have produced a lowering of the potential, caused evidently by an increase of hydrogen concentration on the electrode. It would appear most probable then, that the hydrogen is produced throughout the solution and extracted by the platinum black. The attainment of equilibrium between the platinum and the solution is therefore physically hindered by the slow diffusion of the hydrogen through the developer toward the platinum, and from the liquid into the metal itself. Similarly, the hydrogen must diffuse through the liquid, and from the liquid into the space above, before the partial pressure of the

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[1] Sheppard and Mees, *Loc. cit.*, p. 169.

gas in that space can correspond to that of the hydrogen in the solution.

Since an increase of the concentration of the hydrogen on the electrode makes it more negative with respect to the solution, the potential will continue to change in this direction until the hydrogen gas is in equilibrium with the solution, the platinum of the electrode, and the space above the liquid surface. These considerations alone are evidently sufficient to explain the fact that the single potential of a developer changes very rapidly at first and then more and more slowly, giving curves of the shape shown by Mathews and Barmeier. Therefore the shape of these curves can not be cited in support of their views as to the function of the different constituents of a developer.

Experimental.

All single potentials were measured with the aid of a large potentiometer (Kompensations-Apparat nach Franke[1]) and a very sensitive galvanometer. The potentiometer was frequently adjusted by the use of a Weston cell, which had been made up for more than a year and was compared during the preliminary experiments with a cell certified by the Reichsanstalt. The normal calomel electrode was used, being assigned the value 0.560 + 0.0006 (t — 18), the mercury being considered positive to the solution.[2] All single potentials are given as the potentials of the electrode minus that of the solution ($E_{Pt} - E_{sol}$). The error in the determinations of the potentials is of the order of 0.001 volt or less, usually no more. A saturated solution of potassium chloride was used as the intermediate liquid in all cases.

The first experiments were made with an electrode cell consisting of a 250 cc. bottle, partially filled with developer, and closed with a rubber stopper, through which passed the necessary glass tubes. The solution was a metol-hydrochinon developer recommended for use with Seed plates, having the composition, in grams per 1000 cc. water: metol 1.85 g., hydrochinon 1.85 g., sodium sulfite 13.9 g., sodium carbonate 13.9 g. The carbonate used in this formula was Merck's C. P. dried, which was later found to contain 14.8% water. The sulfite was Baker's analyzed anhydrous, which was that used throughout all our experiments.

The curves, of which Nos. 1 and 2, Fig. 1, are examples, have the slope required by the theory. After several hours the curve begins to rise again (not included in the figure) and the developer becomes yellow, evidently on account of oxidation. The oxygen absorbed has, by its depolarizing effect, distorted the curve, prevented the attainment of equilibrium, and has oxidized the developer so that it is finally unable to

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[1] *Z. Instrumentenkunde*, **23**, 93 (1903).

[2] Ostwald Luther, "Physiko-Chemische Messungen," 3rd ed., p. 443.

produce hydrogen as fast as the latter is oxidized at the electrode, and the potential begins to rise again. Mathews and Barmeier have stated that the existence of the first part of the curve, where the electrode is becoming more and more negative with respect to the solution, is due to the oxidation of the developer, but it is evident that the *later* portion of the curve, where the potential is becoming more and more positive, is really the one where the effect of oxidation appears.

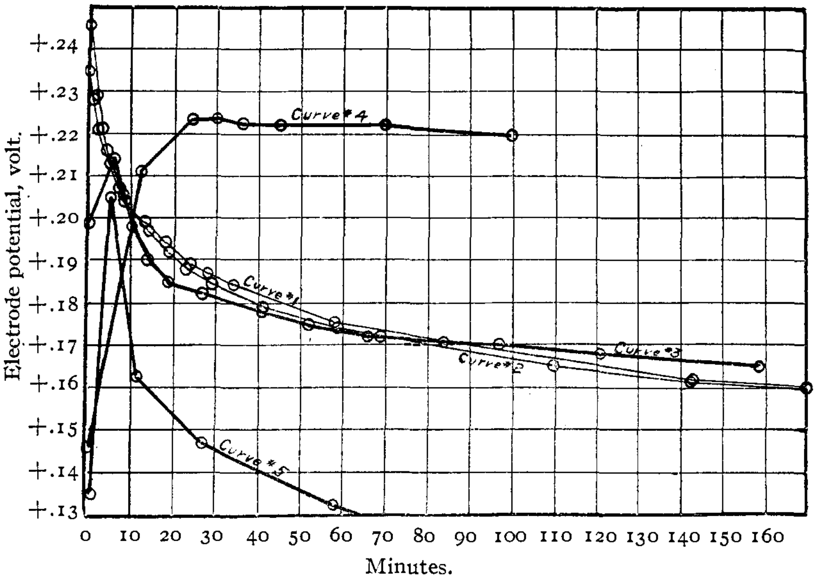

Fig. 1.—Electrode potentials in developers.

To show the effects of oxidation and mechanical agitation, two cells were used which had been set up for some time, and had already attained fairly low values for the electrode potentials. Air was bubbled through one of these, and nitrogen through the other. The results are shown in Curves 3 and 4, Fig. 1. The values plotted at zero time are those taken just before the gas was turned on. In both cases it will be noted that there is an immediate rise in the potential of the electrode, evidently due to the removal of hydrogen from the platinum. Curve 3 shows that when nitrogen is used, and the effect is purely mechanical, this rise is succeeded by a drop, after which the curve tends to become horizontal. The rise at first is apparently due to the agitation, which brings to the electrode a surface layer of developer richer in oxygen. This at once reacts with the hydrogen in the electrode, but the passage of the nitrogen both tends to remove oxygen already in the developer and to prevent more from entering it. The potential then drops rather rapidly as the electrode absorbs hydrogen from the solution, while the nitrogen, by tending to remove this hydrogen, flattens out the curve and soon is able to remove the hydrogen as fast as it is formed. If the nitrogen is now turned off, the curve drops rather suddenly as shown in Fig. 2, since the interfering action of the nitrogen is removed.

Curve 4, Fig. 1, shows the electrode potential when air is bubbled through the solution and the depolarizing effect of the oxygen is thus maintained. The difference between Curves 3 and 4 can only be ascribed to the oxygen in the air, and refutes entirely the claims of Mathews and Barmeier as to the effect of oxidation of the developer. After the two cells had run in this manner for some time, they were interchanged, the one containing nitrogen being now supplied with air, and *vice versa*. The new curves for agitation with nitrogen and air were almost identical with Curves 3 and 4, thus indicating that the shape of these curves was determined entirely by the composition of the gas used.

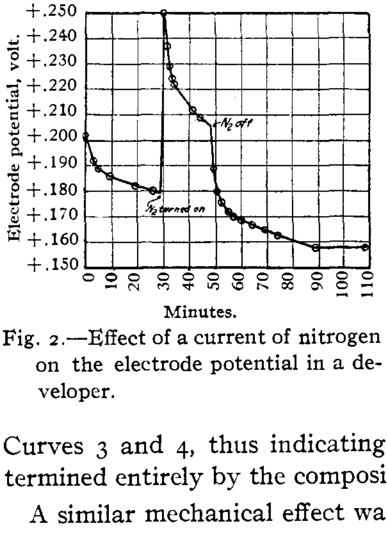

Fig. 2.—Effect of a current of nitrogen on the electrode potential in a developer.

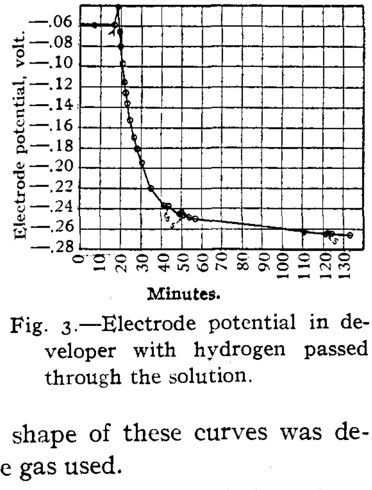

Fig. 3.—Electrode potential in developer with hydrogen passed through the solution.

A similar mechanical effect was observed when a cell was shaken vigorously for half a minute, and the potentials then read at intervals (Curve 5, Fig. 1). If the potential of a developer is taken by means of an electrode dipping into it in an open dish, and the solution is stirred, the results are the same.

A current of hydrogen was passed through a cell which had been set up for several hours and which had attained a nearly constant value of —0.060 volt. The results are shown in Fig. 3; the hydrogen being turned on at point A, 18 minutes after the beginning of the portion of the curve shown. A slight rise, due to depolarization by dissolved oxygen from the surface of the developer, is again observed, followed by a rapid drop, due to the saturation of the platinum with hydrogen. At each of the three points marked S, the cell was shaken vigorously for half a minute, and it will be noticed that the effect, which was slight at first, becomes negligible as the electrode approaches saturation. This is exactly what would be expected from the explanation already given. This curve has the same general characteristics as the previous ones, and those of Mathews and Barmeier, and substantiates the theory of the causes of the retardation of the equilibrium in the determinations of the single potential of developers.

In order to obtain the real single potential of a developer, it is evident that an apparatus, entirely constructed of glass, must be completely filled with the developer and the observations extended over a long time, until it is quite certain that equilibrium is reached. The form of electrode cell finally adopted is shown in Fig. 4. The total capacity up to the stopcock B is about 4 cc. At D is a constriction, so that, after filling, the apparatus may be evacuated and sealed off. E is a small platinized electrode. The side-tube is drawn to a fine point at C, which is plugged with filter paper after the cell is filled. A short piece of rubber tubing with a glass plug closes the end C′. At first these cells were filled as follows: the developer was quickly mixed and drawn up to point F, the stopcock was closed, the cell evacuated with a water pump and sealed off at D. After cooling, C was placed in a small amount of the developer and the stopcock opened, whereupon the cell filled almost completely, leaving only a small bubble of air over the solution. The plug of filter paper was inserted in C, and the apparatus was ready for use. With this cell the Seed metol-hydrochinon developer reached, after six weeks, a fairly

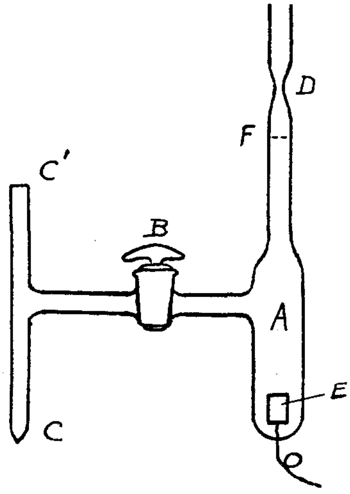

Fig. 4.—Cell for determining the single potential of a developer.

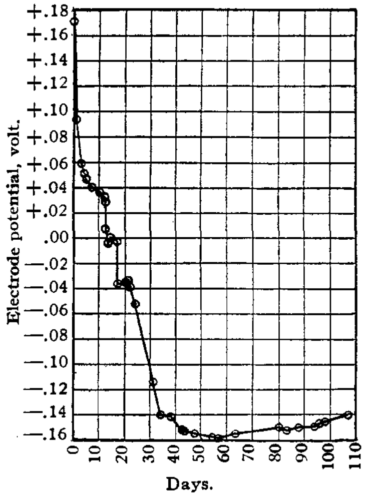

Fig. 5.—Electrode potential of Cell No. 3, Developer No. 1, Jan. 15, to May 2.

constant value of —0.150 volt. Four different cells containing this developer ultimately gave the same reading, maintaining it for a period of nearly two months. Fig. 5 shows the observations on one of these cells. Many minor irregularities are to be noted. As stated on page 2236, the carbonate used in this developer contained about 15% water. On account of the importance of this salt, it was decided that later determinations should be made with thoroughly dried material.

Suspecting from the behavior of the cells that some of the irregularities shown in Fig. 5 might be due to inhomogeneity of the solution, small rods of glass were put in some of the cells to act as stirrers. With the use of these it was at times possible, when a temporary equilibrium appeared to have been reached, to disturb this and start the potential downward. No uniformity could be traced in the results of shaking, although it was observed that there was a certain stage, between +0.035 and —0.040 volt, where the cell was more sensitive to shaking. Some of the cells reached a temporary equilibrium which might have proved very misleading, if only one determination were made. One of the cells containing this developer remained at +0.035 volt for more than ten days, another at about zero for several days, and a third seemed constant at about —0.036 for a week.

With the hope of hastening the attainment of the 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 electrode cells of the same design as shown in Fig. 4, the latter having also been evacuated and washed out with both nitrogen and the developer. The apparatus and its use will be described together. The apparatus is shown in Fig. 6.

The tube V is connected with the vacuum pump, N with the nitrogen supply (made from ammonium nitrite and washed with alkaline pyrogallate in a Liebig potash bulb), and the tube M is connected with the tube C of the cell. All the glass parts have been previously cleaned with chromic acid and washed with distilled water. The tight rubber stopper S is put in place, and the tube now evacuated. H is a stopcock so arranged that the suction can be applied either at J or C. A tight rubber tube and glass plug are placed over C′. For the first part of the operation the suction is applied at J, the stopcock R being open while B is closed. When most of the air has been removed from the mixing apparatus and the cell, nitrogen is slowly admitted at C, and J is closed. The apparatus is allowed to fill with nitrogen, is then evacuated as before and again filled with nitrogen. Tube T is large enough to contain about 75 cc., and should be about 20 cm. long. 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 the stopcocks so arranged that a rather brisk stream of nitrogen will flow through the apparatus from C when S is removed. The stopper S is now removed and about 35 cc. of the boiled water quickly introduced into the apparatus by means of a pipet. The stopper is then again inserted, the nitrogen supply shut off, and suction again applied slowly at J, until the water boils vigorously. A slow stream of nitrogen is now allowed to flow through the apparatus from C, and the boiling *in vacuo* cautiously continued, with gentle heating. After

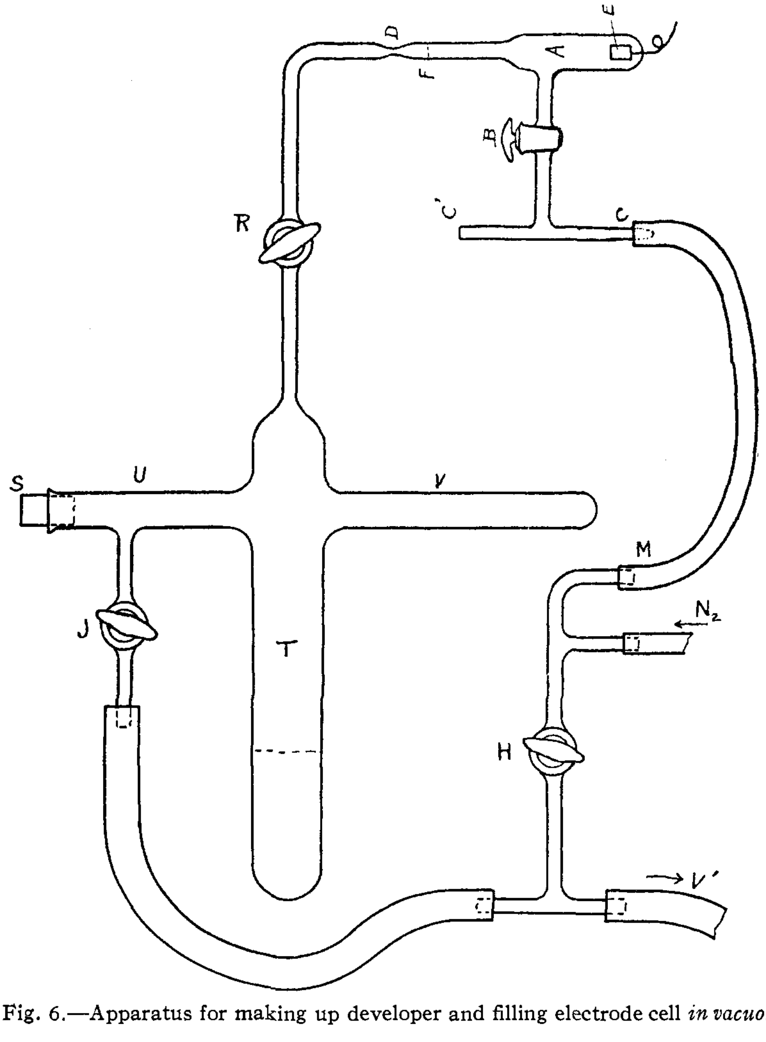

Fig. 6.—Apparatus for making up developer and filling electrode cell *in vacuo*.

boiling ten minutes, the suction is shut off and the apparatus allowed to fill with nitrogen and cooled. The volume of the water should be adjusted to 25 cc. by drawing out the excess through J. The developer, previously accurately weighed into small glass capsules, is now introduced through the tube U, while a current of nitrogen flows through the apparatus 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 tightly, and the apparatus evacuated as far as stopcock B. It is then filled with nitrogen, again evacuated, and again filled with nitrogen. The capsules of developer are then dropped into the water and quickly shaken until the contents are dissolved. Suction is again applied, and the nitrogen dissolved in the water during the solution of the developer is mostly removed. Nitrogen is once more admitted, and the whole apparatus evacuated. By tipping the apparatus, about 3 cc. of developer are allowed to flow into the electrode cell A. R is now closed and the developer shaken around in A to rinse it out. Suction is now applied at C, drawing out the air up to the stopcock B. A little nitrogen 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 then closed, and another portion of 3 cc. allowed to flow over and drawn out by way of C as before. The greatest possible degree of suction is now applied at C, and B is closed. The cell is now filled to a point about 2 cm. beyond the stopcock *B*, leaving a space of about a centimeter above the developer in the cell, so that the liquid will not be too close to the point where the glass is to be sealed together. This part of the operation is sometimes troublesome, but by tapping the tube and applying suction at either J or C, as required, the liquid can be adjusted exactly as desired. R is now closed and nitrogen admitted to tube T through J. The cell is now sealed off at D, and nitrogen admitted to the tube C. After the glass has cooled, the stopcock B is opened and the space above the developer is practically completely filled. The outer part of the electrode, between B, C and C′, is not filled until after the next cell has been sealed on the apparatus and filled. As soon as the first cell has been sealed off, another is sealed on in its place, without in any way disturbing the content of tube T. The second cell is evacuated and filled with nitrogen twice through C, R is opened, the whole apparatus evacuated through C, and this cell rinsed and filled just as the first one was. After sealing this cell off, the remainder of the developer is poured out of the tube T and used to fill the tubes CC′ of the two cells. The tube C is then plugged with filter paper, C′ closed with rubber tubing and a glass plug, and the cells placed in the rack ready for measurements. The mixing apparatus can be used as often as desired, by sealing on new electrode cells.

With the use of the apparatus just described, seventeen electrode cells were filled for the investigation of eight different developers. Of these, only two cells containing amidol, and one containing hydrochinon with tetrathiourea ammonium bromide, appear to have come to equilibrium, although all have stood more than two and a half months. The amidol developer contained 100 g. sodium sulfite and 20 g. amidol dissolved in 1000 cc. water. The hydrochinon developer with thiourea was made according to the formula recommended[1] for the direct production of positives in the camera, and contained, dissolved in 1000 cc. water, 63 g. sodium sulfite, 126 g. sodium carbonate, 10.5 g. hydrochinon, and 0.5 g. tetrathiourea ammonium bromide.

At the end of a week, the amidol developer reached a point where it appeared to be in equilibrium, and both cells have, in fact, remained at about that value since. The average of ten readings from the two cells, extending over a month, is +0.063 volt, the extreme readings being +0.057 and +0.067 volt. One of the two cells containing the thiourea developer was found to have cracked where it was sealed off, and did not come to any equilibrium. The other reached the value —0.255 volt after eight days, maintaining this for a week (readings —0.255, —0.251, —0.253, —0.260). When it was again read, three days later, it appeared to have approached a new equilibrium in the neighborhood of —0.150 volt. This was well maintained, as the readings over a period of six weeks show.

—0.148, —0.157, —0.162, —0.125, —0.144,
—0.120, —0.148, —0.154, —0.154.

It is well known that thiourea compounds are not very stable in alkaline solution; and it is not surprising, when we consider that the whole electrode cell contained only about 0.002 g. of this substance, that its action, while vigorous, was not prolonged; and that at the end of two weeks it appears to have been all decomposed. After this time the cell seems to have come to an equilibrium corresponding to the hydrochinon remaining. The average value for the equilibrium when thiourea was present is —0.254 volt; at the second stage, neglecting two values which are obviously irregularities, the average is —0.152. The average for the Seed metol-hydrochinon developer previously determined (not made up *in vacuo*, page 2238) was —0.149 volt. This is the average of 19 readings from four cells, some of them covering a period of eighty days.

These two values for hydrochinon and metol-hydrochinon developers, respectively, are a good illustration of the fallacy of the direct comparison of single potentials. One would say from the single potentials that the

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[1] Frary, Mitchell and Baker, *Proc. 8th Intern. Congr. Appl. Chem.*, 20, 141.

reducing powers of these developers were identical, although every photographer who has tried them knows that the metol-hydrochinon is much more rapid and apparently more vigorous in its action. By taking the hydrogen potentials and calculating the actual partial pressure of hydrogen, to which the developer is equivalent, as previously explained, we arrive at the relative reducing power of 2.7 : 1 (see Table I), which is photographically reasonable.

Mathews and Barmeier[1] stated that the potential did not change when the developer was made up from oxygen-free water in a vacuum. If this were true, it would upset all our theories, and leave us entirely in the dark as to the cause and nature of the single potentials observed. The procedure required for the use of the apparatus for sealing off the developer in an atmosphere free from oxygen, though slow and laborious, was adopted in order to be absolutely certain to exclude oxidation effects. In each of the seventeen electrodes sealed off in this way the potentials dropped, the curves being similar to those obtained in the presence of air. We are unable to account for the results claimed to have been obtained by Mathews and Barmeier. It will be seen that the oxygen in the water can not be the cause of the change in the electrode potential, while the theory of the production of hydrogen throughout the solution and its slow diffusion toward the electrode, and the presence of a reaction resistance depending on the nature of the reducing agent seem adequate to explain the changes observed.

In order to convert the values obtained for the single potentials of the developers into actual pressures of hydrogen, and so get a definite measure of the reducing power of these developers, it is necessary to determine the potential (E_{H_2}) which a platinized electrode saturated with hydrogen at atmospheric pressure will assume in the same solutions.

For all work on hydrogen potentials in this and the three following papers the form of apparatus shown in Fig. 7 was employed. This gives an electrode of simple construction and one with which reliable results to an accuracy of 0.0001 volt can be obtained. The hydrogen electrode has been thoroughly discussed by Loomis and Acree,[2] and a very extensive bibliography of the subject given.[3] It was our experience that no form of electrode cell was reliable in which rubber stoppers were used, especially if the current of hydrogen stopped. By the use of the apparatus shown in the figure it is very often possible to maintain, at a constant temperature, a potential constant to 0.0001 volt with the hydrogen turned off, provided equilibrium has been previously reached.

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[1] Mathews and Barmeier, *Proc. 8th Intern. Congr. Appl. Chem.*, **20**, 201.

[2] *Am. Chem. J.*, **46**, 585 (1911).

[3] *Ibid.*, **46**, 635 (1911).

A is the main electrode chamber, and E is the electrode of platinized platinum, having a short piece of platinum wire extending down from it as shown. The hydrogen enters at H and bubbles up through the solution to be investigated at D. The gas was made from C. P. sulfuric acid and arsenic-free zinc, and purified by passing through two small glass wash bottles containing acid potassium permanganate and a third flask containing a solution similar to that in the electrode cell itself. The gas leaves the apparatus through the trap K, which contains mercury, the height of which can be regulated by the reservoir M and pinchcock N.

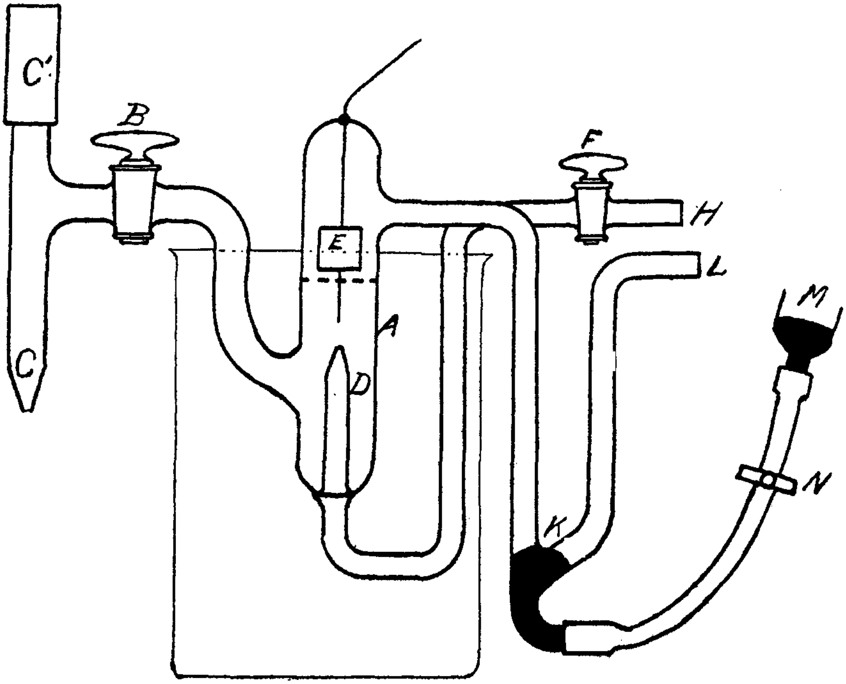

Fig. 7.—Hydrogen electrode.

The meniscus is so adjusted at the angle K that the gas pushes the mercury aside when under slight pressure, so the gas can escape but no air can enter. Connection with the intermediate liquid is made through the tube CC′ as in previous cases. The height of the liquid should be about that indicated by the dotted line. It was found that equilibrium was reached more quickly if the electrode was shaken thoroughly with the solution before use, so as to be sure that the liquid had penetrated the pores of the platinum black. When the electrode was in good condition, the time required to reach requilibrium with a developer varied from four to fifteen minutes. As soon as one determination was completed the cell was washed with hot water, filled with dilute sulfuric acid (1 : 20) and allowed to stand in this condition until again needed. The use of this acid assisted greatly in keeping the electrode in good condition and reduced the time required to reach equilibrium.

The temperature has a great influence on the hydrogen potential. This was controlled in our work by immersing the electrode cell in a beaker of water kept at 25°. The calomel electrode was also kept immersed in a water bath, so that its actual temperature could be readily determined and the appropriate correction made. The correction for barometric pressure was so small as to make it unnecessary to consider it.

In applying the hydrogen electrode to the problem of the reducing power of the developer, it is to be noted that the accuracy of the final result is no greater than that to which the single potential (E_x) of the developer can be determined. Since this can hardly be determined within less than a millivolt, a hydrogen potential of the same accuracy is sufficient. No difficulty was found in obtaining such accuracy, either with duplicate determinations from the same lot of solution, or with different lots made up from the same formula.

The hydrogen potential of the Seed metol-hydrochinon developer was determined at 23.5°, but its temperature coefficient was studied and found to be —0.0004 volt per degree. The value obtained at 23.5° was —0.3096 volt, which gives —0.3102 volt at 25°. Determination of the value of E_{H_2} for the amidol developer gave —0.031 volt and for the hydrochinon developer containing the thiourea salt —0.338 volt at 25°.

As previously shown (p. 2233), we can calculate the pressure of the hydrogen produced by the developer in equilibrium with the platinum electrode at 25° from the formula:

$$E = 0.05909 \log 1/C',$$

where $E = E_{H_2} - E_x$. The results for the developers which came to equilibrium are shown in Table I.

TABLE I.—REDUCING POWER OF DEVELOPERS.

Developer.	E_{H_2}.	E_x.	E.	C' (Atm.).	F.
Hydrochinon	—0.338	—0.152	0.186	0.000712	1.0
Metol-hydrochinon	—0.310	—0.149	0.161	0.00188	2.7
Amidol	—0.031	+0.063	0.094	0.0257	36.0
Thiourea	—0.338	—0.254	0.084	0.0379	53.3

Under Column F are arranged numbers showing the relative reducing powers of the different developers, taking hydrochinon as unity. As previously stated, the values for thiourea and hydrochinon depend on only one cell, and may therefore be somewhat in error, but we feel that the absolute values for the amidol and metol developers of the formula given are quite well established.

For comparison with the above, the results obtained by Sheppard and Mees[1] are of interest. Recalculating them to a basis of hydrochinon = 1.0, their results show the relative reducing power of ferrous oxalate to be 1.6; that of hydroxylamine, 2.0; and that of *p*-aminophenol, 5.4. Their hydrochinon developer was made up with more than two molecules of sodium hydroxide to a molecule of hydrochinon, in order to have present the di-quinolate, which their work showed to have a greater reducing power than the mono-quinolate. As our results above are for a hydrochinon developer made up with carbonate, in which we have been able to show that the anion present is probably mono-quinolate, the value hydrochinon = 1.0 in our table probably represents a considerably smaller absolute reducing power than the same value in their results.

Photographically, it is well known that metol-hydrochinon is a much more rapid and powerful developer than hydrochinon alone. It is also known that the addition of thiourea compounds increases the reducing power of the developer to the point where it is capable of reducing unexposed silver bromide if a sufficient amount of alkali be present. With less alkali, little or none of the unexposed silver bromide is attacked, indicating that the reducing power of this developer is not so very far beyond the limits of ordinary developers. The figure 53.3 for the relative reducing power of the thiourea developer, as compared with hydrochinon, does not seem unreasonable. Amidol, thirty-six times as powerful a reducing agent as hydrochinon, is surprising, but not unreasonable photographically. It is well known that amidol is the only developer commonly used without alkali, that it brings up the image very quickly, and is very difficult to restrain with bromide. In the absence of alkali the gelatin must offer much more resistance to the development of the silver halide than it does with ordinary developers. Chemically, amidol would be expected to be more powerful than *p*-aminophenol, investigated by Sheppard and Mees, as it is a di-phenol and therefore much more subject to oxidation. When we note that amidol is only 13 times as powerful as metol-hydrochinon, and probably only three or four times as powerful as *p*-aminophenol (allowing for the difference in reducing power between our hydrochinon developer and that of Sheppard and Mees) and that both of the former require the use of alkalies in development, the figures above seem still more reasonable.

Summary and Conclusions.

1. The fundamental theory of the single potential of a developer and the conditions which retard the attainment of the equilibrium in its measurement have been discussed and illustrated.

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[1] Sheppard and Mees, "Investigations of the Theory of the Photographic Process," pp. 188–196 (Longmans, Green & Co.).

2. The calculation of the partial pressure of hydrogen, to which the developer is equivalent, seems to be the only way in which the absolute or relative reducing power of developers can be directly measured.

3. The results obtained by the employment of this method seem to be photographically reasonable.

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THE HYDROGEN POTENTIALS OF SODIUM HYDROXIDE SOLUTIONS AND THE DISSOCIATION CONSTANT OF WATER.

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In connection with our work on the single potentials of developers, we noticed that the hydrogen potential (E_{H_2}) of a solution containing sodium carbonate and sulfite would change as much as thirty millivolts on adding the proper amount of hydrochinon to make a satisfactory developer. The change was in such a direction as to indicate that the hydrochinon combined with the sodium carbonate, forming a sodium salt and sodium bicarbonate, thereby decreasing the hydroxyl-ion concentration of the solution. It seemed that electrometric measurements of this nature might give us some very useful information about the reactions taking place when a developer is mixed, but in order to interpret such measurements we needed certain data not accessible in the literature.

It is evident that the mechanism of this reaction involves the hydrolysis of sodium carbonate and the reaction between the sodium hydroxide thus formed and the hydrochinon. As the sodium hydroxide is consumed, the hydrolysis must continue until the product of the bicarbonate concentration by the hydroxide concentration, divided by the concentration of the carbonate, reaches the value characteristic of the equilibrium at that temperature and dilution. In order to be able to determine the extent of the reaction, it is necessary to know both the hydrolysis constant of sodium carbonate and the hydrogen potentials corresponding to the various concentrations of sodium hydroxide. Since these were the fundamental quantities involved in the reaction under consideration, it appeared very desirable, in order to eliminate any errors inherent in the electrometric method, to use this method in their determination. As the hydrogen-ion concentration is the quantity directly susceptible of measurement by the electrometric method, it is first necessary to be able to transform a measurement of the hydrogen potential of the solution into terms of the concentration of sodium hydroxide.

A few measurements of the hydrogen potentials of sodium hydroxide