10^9(mole/cc.)$^{-1}$sec.$^{-1}$, respectively. This is not inconsistent with the assumption that zinc and cadmium atoms can combine with chlorine by association processes analogous to reaction (3). Presumably these reactions would also require triple collisions and have rate constants of the same order as those found for mercury–bromine and mercury–iodine association. Hence under the experimental conditions employed by Polanyi (total gas pressures of a few mm.), the bimolecular velocity constants for the zinc–chlorine and cadmium–chlorine association reactions may be estimated as at most some $10^5 - 10^6$(mole/cc.)$^{-1}$-sec.$^{-1}$. This is very much smaller than the experimentally observed velocity constants for the metathetic reactions, and hence the association plays a negligible role. With mercury atoms and chlorine it appears that the reverse situation obtains, since it can be shown that the process analogous to reaction (1) is about equally endothermic for all halogens. This conclusion is in agreement with the observation of Polanyi that mercury atoms do not initiate chains in hydrogen–chlorine mixtures.

Summary

1. It has been shown that mercury atoms enter into a rapid vapor phase reaction with halogens.

2. At 110° and in the presence of air at atmospheric pressure the mercury–bromine reaction appears to be of the first order with respect to each reactant, and the velocity constant lies between 10^7 and 10^5(mole/cc.)$^{-1}$sec.$^{-1}$.

3. The temperature coefficient is very small, an upper limit of 5 kcal. being estimated for the activation energy.

4. It appears that the mercury–bromine reaction must take place as an association process, most probably in triple collisions with molecules of inert gas. The efficiency of triple collisions appears to be relatively small.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, ALABAMA POLYTECHNIC INSTITUTE]

Photography of Minima in the Magneto-Optic Apparatus

BY GORDON HUGHES

The work of Allison[1] and others on the magneto-optic apparatus has been called into criticism by several investigators[2-4] due to their inability to operate the magneto-optic apparatus successfully. In the face of the many admitted complexities and difficulties encountered in its use the failure of some might be readily expected. The purpose of this investigation has been to develop a completely objective method for the study of the minima of light intensity in the apparatus and thus demonstrate, beyond doubt if possible, the reality of the minima and the validity of the visual results previously obtained with the apparatus. During the course of this study several photographic methods have been employed with only partial success. Their failure has been due entirely to mechanical difficulties. The method described here is free of these inherent defects and with it consistent positive results have been obtained. This method has been made as completely automatic as possible in an effort to reduce the personal factor to a minimum. Since the results obtained by this photographic method may be interpreted into fairly accurate quantitative measurements, this work has had the added purpose of determining the quality of the minima under varying conditions in an effort to improve them for visual work.

(1) Allison and Murphy, THIS JOURNAL, **52**, 3796 (1930).

(2) Slack, *J. Franklin Inst.*, **218**, 445 (1934).

(3) McPherson, *Phys. Rev.*, **47**, 310 (1935).

(4) Farwell and Hawkes, *ibid.*, **47**, 78 (1935).

Experimental Technique

Methods have been devised[2-4] for testing the presence of minima by comparing the light through the apparatus with a sample of light brought to one side of the coils and then joined with the main beam. In these methods one is never sure that both beams suffer the same optical conditions at all times. The Wollaston prism was employed in this study since with it there is no doubt that the treatment of both beams is optically identical. That is to say, the intensity ratio of the two beams is independent of variations in the intensity of the incident light. It has the further advantage that its use doubles the absolute intensity change for the effect, on the hypothesis that the effect is a rotation of the plane of polarization of the incident light.

The apparatus was essentially identical with the conventional one used for visual work except for the substitution of the Wollaston prism, W in Fig. 1, for the analyzing Nicol prism. Before photographic work was started sufficient work had been done visually with the Wollaston to show that minima could be observed with this type of prism as well as with the Nicol prism. The lens L_2 focused the two images of the single vertical slit S sharply on the photographic plate P_2. The Nicol prism N was set with its plane of polarization at an angle of 45° to the horizontal. The Wollaston prism mounted in a revolving head was turned to an angle midway between the angles of extinction of each of its two beams. This procedure gave two ribbon-like beams in a horizontal plane of nearly equal intensity falling on the photographic plate.

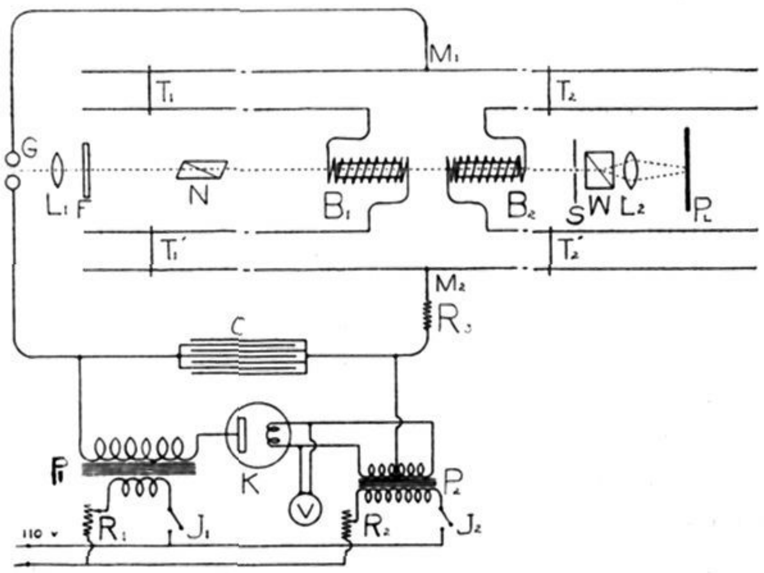

Fig. 1.—Magneto-optic apparatus.

The camera consisted of a simple frame to hold the plate which could be racked along the horizontal track by steps of 4 mm. With this horizontal motion it was possible to take 16 to 20 pictures in a row and a vertical motion of the plate in the frame permitted several rows on a plate. The time of exposure for each picture was made uniform by a synchronous motor timing device which gave to each exposure two and two-thirds seconds or some multiple of that time. At the same time the interval between exposures was kept at a constant one and one-third seconds. Eastman Hyperpress plates were used in this study since only a small amount of blue light was available for an exposure. The Hyperpress plates served admirably when developed with the contrast developer recommended for their use.

The magnesium 4481 Å. line was used. Short exposures were desirable in order that the electrodes of the spark gap should not overheat nor burn away appreciably from one exposure to the next. Exposures which gave a rather dense blackening were found to give more consistent results than those which were less dense. Plates which were not properly exposed were not included in the summary of results below.

The microphotometer employed in determining the densities of the exposures was of the conventional design with vacuum thermocouple and short-period high-sensitivity galvanometer. It was equipped with recording drum and glass scale so that the densities could simultaneously be recorded and measured directly from the galvanometer deflection on the glass scale. Most of the determinations were read directly from the scale as this was less time consuming than recording and then measuring the microphotometer traces.

The electrical system as shown in Fig. 1 is the same as that used for visual work except for the introduction of R_3, an electrolytic resistance of 130 ohms which effectively damped out oscillations in the electrical circuit and made the spark breakdown at G much steadier as well.

The breakdown at G was analyzed by means of a high-speed rotating mirror mounted on a Beams pneumatic top. The light, first focused on a narrow slit, was reflected from the mirror onto a photographic plate. Microphotometer traces of these exposures are shown in Figs. 2 and 3. The

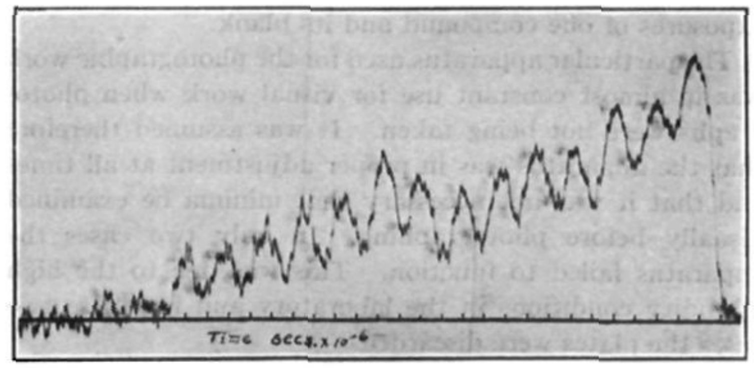

Fig. 2.—Normal spark discharge used for visual work.

time scale is approximate only since no accurate measure of the speed of the top was made. Figure 2 is the type of breakdown obtained when R_3 was not present and shows the highly oscillatory nature of the current in the trolley system and coils. Figure 3 is the breakdown with R_3 inserted. Its damping value is apparent. Photographs of minima were attempted with both types of spark and it was found that only the damped spark gave positive results.

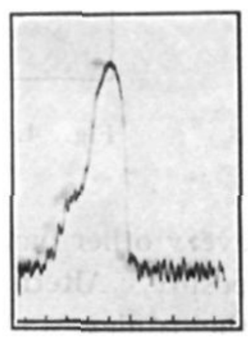

Fig. 3.—Spark discharge with damping resistance.

Since the results of visual work preclude any possible large change in light intensity to be photographed, it was apparent that a true picture of any real effect could be obtained only from the average effect in a large number of pictures. Under optimum conditions, the variable factors, intensity of light, current in the coils, and the optical condition of the liquids, would remain constant from one exposure to the next. It was with these variations in view that exposures were made in rapid succession first with the trolley contacts T_2 and T_2' at the proper position for a minimum and then off this position, alternating for possibly 16 to 20 pictures in a row. The number of rows of pictures starting with an "off" about equalled the number starting with an "on." The "on" position for any given compound had been determined previously from repeated visual observation. In determining a desirable "off" position, a position was taken which was known to be free of minima as shown from a chart of all known minima or a solution of the material to be examined was placed in the apparatus and the regions of the scale on either side of the minimum position were scanned visually to find one location free of minima. In the cases of the compounds used: for lithium chloride the "off" position was 2.1 cm. ahead of the "on" position, for cupric chloride the "off" was 0.9 cm. back of the "on" position, for phosphoric acid "off" was 1.05 cm. ahead of "on." The concentration of compound for all but a few pictures was 1 to 2 parts in 10^5 parts of water. This relatively high concentration was necessary since the Wollaston prism was set so that its two beams were at 45° angles to the plane of the polarizing nicol. Bishop, Dollins and Otto[5] report a reduced sensitivity of the apparatus at this point.

In every case water blanks were photographed prior to compounds. The compound to be studied was added to the same tube which had contained the water blank in order that the optical system should remain intact for all exposures of one compound and its blank.

The particular apparatus used for the photographic work was in almost constant use for visual work when photographs were not being taken. It was assumed therefore that the apparatus was in proper adjustment at all times and that it was not necessary that minima be examined visually before photographing. In only two cases the apparatus failed to function. This was due to the high humidity conditions in the laboratory and for these two cases the plates were discarded.

Discussion of Results

Figure 4 is an enlarged reproduction of some of the exposures on a typical plate. In the top row every other pair of lines represents an "on" exposure. Alternate pairs of lines were made when the trolley was on the position of a minimum and the other pairs when the trolley was off this position as described above. Since the two beams making lines A and B were of nearly equal intensities and were polarized at 45° angles to the light from the polarizing nicol, any rotation of the plane of the light before it reached the Wollaston would have caused a dimming of one of the beams and a brightening of the other. On the assumption that there was a change in the plane of polarization on passing through a minimum, there should have been a momentary difference in the density ratio of the lines A and B as this position was crossed.

Fig. 4.—Enlarged reproduction of typical plate.

Figure 5 is a typical microphotometer trace showing only the peaks or maximum density points for a picture similar to Fig. 4.

Table I presents a set of measurements made on the microphotometer trace of Fig. 5 and the reading on the glass scale for the same plate. The base line in Fig. 5 from which the peaks were measured is arbitrary and is on the opposite side of the peaks from the zero of the glass scale.

TABLE I

MICROPHOTOMETER READINGS H_3PO_4 10^{-5} G./CC. FROM DENSITOMETER TRACES

On minimum			Off minimum		
A cm.	B cm.	A–B cm.	C cm.	D cm.	C–D cm.
3.60	5.00	1.40	3.50	5.05	1.55
3.40	5.30	1.90	3.65	5.30	1.65
4.00	5.05	1.05	3.65	5.45	1.80
3.35	5.05	1.70	2.60	4.85	2.25
3.20	4.75	1.55	3.15	4.90	1.75
3.15	5.10	1.95	2.80	4.95	2.15
3.80	5.35	1.55	2.90	4.80	1.90
3.25	5.25	2.00	3.35	5.50	2.15
Mean "on" 1.63 cm.			Mean "off" 1.90 cm.		

Difference "off" − "on" = 1.90 − 1.63 = 0.27 cm. = G

From Glass Scale

On minimum			Off minimum		
A cm.	B cm.	A–B cm.	C cm.	D cm.	C–D cm.
29.90	28.55	1.35	30.00	28.45	1.55
30.10	28.20	1.90	29.85	28.15	1.70
29.50	28.40	1.10	29.80	28.00	1.80
30.20	28.40	1.80	30.90	28.60	2.30
30.30	28.70	1.60	30.35	28.50	1.75
30.30	28.35	1.90	30.70	28.50	2.20
29.70	28.10	1.60	30.60	28.70	1.90
30.25	28.20	2.05	30.10	27.95	2.15
Mean "on" 1.66 cm.			Mean "off" 1.92 cm.		

Difference "off" − "on" = 1.92 − 1.66 = 0.26 cm. = G

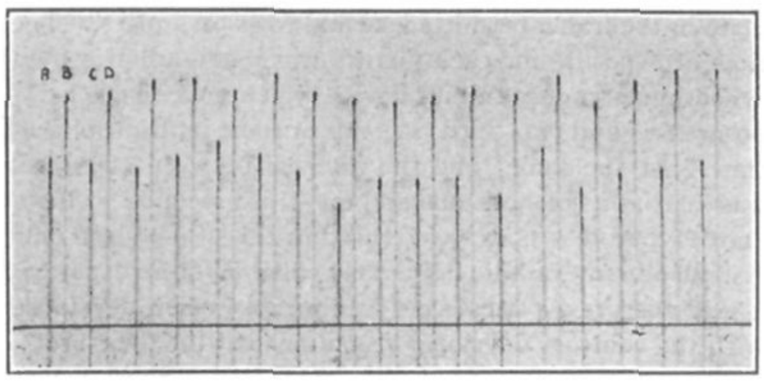

Fig. 5.—Microphotometer trace of maximum density points of typical plate.

The readings on the glass scale are presented to demonstrate the reliability of density measurements made in this manner when compared to the generally accepted method of measuring microphotometer traces. That nearly exact duplication is shown is sufficient justification for the direct measurement of the galvanometer deflection.

The value of G in the above table represents a difference in density which should be obtained if the minima have been photographed. The value

(5) Bishop, Dollins and Otto, THIS JOURNAL, **55**, 4365 (1933).

in centimeters as recorded has no absolute significance since the measurements were made only to show a difference in density "on" and "off" minima and are not a measure of this difference in absolute terms. Table II presents the results of water blanks photographed just prior to the photographs recorded in Table I. The photographs of the acid solution were made with the acid in the identical tube which had contained the blank placed in the apparatus in the same position as the blank. Several series of pictures were made in which different cells were used for the solution and the blank. These blank pictures were not comparable with solution pictures since the collimation of the light was different for different cells.

TABLE II

DENSITOMETER READINGS FOR WATER

On minimum A cm.	B cm.	A-B cm.	Off minimum C cm.	D cm.	C-D cm.
17.70	16.35	1.35	17.50	16.40	1.10
17.65	16.30	1.35	17.60	16.30	1.30
17.50	16.35	1.15	17.40	16.20	1.20
17.40	16.20	1.20	17.40	16.20	1.20
17.80	16.50	1.30	17.85	16.50	1.35
17.50	16.50	1.00	18.00	16.55	1.45
18.00	16.50	1.50	17.80	16.50	1.30
17.55	16.45	1.10	17.80	16.65	1.15
Mean "on" 1.24 cm.			Mean "off" 1.26 cm.		

Difference "off" − "on" = 1.26 − 1.24 = 0.02 cm. = G

If the minima are characteristic of the compound in the cell, it is necessary that the value of G for the blank be lower than this value for a compound. Such is the case in Tables I and II. The data in Tables I and II are the results of two lines of eight pictures each. Since some 90 lines each containing as many and more pictures to the line were recorded, a more complete view of the average result is seen in Table III wherein are the averages of a few typical lines under various conditions.

The value G for a compound and the corresponding value for the water blank may be compared directly since the two sets of pictures were made and microphotometered at the same time. The value of G for one blank may not be compared with that for a different compound since the various pictures of compounds were taken at different times, on different plates, and were examined with the microphotometer at different sensitivities. A fair comparison may be made between the percentage by which the value of G differs from the value of the "off" reading for any water picture and this percentage for any compound. The sign of this percentage is purely conventional. It is taken as positive when the value of "on" is greater than the value of "off." This difference in percentage between water and compound was employed in a previous publication on this work[6] as the criterion of the minima having been photographed. Although it is an unsatisfactory measure and has no quantitative meaning, nevertheless it does indicate a density difference between "on" and "off" pictures of compounds and blanks which is sufficient proof of the reality of the minima.

The seeming discrepancy in the sign of the percentage between lines number 1 and 2 of the first group of Table III and the other lines of the group and a similar discrepancy in line number 6 of the second group is explained in Fig. 2. Considering the case of lines 1 and 2 let the rectangular figures represent the density curves of a pair of lines of a picture "off" a minimum. As represented A is somewhat brighter than B. These curves from the data of Table III will look as A′, B′ for the picture "on" a minimum. For such a case the percentage would have a positive value since A−B is smaller than A′−B′. Examples of this condition are lines numbered 3, 4 and 5. For lines 1 and 2 the direction of the intensity change in each beam is the same as that of lines 3, 4 and 5 but the initial intensity ratio of the two beams is reversed. For these two lines the density curves would be as in Fig. 6. The percent-

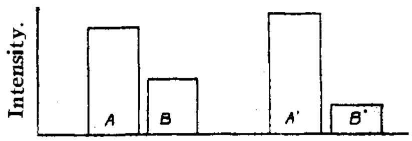

Fig. 6.—Percentage positive.

age in this case is negative. Many pictures were made at each of the two settings and the sign of the percentage was consistent for all pictures at each setting. The value of the percentage for water was found to be nearly zero and to vary with no regularity in sign as may be seen in Table III.

Duplicate exposures were made with the current in the coils B_1 and B_2 in Fig. 1 reversed to its original direction in order that any characteristic of the electrical circuit or optical system that might be giving these results should be detected.

(6) Hughes and Goslin. *Phys. Rev.*, **47**, 317 (1935).

TABLE III

FIELDS ASSISTING, CURRENT IN REGULAR DIRECTION

No.	Material	Compounds On cm.	Compounds Off cm.	Compounds G cm.	Compounds %	Compounds No. of pairs	Blanks On cm.	Blanks Off cm.	Blanks G cm.	Blanks %	Blanks No. of pairs
1	H_3PO_4	5.61	6.37	0.76	−11.9	14	6.26	6.14	0.12	+1.9	14
2	$PbCl_2$	6.84	7.54	.70	− 9.2	12	5.76	6.08	.32	−5.2	14
3	Li_3PO_4	2.23	1.99	.24	+12.0	10	1.57	1.53	.04	+2.6	14
4	HBr	2.83	2.62	.21	+ 8.0	12	1.88	1.90	.02	−0.52	13
5	LiBr	1.93	1.77	.16	+ 9.0	13	1.41	1.37	.04	+0.21	13

FIELDS ASSISTING, CURRENT IN REVERSED DIRECTION

No.	Material	Compounds On	Compounds Off	Compounds G	Compounds %	Compounds No. of pairs	Blanks On	Blanks Off	Blanks G	Blanks %	Blanks No. of pairs
6	H_3PO_4	4.57	4.14	0.43	+10.5	14	2.19	2.17	0.02	+0.91	13
7	HBr	6.79	7.19	.40	− 5.5	14	4.49	4.50	.01	−2.2	14
8	LiBr	5.22	5.50	.28	− 5.2	14	4.08	4.13	.05	−1.2	14
9	H_3PO_4	1.12	1.25	.13	−10.4	20	0.61	0.61	.00	0.0	17
10	$CuCl_2$	0.87	0.95	.08	− 8.4	17	1.45	1.41	.04	+2.7	20

The two groups in Table III show the effect of reversing the direction of the current. Minima were photographed when the two magnetic fields were in the same direction, that is, when the two adjacent ends of B_1 and B_2 were N and S, respectively, and when the fields were in opposite directions. The results listed in Table III are for fields in the same direction. Pictures were made with the current in either direction when the fields were in opposite directions. No appreciable difference was noted in the quality of the minima for the different directions of the fields or current.

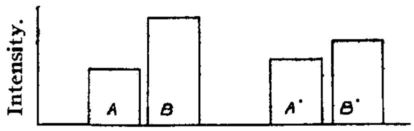

Fig. 7.—Percentage negative.

Since the purpose of this work was to show by a photographic test that minima are real it is necessary to consider the results of all the pictures which have been taken for this purpose, excluding only those which for valid reasons would not be expected to give positive results. The following reasons were considered valid for discarding pictures and the results of pictures taken under such conditions were not included in the means, percentages or totals given below.

1. Pictures taken with an unsteady spark were discarded. If the spark was unsteady for an entire plate the entire plate was discarded. If in a plate the spark was noticeably unsteady for a single line on the plate and with the proper adjustment became steady for the later pictures on the plate only the bad line was excluded. If for one picture in a line the spark was unsteady and that unsteadiness for the particular picture was recorded in the notes, the one picture affected was not included in the average for the line.

2. Plates were discarded which did not have the proper development or which showed slight scratches due to handling.

3. Plates which had an improper exposure as described above were discarded.

4. Plates were discarded which had an improper spacing between the lines. The lines on these plates were too close together due to an improper distance between camera and lens.

5. When it was found that positive results were never obtained when the resistance R_3 was omitted from the circuit those pictures taken without it were discarded.

6. This report does not carry the results of 200 pictures obtained before an automatic timing device was used. These results are positive but since the timing was uncertain they are not included.

7. A few lines of pictures taken when the concentration of material present was too low to give minima are not included.

8. Those pictures are not included for which visual observation showed the minima of an impurity present in the solution to be close to the "off" position of the minimum under consideration.

9. The pictures which were taken under conditions of high humidity are not included. Visual work has shown minima under such conditions to be very poor and with extreme humidity to disappear completely.

Table IV presents the average percentage difference for all pictures of compounds and water except those specified above with each of the four possible electrical connections. In determining the mean percentage for compounds the sign of the individual percentages is not considered since it must necessarily change with the electrical connection. In the case of water, however, an algebraic mean is given since the percentages appeared positive and negative in all connections.

TABLE IV

		Compounds		Blanks	
Fields	Current	%	No. of pictures	%	No. of pictures
Assist	Regular	+ 7.8	730	+1.46	208
Assist	Reversed	− 9.5	255	+1.0	109
Oppose	Regular	−11.5	265	−1.0	190
Oppose	Reversed	+12.3	246	+0.76	53

Mean per picture 9.4% Mean per picture +0.46%
Total pictures 1496 Total pictures 560

TABLE V

		Compounds		Blanks	
Fields	Current	%	No. of pictures	%	No. of pictures
Assist	Regular	+10.8	137	+0.45	89
Assist	Reversed	− 9.9	103	−1.44	54
Oppose	Regular	− 8.0	30	−0.82	46
Oppose	Reversed	+ 9.1	68	−0.11	36

Mean per picture 9.9% Mean per picture −0.35%
Total pictures 338 Total pictures 225

Table V is reproduced from a previous publication on this work.[6] The results presented have been incorporated in Table IV. It is of interest to note that the percentage for compounds varied only 0.5% with the addition of 1158 new pictures while the water, which shifted on either side of zero for the different connections, changed the sign of its earlier mean value with the addition of only 325 new pictures.

The water blanks tabulated above were made with samples of very pure water. The difference in conductivity between this water and a solution of an acid of a concentration of 1 part in 10^5 parts of water is large, and it has been suggested that the minima might be due to this change in conductivity. To investigate this point pictures were taken with the trolley on and off the position of the phosphoric acid minimum when only 1 part of cupric chloride in 10^5 parts of water was present in the tube. The percentage for 56 of these pictures was 0.91, showing conclusively that minima can be obtained for a particular substance only when the trolley is at the proper position regardless of the other materials present in the tube.

Since the differences in density to be measured in this procedure are small, it was found that the utmost care had to be exercised in the handling and development of plates and in their examination with the microphotometer. The plates were carefully inspected before placing in the microphotometer and any dirt or lint in the exposed area was gently brushed aside. In those cases where lint was found on the plate after the lines had been measured the line or lines in question were remeasured along with neighboring lines so that a proper comparison could be made. For example, in a particular strip of picture the "on" pictures were all larger than the "off" pictures except one pair. A bit of lint was found on one of the four lines of this pair of pictures and whereas the density differences read

	A	B	Diff.
on	14.43	14.10	0.33
off	14.50	14.10	.40

before cleaning, they read

on	13.70	13.39	0.31
off	13.58	13.34	.24

after cleaning, in accord with the other pictures in the strip.

The difference in actual galvanometer deflection recorded as A and B above for the two readings of the same lines may be due to a motion of the

TABLE VI

DIFFERENCES FOR PICTURES ON MINIMUM

	Trial 1 cm.	Trial 2 cm.	Trial 3 cm.	Trial 4 cm.
	1.08	1.10	1.10	1.10
	1.09	1.16	1.00	1.00
	1.08	1.10	1.10	1.00
	0.92	1.01	1.10	1.05
	1.17	1.19	0.90	0.90
	1.31	1.37	1.10	1.05
	1.07	1.17	1.35	1.45
	1.11	1.22	1.10	1.10
	1.20	1.38	1.30	1.30
	1.14	1.32	1.20	1.35
Mean	1.117	1.202	1.115	1.130

DIFFERENCES FOR PICTURES OFF MINIMUM

	Trial 1 cm.	Trial 2 cm.	Trial 3 cm.	Trial 4 cm.
	1.20	1.24	1.10	1.35
	1.26	1.29	1.15	1.30
	1.24	1.32	1.35	1.25
	1.15	1.25	1.10	1.00
	1.26	1.30	1.45	1.30
	1.35	1.44	1.40	1.35
	1.29	1.32	1.15	1.20
	1.25	1.35	1.28	1.20
	1.16	1.26	1.15	1.20
	1.32	1.41	1.35	1.35
Mean	1.248	1.318	1.248	1.250
Percentage	10.4	9.9	11.2	10.3

plate in its holder on the microphotometer causing a slightly different length of the line to have been measured. Many strips of pictures were examined along different sections on the length of the lines and although the lines varied in density along their length the density difference between the lines of a pair varied but little. Table VI presents the results of one strip measured four times.

Only the differences between the lines are recorded since it is these values that determine whether the minima have been photographed or not. Trials 1 and 3 were made on the top edge of the strip while 2 and 4 were made on the lower edge. To determine the constancy of the microphotometer Trials 3 and 4 were made several days after 1 and 2. Due to the removal of the plate from the microphotometer after each trial, a variation in the individual values recorded is to be expected. The percentages recorded in the table indicate in a measure the quality of the minima and from their values it will be observed that the minima vary but little along the length of the lines in a series of pictures. These percentages also indicate with what error a series of lines may be read over a period of time.

The means recorded in Tables I and II are simple arithmetic means. Such averages used in the course of this study gave results confirming visual work. It has been pointed out, however, by critics interested in this investigation that the simple averages used were obtained from data many of whose individual members deviated widely from the mean, and that this large deviation might be the major factor in giving the desired result. The author appreciated from the first of this study that the effect obtained was a small one and close to the experimental error. For this reason a very large number of photographs were taken with as many variations as possible. The fact that these many pictures gave the desired result was not considered sufficient evidence for the proof of this effect because all of the groups of pictures contained pictures which deviated widely from the mean. A recalculation of all the results was therefore made in which the extreme cases in the data were discarded in an effort to obtain a result free from such cases.

Using the average deviation of the individual pictures from their simple average it was found that 0.1% of all the pictures deviated from the average by more than three times the average deviation, 11.0% deviated by twice the average deviation and 34.0% by more than the average deviation. There was no appreciable difference in the number nor magnitude of the deviations for any group of pictures as compared to any other group.

The data presented in Table IV, recalculated, using only those pictures which are within twice the average deviation are presented in Table VII.

TABLE VII

SELECTED DATA FROM TABLE IV

Fields	Current	Compounds %	Compounds No. of pictures	Blanks %	Blanks No. of pictures
Assist	Regular	+ 9.9	662	+0.03	184
Assist	Reversed	−15.0	234	+1.1	101
Oppose	Regular	−12.3	245	−0.6	169
Oppose	Reversed	+13.1	219	+ .67	47
Mean per picture 10.5%		Total 1320		Mean per picture +0.09% Total 506	

On the basis of this calculation the minima appear better than before. The general effect on the individual strips was to raise the percentage. For some strips the percentage was lowered but in no case was there a change of sign of the percentage for compounds. In the strips for water there were many changes of sign and the direction of the change in percentage followed no general trend. This statistical treatment of results shows that the effect of the minima is superimposed on a changing background and that without this background the effect would appear larger and more pronounced than these results seem to indicate. A second recalculation using only those pictures within the average deviation gave results only slightly different from those in Table VII. Since one of the purposes of this investigation was to picture photographically that which the eye sees visually, one is hardly justified in discarding any data except the very extremes. It is the opinion of the writer that the truest picture of this effect is obtained when the result is calculated from data which come within twice the average deviation.

The Absolute Intensity Change for a Minimum

A study was made to determine the absolute value of the intensity change occurring when the trolley was moved to the position of a minimum from off this position. The measurement of the absolute value of this change was accomplished by imposing a 1% change on the intensity of each of the beams from the Wollaston prism by rotating the prism through an angle of 17′ which in accord with the cosine squared law gives the desired change. The mounting of the Wollaston was equipped with a divided circle with a vernier. Stops were placed on the vernier so that the Wollaston could be rotated readily through 17′ and a series of pictures was taken with the prism alternately at 45° and 45°17′. The 1% changes could be compared directly with pictures "on" and "off" minima. In setting up a plate in the microphotometer there is always some doubt as to the section along the length of the line that is being measured. For this reason it was thought that a proper comparison might not be made between the 1% changes and the minima pictures and a second series of pictures was made therefore in which the 1% changes were made in the same strip as the minima pictures. The sequence "on," "off" and 1% was repeated throughout the strip. The absolute value of the change thus determined was 0.7%. This value is the average of 168 pictures of compounds compared with 150 pictures of the 1% change. The maximum value of this change photographed for a series of two or more pictures was 1.0%. The value of the change when the data are treated as above using only those values which come within twice the average deviation is 0.8%. This is the average of 155 pictures compared with 145 pictures of the 1% change.

A small number of pictures were made on more dilute solutions to determine the manner in which the absolute change varied with concentration. To the average eye the apparatus as adjusted for photographing is sensitive to about 1 part of salt in 10^5 parts of water. When a dilution of 1 part in 10^7 parts of water was used a small positive effect of 0.3% was observed. A dilution of 1 part in 10^9 parts of water gave erratic results similar to a blank run.

Criticism has been made on the magnitude of this change in light intensity on the basis that such a small change could not be detected in visual work. The author appreciates that the small 0.7% change in light intensity is below the limit of a simple intensity change the normal eye can detect. A critical examination of this photographic measurement of the change in light intensity for a minimum shows however that such a measurement may be in error in itself and further that it may be in error when compared with the same effect measured by other means.

The several known facts about the minima themselves make it appear that the individual changes which over a long period of time cause the minima, must be in themselves very short lived. The very high resolving power of this apparatus is an indication of this short-timed effect. Minima which are separated by as little as 3 cm. on the trolley or 1×10^{-10} second are seen as separate minima. The photographs of the spark, plates 1 and 2, indicate that the light used in making the photographs comes in flashes of the order of 10^{-6} to 10^{-5} second duration. The composition of the light making up the minimum then must be a change in the intensity of the flash from the spark for a very small fraction of the total life of the flash.

The photographic effect of such a change is unknown but from the complicated effect of the flashes themselves it is probable that the change is not a simple one. Now in the above measurement the complex change of the minimum has been compared with the effect of flashes whose intensity has been changed by 1%. If the change for a minimum had been a simple change in the intensity of a continuous light then the procedure used would be valid but in view of the complex nature of the changes in the light in this experiment it is doubtful that a measurement in this manner gives the correct value.

The appearance of minima from the descriptions of many different observers indicates that any static measurement for the intensity change for a minimum over any appreciable period of time probably would not be an accurate measure of what the eye sees as a minimum. To one class of observers the minima appear as a gradually darkening field for a length of a few millimeters on the trolley. Minima appear best when observed with the trolley moving over them so that the change is seen by contrast. With the trolley moving in this manner the minima appear to shift slightly with the trolley. Now if a photograph is made with the trolley stationary at one point and the minima really do move slightly in their positions then the change for a minimum measured by such a photograph would show a change only for the time the minimum appeared at that setting of the trolley. This might be but a small fraction of the sudden change the eye would detect as the trolley passes over the proper position for a minimum.

A second class of observers sees the minimum as a shadow or dark band moving in the field of view as the trolley passes the position of a minimum. This change might be considered as a redistribution of the light in the field with little net change over the entire field. A photographic plate would record such a change as a very small one if the light from the entire field were focused to one point on the plate. Such a change would be easily discernible to the eye since vision would permit one to detect a darkening throughout different portions of the field.

There can be little doubt that the only valid way to measure the change the eye sees as a minimum is to use the eye to compare the minimum with a similar known change. Since the exact mechanism of the production of this effect is unknown at this time, it is impossible to produce a proper synthetic light change for comparison. Investigations are now under way to determine the mechanism of this effect.

Conclusion

The success of this photographic technique in detecting the small changes in light intensity due to minima over the other techniques which have been employed is due to the ability of the Wollaston prism to discriminate between the small changes in intensity due to minima and the changes in the incident light.

The observed photographic effect showed the following characteristics when tests were applied to prove the effects obtained were not due to changes in the electrical circuit or optical system:

1. No appreciable effect was obtained when blank solutions were used and the effect was only obtained for compounds when the trolley was placed at the proper position for one of the minima of a compound.

2. Minima were obtained when the setting of the trolley off the position of the minimum was taken on either side of the minimum position.

3. A decreasing absolute change in light intensity was found for decreasing concentrations of the compound.

4. The direction of the change in light intensity was found to change with the reversal of the direction of the current in the coils.

5. The direction of the light intensity change was found to reverse with the setting of the Wollaston prism on either side of the critical 45° position.

These five characteristics of the 2300-odd pictures taken in this investigation indicate that there is a small photographic effect in the magneto-optic apparatus which is characteristic of the compound present in the apparatus. This photographic effect was found to occur only at the positions of minima previously determined from repeated visual observation. The absence of minima in blank solutions; the absence of minima except at the proper trolley positions for a particular compound; and the reversal of the effect with the reversal of the direction of the current in the coils, have been observed in visual work. It is concluded therefore that the effect photographed is identical with the visual effect and that this effect is valid and characteristic of the compound present in the apparatus.

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Summary

A photographic method has been developed to demonstrate the reality of minima in the magneto-optic apparatus. Microphotometer measurements of the difference in density of exposures taken on and off the positions of minima are attributed to variations in light intensity due to minima. The slight excess of the photographed effect over the experimental error necessitated a statistical study of the 2300 pictures taken in this investigation. This study showed only that the photographed effect was obscured by a background of changing light intensity. The measured change in intensity for a minimum was 0.7%. Water blanks showed approximately zero percentage change. The presence of foreign materials did not change the magnitude of the intensity change for a minimum. The direction of the effect was found to be dependent on the direction of the magnetic field in the coils.

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