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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 Elmer T. Fagan for the degree of Master of Science. They approve it as a thesis meeting the requirements 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.

E. K. Strachan
Chairman
Arthur A. Hirschfelder
Sterling Temple

May 23, 1916

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AN ELECTROMETRIC STUDY OF DEVELOPERS.

A Thesis submitted to the faculty of the Graduate
School of the University of Minnesota by
Elmer T. Fegan
in partial fulfillment of the require-
ments for the degree of
Master of Science.

May 1916.

The University of Minnesota

Minneapolis

May 18, 1916

MEMORANDUM FROM MR. FORD TO PROF. STRACHEN:

SUBJECT:

Enclosed I am sending you a copy of the ^{Doctor's}~~Master's~~ thesis, upon which you have already been asked to pass your judgment, as a member of the Thesis Committee. The judgment of the Committee will be reported through the Chairman and if favorable, certified by your signature to the blank, which has been sent him. All copies of theses should be returned to this Office and they will later be distributed to the proper persons.

Sincerely, .

Guy Stanton Ford, Dean.

AN ELECTROMETRIC STUDY OF DEVELOPERS.

An exact and reliable method for measuring the reducing power of photographic developers has not yet been successfully devised. Sheppard and Mees¹ have by an indirect method, based on the restraining power of potassium bromide, obtained relative values for a few developers. Mees² later suggested a method based on single potentials of the developing solution. Mathews and Barmeier³ measured the single potentials of a few developers for the period of only a few hours. Their results can not be compared directly with ours because a wrong value for the normal calomel electrode cell was used throughout their work. Moreover sufficient time for the cell to reach equilibrium was not allowed. Lidbury⁴ has worked along this line, but the same errors have been made by him as were made by Mathews and Barmeier. Neither of the latter two workers suggested a method by which the reducing power could be calculated from their data.

Frary and Neitz⁵ have recently published the results of some work on this subject, using the potential method. Their work showed that the conclusions of Mathews and Barmeier, that the potential becomes more negative with increasing time due to the oxidation of the sulfite, are erroneous. Their

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- 1-Sheppard and Mees, "Investigation of the Theory of the Photographic Process", pp 188-196.
 2-Mees, Journal Am. Chem. Soc., 35,1731 (1913)
 3-Mathews and Barmeier, Proc. 8th Int. Cong. Applied Chem., 20, 201
 4-Lidbury, Proc. 8th Int. Cong. Applied Chem., 20 189-197
 5-Frary and Neitz, 37,2273 (1915) J. Am. Chem. Soc.

work contains a very good discussion of the fundamental theory of the single electrode potential of the developer and of many of the conditions which effect the equilibrium. They determined the single electrode potential of the developer; also the potential of a hydrogen electrode in the same solution. As the partial pressure of the hydrogen in the hydrogen electrode was one atmosphere, that in the single electrode was calculated by the equation:

$$E = \frac{RT}{nF} \log \frac{C}{C'}$$

in which C and C' represent the hydrogen pressures; T is 298° Absolute; n is the valency of the ion of the electrode; R is the gas constant and F signifies the number of faradays. Since according to the conditions C , n and f all equal 1, the equation becomes

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

E in this case, being the difference between the hydrogen potential and the single potential of the developer or $E = E_{H_2} - E_D$. The lowest potential developed in the single cell was taken as the maximum reducing power, and this value used as the E_D in the calculations.

The following work was begun for the purpose of investigating and determining the rate of change of the single potential with time, and of examining and interpreting the various fluctuations of the single potentials of cells of the type employed by Frary and Neitz. In addition a study of the two sodium salts of hydroquinon was planned, and a discussion of the function of the sodium sulfite in the developer.

APPARATUS.

The single electrode cells used in all of the work are of the glass type illustrated in Fig. 2. Each cell holds about five or six cubic centimeters. After being thoroughly cleaned and dried, the cells were filled as described by Frary and Neitz;¹ sealed off and the stop cock closed. The cells named in Table No. I were filled in an atmosphere of nitrogen while all the other cells were filled in the air.

The hydrogen potentials were taken in the all-glass cell of the type shown in Fig. 1. This same type was used by Frary and Neitz last year. The hydrogen gas was generated in a Kipp apparatus from pure sulfuric acid and arsenic free zinc. This gas was freed from oxygen by passing it through a heated copper tube containing copper filings. It then entered the cell at A, bubbling through the solution at B. The gas leaves the cell through the trap T, which contains mercury, the height of which is controlled by the reservoir R. This mercury trap prevented any air from diffusing back into the main chamber C, which contained the platinumized-platinum electrode E, which dips into the solution. Connection with the calomel cell is made through the side arm S, which dips into the saturated potassium chloride solution. The electrode cell when not in use, was filled with weak (1 : 20) sulfuric acid, which kept the electrode in good condition. Equilibrium with this type of cell can be reached in fifteen minutes with an acid solution, but more time is required for alkaline solutions.

All measurements of potentials of the cells and of the

¹-Frary and Neitz, J. Am. Chem. Soc., 37, 2256 & 2257 (1915)

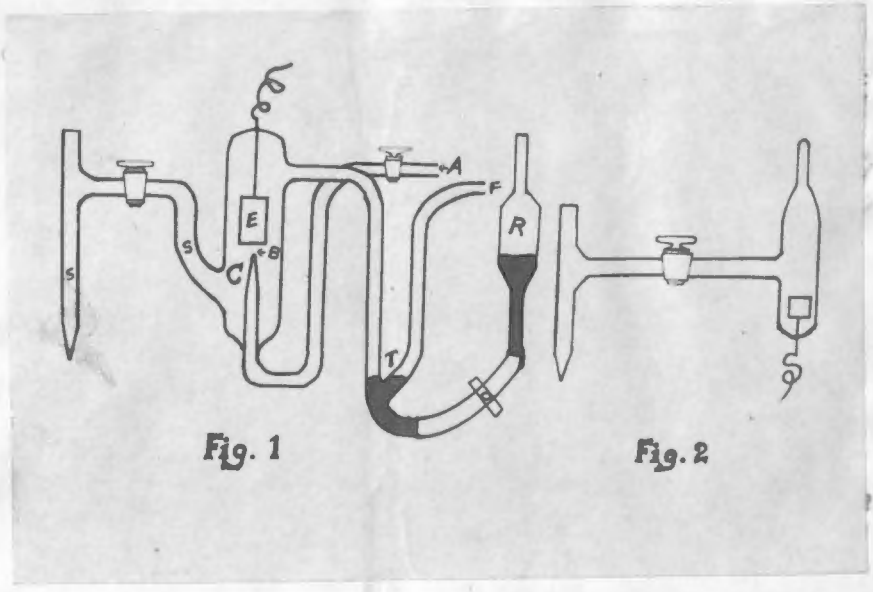
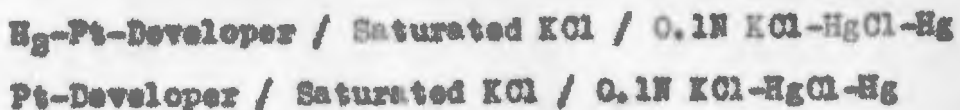


Fig. 1

Fig. 2

hydrogen electrodes were taken by setting up the following systems:



The electromotive force of these systems was measured by means of a large potentiometer¹ ("Kompensation-Apparat" from Fritz Koehler of Leipzig) and a sensitive galvanometer. A standard Weston cell, which had been made up for three years, and had been checked with a cell, certified by the Reichanstalt of Berlin and the Bureau of Standards, was used to adjust the potentiometer before and between readings.

The value $+0.6124 + .0008 (t - 18^{\circ}C)$ volt was employed as the potential of the 0.1 normal calomel electrode. Two of these cells were made up at different times and at present writing they differ from each other by only .0001 volt. Clark, Myer and Acree² have shown that the 0.1N KCl-HgCl-Hg system is very stable and reproducible. To check these calomel cells, the following chain was set up:



The E. M. F. of this chain in the case of calomel cell (a) was found to be 0.4272 volts and in case of calomel cell (b) 0.4273 volts. These results agree very well with the value 0.4273 volts at 25°C, and 760mm pressure, which Clark, Myer and Acree² obtained for this system.

It is possible with this apparatus to obtain readings with the accuracy of 0.1 millivolt, in fact all readings were

1- Zeitschrift der Instrumentkunde, 23 93
 2- Clark, Myer & Acree, J. Phy. Chem., 20 243, (1916)

made to the fourth place. The error of determination is about the order of 1 millivolt. This fact, together with the fact that the duplicate cells did not check to the third place, made it unnecessary to read closer than millivolts. The room temperature, while the readings were being made, was adjusted between 24°C. and 25°C. The temperature coefficient of the cells is about .0008 volts per degree and in the same direction as that of the calomel. For these reasons a thermostat is unnecessary and was not used.

In Table No. I (page 7) are listed the developers prepared by Frary and Neitz in 1915. In the first column are listed the numbers of the developers, and in the second the cell numbers. The following four columns give the composition of the developer. With the exception of cells #3, #5 and #6 of developer 1a, all were prepared in the absence of air or oxygen by Frary and Neitz. The readings of these cells are shown in Table No. II (page 8). The readings up to and including those of June 19th, 1915 were made by Frary and Neitz. The first two columns of Table No. II are the same as the first two in Table No. I, and the following ones give the potentials of the cells on the stated dates.

Figures #3, #4, #6 and #7 were obtained by plotting the values of the potential shown in Table No. II against the time. With the exception of the curves in Figure #7, all follow the same general course. Those in Fig. #7 show the potential of the amidol cells, which dropped rapidly for fifteen days to a value of about +0.080 volts, is maintained for over a year. There are only slight variations of the potential from this value during the entire period.

Table I.

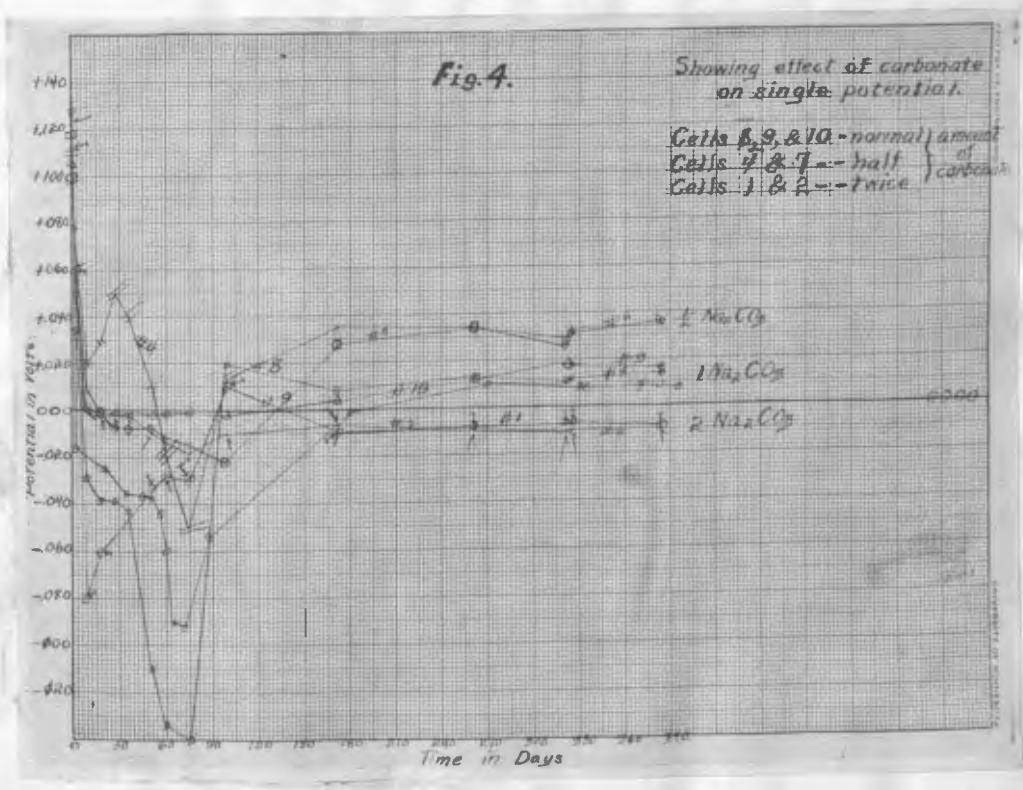
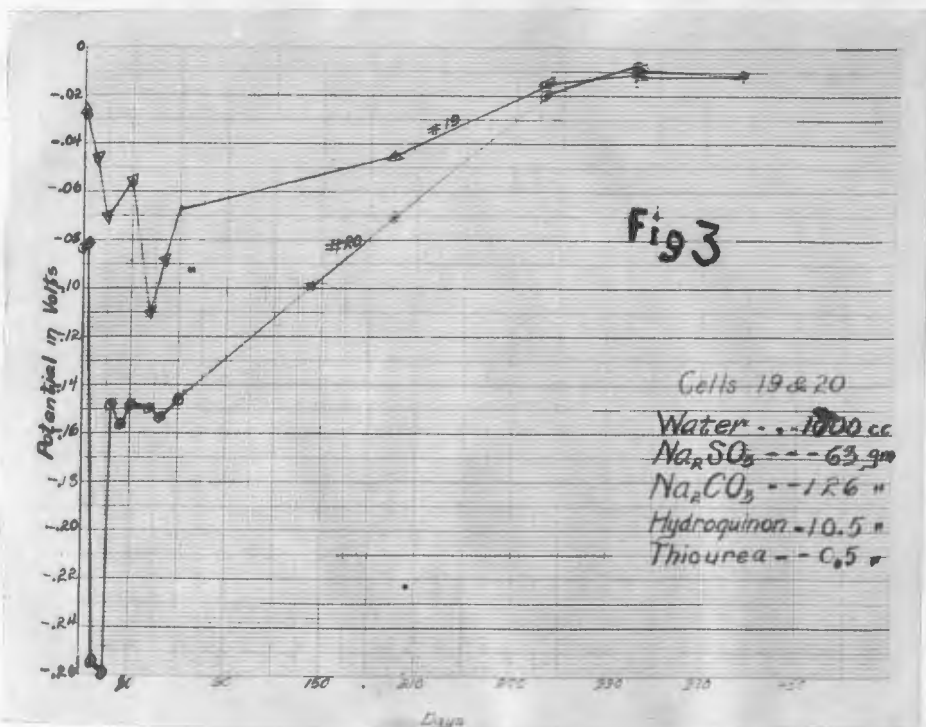
Number	Cell	Water	Na ₂ CO ₃	Na ₂ SO ₃	Developing agent	Remarks
1b	14		13.9gms		Hydroquinon 1.85g	
	16	1000cc	Merc's	13.9gm		
1a	3		13.9gms		Hydroquinon 1.85g	Contains
	5	1000cc	Merc's	13.9gm		15% more
	6		dried		Metol.....1.85g	carbonate
6a#1	8					
	9	1000cc	150 gms	50 gms	Hydroquinon.. 7gm	
6a#2	10		dried			Contains
	4	1000cc	75 gms	50 gms	Hydroquinon 7gms	as much
	7		dried			carbonate
6a#3	1					as 6a#1
	2	1000cc	300 gms	50 gms	Hydroquinon 7gms	Contains
			dried			twice the
6a#4	13					Carbonate
	15	1000cc	150 gms	50 gms	Hydroquinon 7gms	in 6a#1
7	11		0	100 Gm	Amidol-----20gms	Contains
	12	1000cc				4.6 gms
9	19	1000cc	126 gm	63 gm	Hydroquinon 10 1/2 gm	of KBr.
	20		dried			
						tetrathio- urea.

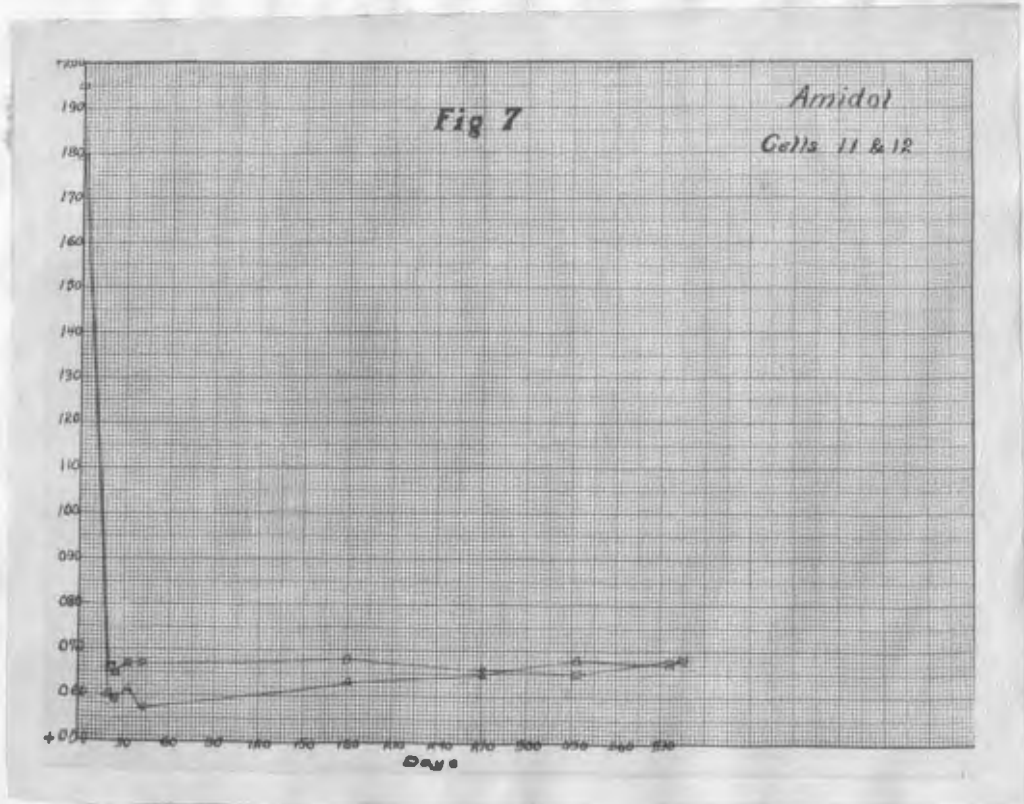
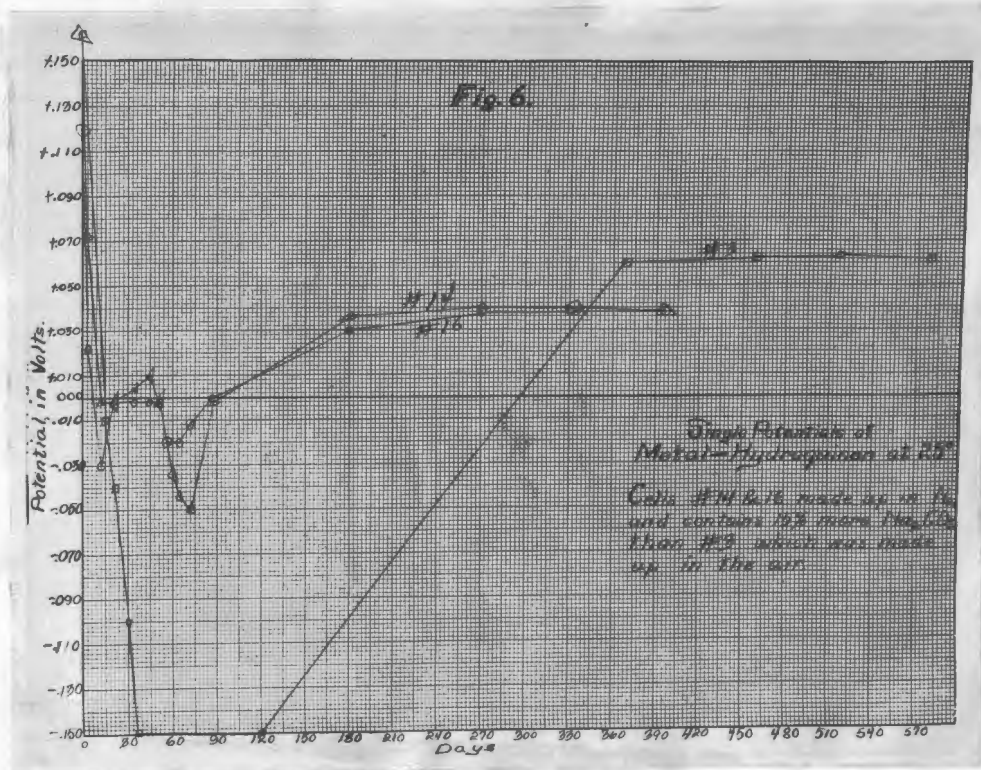
Table II.

The potential of the cells

No. of Dev.	No. of Cell.	1st	2d	3d	4th	5th	6th	7th	8th	9th	10th	11th	12th	13th	14th	15th	16th	17th	18th	19th	20th	21st	22d	23d	24th	25th	
6a#1	0	.118	-.039	-.039	-.038	-.046	-.052	-.079	-.142	-.008	-.013	-.010	-.012	-.014	-.014	-.014	-.014	-.014	-.014	-.014	-.014	-.014	-.014	-.014	-.014	-.014	-.014
6a#1	9	.106	+.001	.000	-.007	-.007	-.005	-.006	-.007	+.004	+.012	+.019	+.017	+.016	+.015	+.015	+.015	+.015	+.015	+.015	+.015	+.015	+.015	+.015	+.015	+.015	+.015
6a#1	10	.128	-.018	-.035	-.031	-.036	-.044	-.091	-.054	-.001	+.010	+.007	+.008	+.008	+.008	+.008	+.008	+.008	+.008	+.008	+.008	+.008	+.008	+.008	+.008	+.008	+.008
6a#2	4	.112	+.027	+.051	+.072	+.052	+.017	-.008	+.013	+.037	+.034	+.035	+.035	+.035	+.035	+.035	+.035	+.035	+.035	+.035	+.035	+.035	+.035	+.035	+.035	+.035	+.035
6a#2	7	.106	+.009	-.001	-.008	-.007	-.007	-.016	-.018	+.028	+.033	+.025	+.032	+.036	+.035	+.035	+.035	+.035	+.035	+.035	+.035	+.035	+.035	+.035	+.035	+.035	+.035
6a#3	1	.119	+.082	-.060	-.055	-.010	-.039	-.029	-.015	-.010	-.009	-.008	-.006	-.009	-.006	-.006	-.006	-.006	-.006	-.006	-.006	-.006	-.006	-.006	-.006	-.006	-.006
6a#3	2	.122	+.000	-.006	-.010	-.007	+.001	-.014	-.015	-.007	-.010	-.011	-.009	-.008	-.008	-.008	-.008	-.008	-.008	-.008	-.008	-.008	-.008	-.008	-.008	-.008	-.008
6a#4	13	.139	+.048	+.029	+.012	+.019	.000	-.022	-.050	+.020	+.014	+.016	+.016	+.016	+.016	+.016	+.016	+.016	+.016	+.016	+.016	+.016	+.016	+.016	+.016	+.016	+.016
6a#4	15	.122	+.057	+.055	+.040	+.028	+.016	+.027	+.019	Broken	Broken	Broken	Broken	Broken	Broken	Broken	Broken	Broken	Broken	Broken	Broken	Broken	Broken	Broken	Broken	Broken	Broken
No. 7	11	.195	+.055	+.055	+	+	+	+.067	+.067	+	+	+.053	+.056	+.055	+.055	+.055	+.055	+.055	+.055	+.055	+.055	+.055	+.055	+.055	+.055	+.055	+.055
No. 7	12	.179	+.050	+.059	+	+	+	+.051	+.057	+	+	+.053	+.056	+.055	+.055	+.055	+.055	+.055	+.055	+.055	+.055	+.055	+.055	+.055	+.055	+.055	+.055
No. 9	19	-.086	-.046	-.079	-.014	-.029	-.055	-.088	-.097	-.045	-.015	-.011	-.010	-.012	-.012	-.012	-.012	-.012	-.012	-.012	-.012	-.012	-.012	-.012	-.012	-.012	-.012
No. 9	20	-.083	-.255	-.260	-.148	-.157	-.144	-.154	-.101	-.071	-.030	-.008	-.012	-.012	-.012	-.012	-.012	-.012	-.012	-.012	-.012	-.012	-.012	-.012	-.012	-.012	-.012
1b	14	+.166	+.004	-.005	+.013	+.024	+.005	-.045	-.050	+.036	+.037	+.040	+.038	+.037	+.038	+.037	+.038	+.038	+.038	+.038	+.038	+.038	+.038	+.038	+.038	+.038	+.038
1b	15	+.121	-.005	+.004	+.010	-.006	-.005	-.021	-.001	+.030	+.040	+.039	+.039	+.039	+.039	+.039	+.039	+.039	+.039	+.039	+.039	+.039	+.039	+.039	+.039	+.039	+.039
1a	3	Averaged	over	this	period	as	151	volts	+.050	+.055	+.054	+.054	+.054	+.054	+.054	+.054	+.054	+.054	+.054	+.054	+.054	+.054	+.054	+.054	+.054	+.054	
1a	5	"	"	"	"	"	-.149	"	+.055	+.059	+.058	+.058	+.058	+.058	+.058	+.058	+.058	+.058	+.058	+.058	+.058	+.058	+.058	+.058	+.058	+.058	
1a	5	"	"	"	"	"	-.141	"	+.030	+.035	+.034	+.034	+.034	+.034	+.034	+.034	+.034	+.034	+.034	+.034	+.034	+.034	+.034	+.034	+.034	+.034	

The readings up to and including those of 6/19/15 were made by Frary and Helter.





The potentials of the other cells began approximately at the same point, and dropped rapidly as do those in Fig. #7, but instead of continuing in a horizontal direction, they varied as shown by the fluctuations in Figures #3, #4 and #6. In most cases the potential reached a minimum point, which remained approximately constant for days. This minimum was usually reached in about two or three months. After the cell had been made up six months, the potential became more positive. Looking at the curves again, it will be noticed that they ascend quickly at first, but gradually flatten out, until an upper or maximum value is attained. These potentials, one year after the cell had been prepared, seemed to indicate a true equilibrium.

Frary and Neits¹ calculated their results from the lowest potential, assuming that it corresponded to the highest hydrogen pressure generated by the developer. Their observations did not extend over as long a time as ours have, consequently the latter equilibrium did not come to their notice. The question now arises which of these values is the one to be used in calculating the reducing potential.

As previously discussed, the pressure of the hydrogen produced on the platinum electrode at 25°C. can be calculated from the equation

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

where $E = E_{H_2} - E_D$. The E_{H_2} may be determined in a very short time to the accuracy of 0.1 millivolt by the apparatus shown in Fig. 1. The term E_D is variable and can not be

determined so accurately. By averaging the maximum values of the single potentials of the two or three cells for each developer, a maximum single potential is obtained. This is shown as the upper figure in the third column of Table No. III page 13. The lower figure in this same column the the minimum value attained by the electrode during the entire period. The second column gives the hydrogen potential of the developer. The fourth column gives the maximum and also the minimum difference in potential. In the fifth column is the calculated maximum and minimum hydrogen pressure on the electrode. In the last column is given the relative reducing power, taking the hydroquinon developer with KBr. as unity in the case of the minimum value, and the metol-hydroquinon developer as unity in the case of the maximum equilibrium value.

These results do not seem reasonable except in the case of developers 6a71, 6a72, 6a73 and 6a74, which vary in amount of sodium carbonate. The factors in these cases look photographically reasonable. This same order of relationship may also be obtained by looking at the curves of the same developers in Fig. 4. The series taken as a whole certainly does not indicate the true relation in which these few developers stand to each other.

These results are however to be expected after theoretical consideration. If R. is the active portion of the developing agent, e. g., metol or hydroquinon, the production of hydrogen in the solution may take place in the following manner:

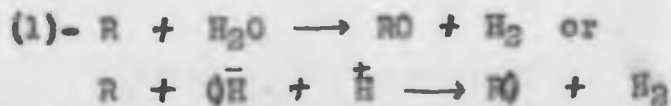
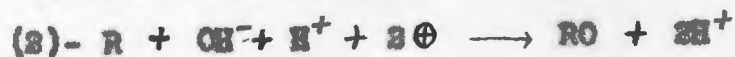


Table No. III.

Developer	Hydrogen potential	Single Potential	Potential Difference	Calculated hydrogen pressure.	Factor.
1b	Maximum	0.037	0.357	0.00000912	1.7
	Minimum	-0.3200	-0.057	0.000035	2.5
1a	Maximum	0.060	0.370	0.00000549	1.0
	Minimum	-0.3100	-0.150	0.0018	122.0
6a#1	Maximum	0.015	0.353	0.0000013	3.2
	Minimum	-0.3380	-0.142	0.0000483	34.5
6a#2	Maximum	0.035	0.358	0.00000828	1.6
	Minimum	-0.3236	-0.051	0.000025	1.8
6a#3	Maximum	-0.009	0.340	0.0000017	3.1
	Minimum	-0.3496	-0.092	0.000045	3.2
6a#4	Maximum	0.015	0.353	0.0000012	2.2
	Minimum	-0.3380	-0.051	0.000014	1.0
# 9	Maximum	-0.011	0.327	0.0000039	5.4
	Minimum	-0.3380	-0.254	0.0379	2700.0
# 7	Maximum	0.066	0.097	0.0228	4222.2
	Minimum	-0.031	0.063	0.0257	1835.

These equations may be resolved into the following ionic ones:



Equation (2) represents the reaction of the developing agent with the ions of water yielding hydrogen ions and an oxidation product of the developer. For convenience the formula

of the oxidation product is written RO., although the validity of the following discussion does not depend on the number of oxygen atoms which combine with the developing agent. An

electrode, which was perfectly reversible with respect to this reaction, when in equilibrium with the developer solution, would have a potential E_D , which would bear the relation to the concentrations of the reacting substances that is demanded by the equation

$$(4) E_D = e'_d + \frac{RT}{2F} \log \frac{(RO)(H^+)}{(R)(OH)}$$

E'_d signifying the potential of a normal electrode and the symbols in parenthesis the concentrations of the reacting substances. In similar manner the potential E_{H_2} of a hydrogen electrode in equilibrium with the developer solution

can be represented by the equation

$$(5) E_{H_2} = e'_{H_2} + \frac{RT}{2F} \log \frac{(H^+)^2}{(H_2)}$$

and where both electrodes are in equilibrium with the solution their potentials are equal or

$$E_D = E_{H_2}$$

It is apparent then, that the single electrode potential of a developer, E_D , is a function of the concentration of (RO) as well as those of (R), (H^+) and (H_2) . The same conclusion results on application of the mass action law to this system.

It follows from equation (1)

$$\frac{(RO) (H_2)}{(R) (H^+) (OH^-)} = K$$

hence it is apparent that (H_2) is a function of (RO) as well as the other substances taking part in the reaction. Therefore, as the potential of the system may be justly regarded as a measure of its tendency to react. It is apparent that

the reducing power of a developer is an indeterminate quantity unless the concentration of the oxidation product is fixed.

With this in mind it is easy to explain the form of the curves shown in Figures 3, 4, 5, 6, and 8. Theoretically

at least, a freshly prepared developer solution would contain none of the oxidation product, and equation (4) would lead us to expect a potential of minus infinity. Practically

this state is never realized, as even a freshly prepared developer is sure to contain some oxidation product, even if it is made up in an atmosphere of nitrogen. Moreover as the developer comes to equilibrium with the electrode very slowly, there is abundant time for any oxygen, that may be present, to react with the developing agent. Such oxygen might enter

the cell, even if the cell was filled with nitrogen, as occluded gas in the pores of the platinum black electrode or in the solid developing agent. Only a very little of it would

be sufficient to cause a great percentage change in $\frac{(RO)}{(R)}$.

Such a behavior would produce the curves of the type shown in Figures 3, 4, 5, 6, and 8. First the potential of the

electrode would increase gradually to that of the solution, then the effect of the increasing $\frac{(RO)}{(R)}$ would become apparent and the potential would increase again, and gradually reach a constant value after all available oxygen had been used up.

It has been assumed for the purpose of the above discussion that the developing agent combined with a single atom of oxygen. The argument would follow the same lines and would be just as valid if two or more atoms of oxygen combined with the developer.

Indeed it is quite certain that the reaction is not as simple as that typified by equation (1).

Andresen¹ has shown that hydroquinone in the presence of sodium sulfite will reduce four molecules of silver bromide, while Bancroft and Gordon² have shown it will reduce as many as nine molecules of silver bromide under certain conditions. Both

of these workers sought to attain the complete oxidation of hydroquinone. It is not improbable, however, that the first step in the oxidation process is the formation of the quinone by the reaction of one atom of oxygen with a molecule of hydroquinone.

A number of single electrode cells of various developers have been made up. The results of a few cells have been

plotted in Fig. 5. The data for plotting these curves is tabulated in Table No. V. Table No. VI gives the composition of developers plotted in Fig. 5.

Although some of the cells have been made up two hundred days, equilibrium has not been reached. As a result nothing further can be cal-

1-Andresen-Eder's Handbuch der Photographie, 5th Ed. (3) 312, 1903
2-Bancroft & Gordon-8th Int. Cong. Applied Chem., 20 101.

TABLE NO. V.

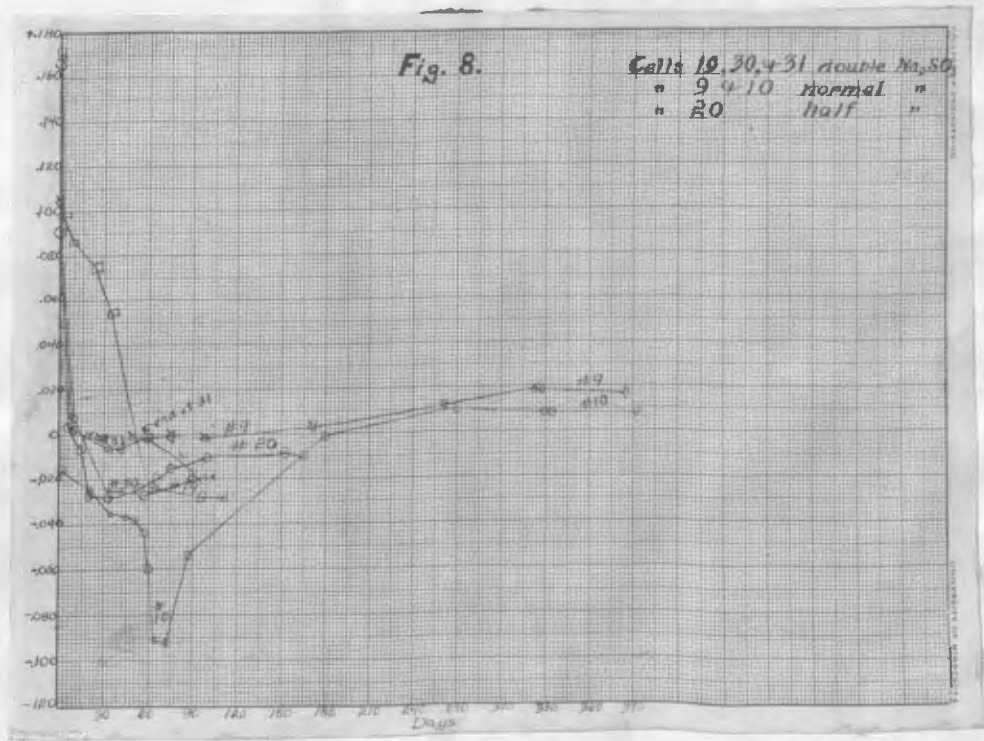
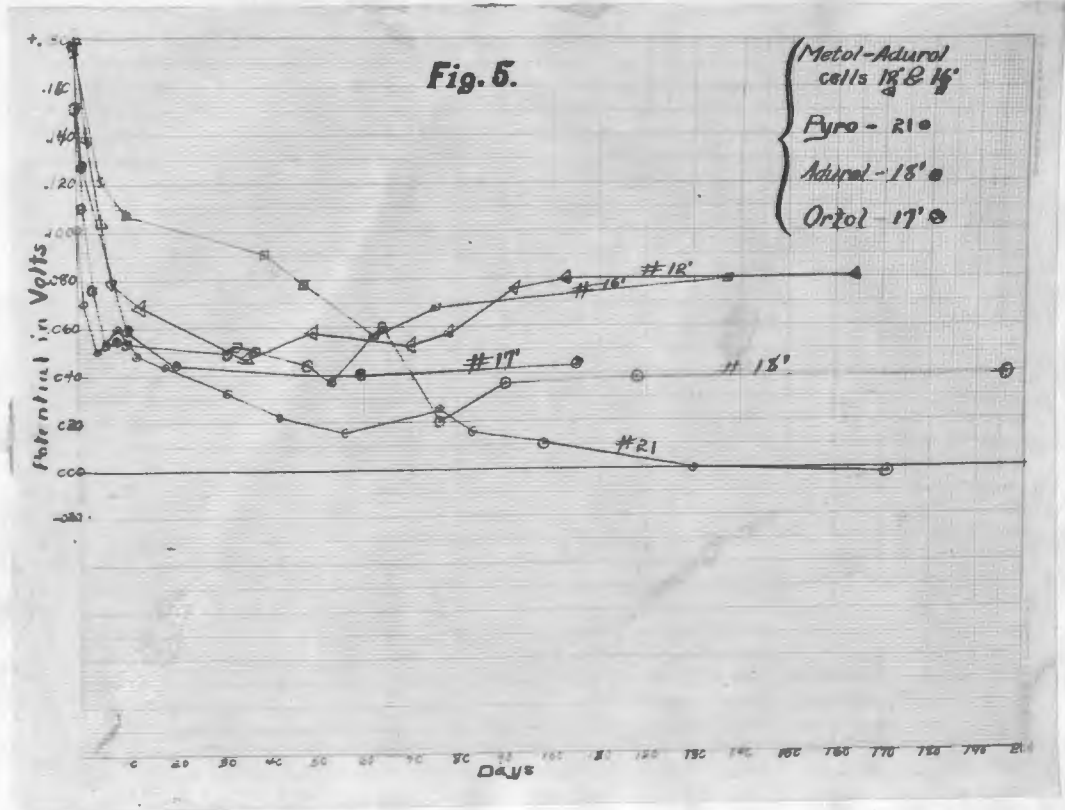
Potentials of the cells in Figure 5.

Date	Potentials				
	Cell #12	Cell #16	Cell #21	Cell #18	Cell #17
10/20/15:	:	:	:	:+0.1523 :	:
21 :	:	:	:	.1138 :	:
23 :	:	:	:	.0767 :	:
26 :	:	:	:	.0536 :	:
30 :	:	:	:	.0543 :	:
11/ 5/15: 0.	:	:	:+0.1007 :	.0530 :	:
6 :	:	:	.0708 :	:	:
8 :	:	:	.0500 :	:	:
10 :	:+0.1811 :	:	:	:	:
12 :	.1386 :	:	.0611 :	:	:
15 :	.1047 :	:	.0492 :	:	:
17 :	.0796 :	:	:	:	:
21 :	:	:	:	.0495 :	:
23 :	.0693 :	:	.0438 :	.0590 :	:
12/ 6/15:	:	:	.0317 :	:	:
10 :	:	:+0.1765 :	:	.0439 :	:
15 :	.0465 :	0.1219 :	.0227 :	:	:
20 :	:	.2072 :	:	.0375 :	:
29 :	.0595 :	:	.0167 :	.0600 :	:
1/10/16:	:	:	:	.0204 :	:+0.1775
11 :	:	:	:	:	.1280
20 :	.0517 :	.0902 :	.0250 :	:	.0598
24 :	:	:	:	.0360 :	:
27 :	.0587 :	.0790 :	.0157 :	:	:
30 :	:	:	:	:	.0443
2/11/16:	.0765 :	.0560 :	.0110 :	:	:
22 :	.0800 :	.0625 :	:	.0385 :	:
3/14/16:	:	:	:	:	:
4/24/16:	.0801 :	.0788 :	-0.0030 :	.0390 :	.0435

TABLE NO. VI.

Composition of Developers in
Cells #12', #16', #17', #18' & #21.

Cell No.	water	Na ₂ SO ₃	Na ₂ CO ₃	KBr	m.KHSO ₃	Developing Agent
12 } 16 }	1050 cc.	24 gms	57 gms	0	0	{metol...-2.5 gms {adurool...-5.0 "
18	1000 cc	40 gms	50 gms	0	0	adurool...-5.0 gms
21	1000 cc	48 gms	25 gms	0	0	pyro....-6.3 gms
17	1050 cc	22 gms	63 gms	2 gms	4 gms	ortol...-7.5 gms



culated until the cell reaches equilibrium.

The last part of this work deals with a study of the sulfite in the developer. It is the generally accepted opinion that the sodium sulfite is added to a developer merely to prevent too rapid oxidation of the developing agent by the air.

This opinion is largely the consensus of judgment of a great number of professional photographers who have failed to detect any difference in the density of the finished negative or the speed of the developing solution, which differ from each other only in their sulfite content.

Hurter and Driffield¹ developed a number of negatives for the same length of time with pyrogallol developers which contained different amounts of sulfite, and found the density of the negatives to be independent of the amount of sulfite in the developer. Andresen² confirmed their results for pyrogallol, but with hydroquinone and adurol (Chlorhydroquinon) found that the density of the negative varied measurably with the sulfite content of the developer. The lower curve of Fig. 10 page 20 shows the relation between the density of the negative and the concentration of the sulfite, as found by Andresen for hydroquinon developers.

An examination of the data of Table No. IV, page 21, shows that the hydrogen electrode may have a different potential in two developing solutions, which are identical except in their sulfite content. This denotes a difference in alkalinity of the solutions brought about by difference

1-Hurter and Driffield-Eder's Jahrbuch 1899, S. 225
2-Andresen-Photo. Correspondence 1900, 197.

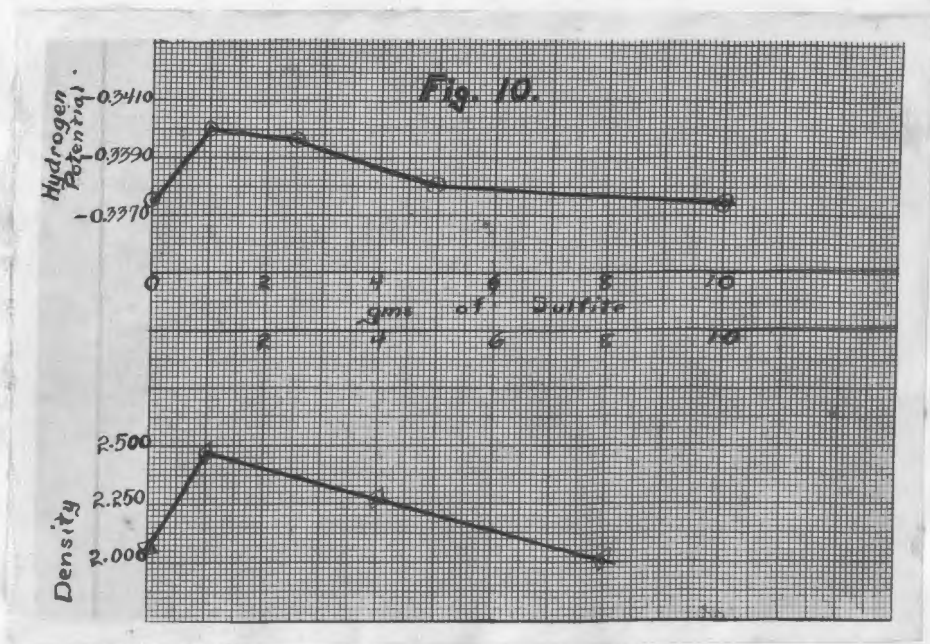


Table No. IV.

Developer number	Cell No.	Hydrogen Potential	Composition of Developer.				Remarks.
			Water	Na_2CO_3	Na_2SO_3	Hydroquinon	
6a#5	--	-0.3375	1000 cc	150 gms	0	7 gms	:no sulfite
6a#6	--	-0.3400	1000 "	150 "	10 gm	7 "	:
6a#7	20	-0.3388	1000 "	150 "	25 "	7 "	:
6a#8	9	-0.3380	1000 "	150 "	50 "	7 "	:normal sulfite
6a#9	10						:
	19	-0.3375	1000 "	150 "	100 "	7 "	:maximum sulfite
	30						:content
	31						:

in their sulfite content. When plotted graphically this data yields the upper curve in Fig. 10. The parallelism of the curves in Fig. 10 suggests at once that the effect of the sulfite in the developing power of the hydroquinone is only a secondary one, and is due to the effect of the sulfite on the alkalinity of the solution. On account of the great complexity of the ionic equilibrium in a mixture of ternary electrolytes, no explanation is offered for the form of the upper curve in Fig. 10.

The results of the single electrode potentials of three of the sulfite developers are shown in Fig 8. on page 18. These cells must be allowed to stand at least six more months before equilibrium is reached.

The developers, 6a#5, 6a#6, 6a#7, 6a#8 and 6a#9, the composition of which is shown in Table No. IV, page 21, were tested photographically with a Chapman-Jones plate tester. With this apparatus, a photographic dry plate or film is exposed behind a special slide or plate having squares of graduating densities from clear glass to total opacity. These squares are numbered in order of the amount of light that is transmitted to the plate. On the finished plate, a picture of which is shown in Fig 9., a certain number of squares appear, depending on the kind of plate, the exposure, the temperature and kind of the developer. The plates used in this experiment were Seed 26, and the temperature of the developer was regulated at $19\frac{1}{2}^{\circ}\text{C}$. The standard light was a standard candle (as used for official gas-testing) at one foot distance. Consequently if each plate was

developed the same length of time, (three minutes in each case) any observed difference in density would be due to the kind of developer used. The five developers named above did not produce on development an observable difference in density. However, the most alkaline developer 6a#6 produced the first appearance of the image, two seconds sooner than the others. Therefore it may again be stated that the sulfite does effect the reducing power of the developer, but only secondarily due to the change in alkalinity which the sulfite produces.

Conclusions.

- 1----The single electrode potential of a developer solution may change continuously during a period of twelve months.
- 2----All of such solutions, with a few exceptions, that were investigated showed a minimum potential within three months, and afterwards increased gradually to a constant value which was reached in twelve months.
- 3----It is apparent then that equilibrium is not established in the single electrode cell until at least twelve months after it has been prepared.
- 4----It has been shown that the reducing power of a developer is a function of the concentration of its reaction products, and consequently it has an indeterminate value unless the latter are known.
- 5----Sodium sulfite indirectly affects the reducing power of a hydroquinone developer by changing the alkalinity.

ity of the developer solution.

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E. T. F. ~