changes which occur during those (end) portions of the cycle when the magnetic phenomena are most nearly reversible are precisely opposite in the two materials. The thermal energy of the steel increases on demagnetization and decreases on magnetization, while that of nickel decreases on demagnetization and increases on magnetization. The phenomenon is the subject of further research in this laboratory.

In conclusion the writer desires gratefully to acknowledge her indebtedness to the Physics Department of Columbia University for the facilities generously placed at her disposal; to the officers of the International Nickel Company, who were at considerable pains to secure the specimens used in the research; to Dr. S. L. Quimby, who suggested the problem; to Dr. W. B. Ellwood, for his counsel during the early stages of the work; and to Mr. C. F. Wiebusch, for his assistance throughout its progress.

FEBRUARY 15, 1935 PHYSICAL REVIEW VOLUME 47

An Investigation of the Magneto-Optic Method of Chemical Analysis

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(Received December 21, 1934)

An apparatus similar to that used by Allison in his magneto-optic method of chemical analysis was set up in an effort to verify the existence of the sharp Allison minima. Many visual observations were made, but only occasionally did readings of possible minima occur in more than random groupings. Where these apparent minima did occur, it was thought that they could be explained as being due to such factors as sticky places on the trolley felt by the hand on the hand wheel control. When a motor control was used on a later apparatus, the distribution of readings of possible minima was no more than a chance distribution. Objective tests were made of the variation of intensity of light with trolley position by a photographic method. In this photographic method the effect of spark fluctuations was eliminated by comparing the intensity of the light passing through the cells with that of a comparison beam direct from the spark. Individual runs by this method showed no minima and were good to three percent. When several runs were averaged, the resultant intensity curve showed no variations greater than one percent. Eye tests showed that the writer could not have detected an intensity change visually of less than three percent on the magneto-optic apparatus. These results indicate that the minima occasionally seen by the writer on his apparatus have no objective reality. A broad minimum of the type described by Slack and by Webb and Morey was obtained by the photographic method for CS_2.

In an effort to verify the existence of the sharp minima seen on the "magneto-optic apparatus" by F. Allison and others, an apparatus similar to that of Allison was set up in the physics department in September, 1933. The apparatus is shown schematically in Fig. 1. P is a 25,000 volt Thordarson type R transformer. G is a 4 mm spark gap between magnesium rods 4 mm in diameter. The size of the rods and the gap length were both varied at different times. L is a lens to form parallel light, F a filter to give monochromatic blue light. N_1 and N_2 are nicol prisms. B_1 and B_2 are cylindrical Pyrex cells, B_1 containing CS_2 and B_2 containing a water solution of some inorganic acid or salt. H_1 and H_2 are two similar helices, of from 20 to 90 turns (usually 50 turns) of No. 18 copper wire wound on Bakelite cylinders 3.5 cm in diameter and 14 cm long. T_1 and T_2 are trolleys to vary the relative lengths of the parallel wire paths to the coils. The trolleys are of No. 18 copper wire, the wires being spaced 20 cm apart. The length of the fixed trolley was varied from 2 to 7 meters. Sliding copper bars were used as contacts on the movable trolley. Values of the capacity C were varied from 0.0008 mf to 0.005 mf, both glass and mica condensers being used.

The Allison minima have been reported[1] to appear when a certain difference in wire path length to the two coils is obtained, these differ-

[1] F. Allison and E. J. Murphy, J. Am. Chem. Soc. **52**, 3796 (1930).

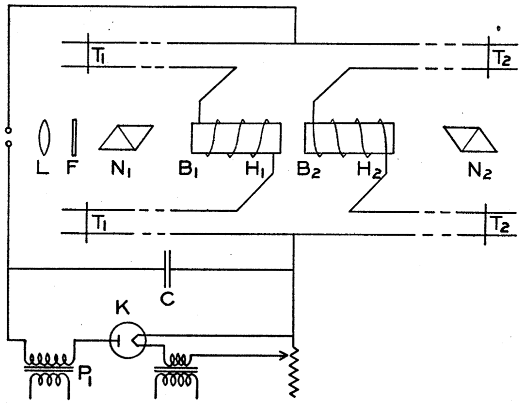

FIG. 1. Magneto-optic apparatus.

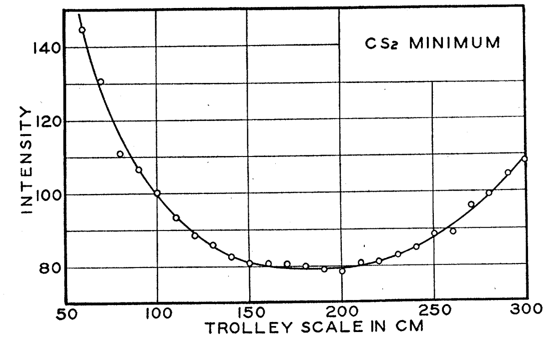

FIG. 2. Minimum with CS_2 in both cells, by photographic method.

ences being characteristic of the compounds in cell B_2. Since in practice one trolley is kept fixed, the minima appear at certain scale readings on the movable trolley.

These minima are reported to have been observed with several arrangements and variations of the above apparatus. The methods that have been tried by the author will be listed. The original method[1] is with "nicols crossed and coils opposed." That is, the two nicol prisms N_1 and N_2 have their planes of polarization perpendicular and the magnetic fields in the two helices are in opposite directions. In this method only light which experiences a net rotation in the two cells passes the second nicol prism. Another arrangement for viewing the minima[2,3] is with "nicols parallel and coils aiding," i.e., the planes of polarization of the two nicol prisms are parallel, and the currents in the two coils are such that the magnetic field goes in the same direction through each coil. In this case the effect of a rotation in either cell is to diminish the intensity of the light. A third nicol is used to cut down the intensity to the desired low value. With this method the minima have been reported with a variation of the apparatus in which the main spark current does not flow through the coils.[4] In this case the trolley system is connected across the spark gap through two small condensers.

Minima have been reported with a steady source of light, the spark still being used in connection with the electrical circuit, both with nicols crossed[1] and parallel.[5] They were seen when only one-half of the bilateral trolley system was used,[5,6] and have been reported with unrectified current to the spark.[6] Allison observed the minima with the trolley in motion. Latimer and Young used a static method in which the trolley was moved along in 2 mm steps, the observer looking at the spark only when the trolley was stationary.

In trying to locate the minima, the writer took repeated observations with a dilute solution of HCl in the cell B_2. The arrangement with "nicols crossed and coils aiding" was used. In each observation the observer would move the trolley by means of a hand wheel through the region in which minima were expected from published results, stopping whenever the light appeared less intense, and recording the position of the trolley. No assistant was needed, as the trolley position was read by the observer through a telescope which was directed on the scale by a system of mirrors. The results of a number of runs were then examined for coincidences in readings, and the positions of these were carefully examined. For several months no "minima" were seen that survived this scrutiny, though many combinations of the values of the various constants of the circuit were tried.

[2] F. Allison, J. H. Christensen and G. V. Waldo, Phys. Rev. **40**, 1052 (1932).
[3] E. R. Bishop, C. B. Dollins and I. G. Otto, J. Am. Chem. Soc. **55**, 4365 (1933).
[4] L. B. Snoddy, Phys. Rev. **44**, 691 (1933).
[5] G. M. Wissink, Physics **5**, 31 (1934).
[6] Fred Allison, J. Chem. Ed. **10**, 70 (1933).

Finally, however, early in January, 1934, after changes in the trolley contacts and in the helices had been made that were thought to be crucial, two minima that persisted for several days were observed in approximately the correct position for HCl. At this time a photographic method for recording minima was devised by Professor R. B. Brode and was used. This method in its final form will be described later. A series of tests by this method showed that there were no minima greater than 3 percent in magnitude, which was as far as the accuracy of the method was extended at that time. Further visual tests in the region showed that the minima seen were not persistent in respect to position of the trolley.

The broad minimum for the case of CS_2 in both cells was photographed and the curve for this is shown in Fig. 2. As can be seen, this minimum extends over several meters. This type of minima is adequately discussed by F. G. Slack[7] and by J. S. Webb and D. R. Morey.[8]

Then there followed a series of alternate visual and photographic tests for different solutions and varying spark conditions. In no case were possible visual minima confirmed by the photographic method, nor did they persist visually after negative results from the photographic method had been obtained.

Tests were made to determine how small a variation in intensity could be detected on the Allison apparatus, and with what optical arrangement this could be done. The intensity of the spark or of a steady mercury source was regulated to the usual value by two nicol prisms nearly crossed. A third nicol prism was mounted so that it could be rotated between two positions with respect to the second nicol, introducing an artificial minimum of any desired magnitude. Care was taken so that the observer could not see the assistant operating the nicol, nor could he see any movement or change except such as might appear in the intensity of the beam of light. In most of the tests the assistant called out a series of two or more numbers or letters. As one of these numbers was called, the assistant would turn the nicol to the position which gave the minimum, leaving it at the maximum setting during the calling of the rest of the numbers. The numbers were repeated in cyclical order until the observer made a guess as to which number corresponded to the minimum. Occasionally it was found that the observer could tell from the assistant's voice which was the minimum. On these occasions the observer would call the numbers, the assistant remaining silent, but turning the nicol at any particular number he chose.

Results show that 3 percent was the smallest change that the author, who did most of the observing for the Allison minima, could detect, and this with no reliability. Out of 62 trials at 3 percent taken in seven tests over a period of two months, he was right 42 times and wrong 20 times, the reliability varying from day to day. Usually anything over a $4\frac{1}{2}$ percent change could be detected with certainty, although on one day a 13 percent change was indistinguishable. Results were somewhat more consistent with a steady source than with a spark source, but the limit appeared to be the same. Tests of different types of comparison fields showed that, of those available, the best was a Lummer-Brodhun cube in which a central elliptical field was compared to an annular ring about it. The presence of the comparison field lent a greater degree of certainty as to the presence of the intensity change, especially for "inexperienced observers," but did not greatly extend the range of detectability. A change of 2.2 percent was the smallest change successfully "guessed at" by any observer under the conditions of the experiment. The use of extremely low intensities did not aid in observing these known changes.

It is interesting to note that when the control nicol prism was shifted between two positions "A" and "B" for which there was an intensity change too small to be easily distinguished, the light could be made to appear to change in intensity at each reversal of position, quite regardless of the actual direction in which the change was taking place. The only stimulus required for this apparent intensity change was the knowledge that the nicol was being shifted in position.

A visual trial was made of a variation of the apparatus reported to give minima recorded by a

[7] F. G. Slack, J. Frank. Inst. **218**, 445 (1934).
[8] J. S. Webb and D. R. Morey, Phys. Rev. **44**, 589 (1933).

photo-cell,[5] in which a steady mercury arc was used for a light source with nicols parallel and coils aiding. A spark was used as before in the electrical circuit. With this arrangement, it was impossible to distinguish visually any change in intensity of the blue mercury light as the spark was turned on. Nevertheless, a series of runs was made over the regions of expected minima, with readings of "minima" recorded in the usual manner. A toothed cardboard wheel of equal open and closed sectors was rotated by a synchronous motor so that it cut out the light passing through the cells for half a cycle. Just as great consistency was obtained in the readings of minima when the closed sectors cut out the light during the active half of the cycle as during the inactive half, the observer not knowing until after the run had been made whether the stroboscope was in or out of phase with the spark. In neither case were readings any more grouped than might be expected from a random distribution.

Using the spark as a source of light, coincidences in minimum settings were sometimes obtained that were unlikely to occur by chance. In one case when a possible minimum at a trolley scale reading of 148.7 cm was reported twice by a visitor to the laboratory, especial care was taken to avoid subjective influences. The writer acted as observer, operating the hand trolley, while W. H. Thurston watched the trolley scale and recorded the positions at which minima were called. The observer did not know the position of the trolley at any time during the run, and after announcing each minimum he moved the trolley about arbitrarily to try to lose any muscular sense of the exact position of that minimum. The fact that the observer thought that the trolley was progressing down the scale between each recorded position shows that this attempt was successful. The positions of the reported minima were:

150.6 150.7 150.7 150.0 (weak) 148.7

At the time this was regarded as fairly convincing evidence of a minimum at 150.7 and possibly one at 148.7, with three coincident readings of each out of seven tries. Failure to confirm either as a true minimum led us however

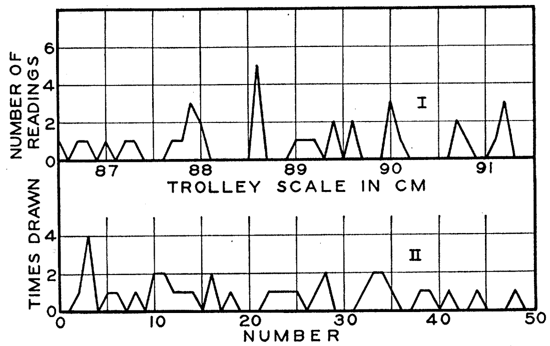

FIG. 3. Curve I gives the number of readings of minima recorded by the author at different positions of the trolley in the region in which the $CaCl_2$ minima were expected. Curve II is a random curve for comparison, obtained by drawing numbers.

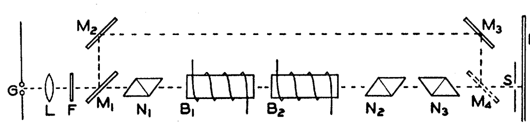

FIG. 4. Optical arrangement used in the photographic method.

to explain them as "sticky" places on the trolley wires, which, felt unconsciously by the hand through the control wheel, gave sufficient stimulus to cause one to "see" the looked-for effect. Another subjective trouble that was noticed occurred when the observer tried to set accurately on a minimum. Whenever a prospective minimum was located by a progressive motion along the trolley, he would try to set on it by rolling the trolley slowly back and forth through the approximate position. At the center of each swing a "subjective minimum" was automatically seen, unless carefully guarded against.

Partly on account of these two difficulties a new trolley system was set up in which the trolley was moved by an electric motor. Other changes were made in the apparatus in the new arrangement, such as in the form and length of the trolley wires, in order to try to avoid any unknown fundamental defects in the particular apparatus. With the new arrangement, a dilute solution of HCl and $CaCl_2$ was examined for possible minima in the expected regions, using the apparatus with the nicols parallel and coils aiding.

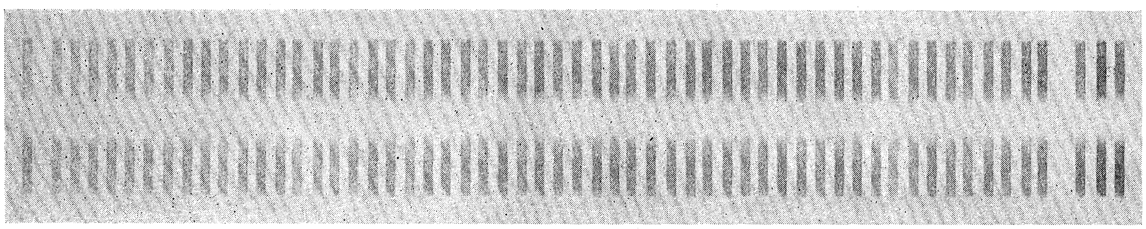

Fig. 5. A photographic plate used in intensity measurements. Microphotometer measurements of this plate gave the intensity curve II, Fig. 6.

Readings were taken over the 5 cm trolley interval in which the $CaCl_2$ minima were to be expected. In the course of 15 runs over this interval a total of 36 minima including repetitions were observed, there being 1 to 4 observed minima in each run. The frequency distribution of these 36 readings is shown in curve I, Fig. 3. That this is comparable to a chance distribution is indicated by comparison with curve II, Fig. 3. This second curve was obtained by placing in a box 50 numbers corresponding to the 50 possible settings on the 5 cm trolley interval. Thirty-six numbers were then drawn from the box 1 to 4 at a time to correspond to the 36 minima recorded in groups of 1 to 4 found in each actual run through the region. The numbers were replaced after each drawing. Curve II is the frequency distribution of the numbers drawn.

A final series of photographic tests was made over this and other regions of the trolley. These tests were based on the static method of observation used by Latimer and Young. The light passing through a 1 mm slit S (Fig. 4) fell on a $1\frac{1}{2}$ by 6 inches Eastman 33 photographic plate. The upper half of the slit was illuminated by light passing directly through the cells B_1 and B_2. The lower half of the slit was illuminated by a comparison beam that did not pass through the cells. This comparison beam was reflected from the main beam to a side path by the plane glass plate M_1 and the mirror M_2, and was reflected back into the original line of direction by the mirrors M_3 and M_4. An exposure of 20 seconds was made in one position of trolley and plate. The plate was then moved 2 mm, the trolley moved 1 mm, and another exposure taken. Thus two series of shadow images of the slit were formed on the plate (Fig. 5), one depending on the light intensity coming through the cells and the other showing the relative intensity of the spark during this time. On each plate there were several exposures taken with a piece of plane glass in the main beam, introducing an artificial 9 percent minimum for calibration purposes. Each series of images was then microphotometered, and the throw of the microphotometer measured for each image. The ratio of the throw for any image formed by the main beam to the throw for the corresponding image of the comparison beam gives a measure of the light coming

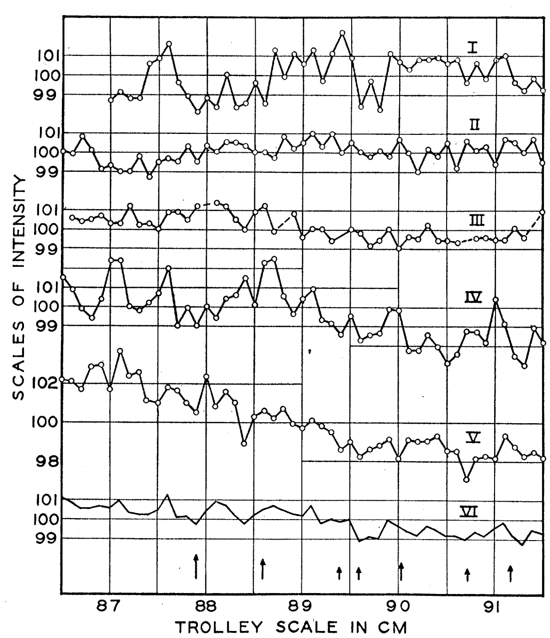

Fig. 6. Curves I to V are intensity curves from individual photographic plates. Curve VI is the average of these. The arrows indicate positions of possible visual minima. There is no apparent consistency between the visual minima and the intensity curves.

through the cells that is independent of spark fluctuations. By a suitable factor determined for the plate from the 9 percent calibration minima, this ratio was converted into percent variation of the light intensity. The spark was adjusted to a more steady state before each run by varying the resistance in series with the filament of the kenetron so that a definite number of condenser discharges per cycle (usually 2) took place, as determined by the number of sparks seen in a revolving mirror driven by a synchronous motor.

Curves I, II, III, IV and V, Fig. 6 are individual runs over the same 5 cm region in which $CaCl_2$ minima were expected. Curve VI is the average of these. As can be seen, there is no correspondence in minima of more than a random nature between any of the curves of Fig. 6. The arrows in Fig. 6 represent visual minima observed in 15 runs over the same region. The length of each arrow represents the frequency of observation of the minimum. These are the same minima shown in Fig. 3. Since the accuracy of locating minima visually was 3 percent at best, and since the photographic method is good to 2 or 3 percent on individual runs and good to about 1 percent when several runs are averaged, it is clear that this objective test does not reveal the existence of any real minima on the apparatus used. The author believes, as a result of these tests, that such minima as he saw from time to time can be explained as due to physiological or psychological factors.

As the final photographic tests described were being made and after all visual work had been completed, an article by F. G. Slack[7] in the *Journal of the Franklin Institute* appeared. This article contains a very complete bibliography of the subject. It is interesting to note that although these two investigations were carried out completely independently and initially with different viewpoints, the observations made and the conclusions drawn from them by the observers are in essential agreement.

In conclusion, the author wishes to express his appreciation to Professor R. B. Brode, who proposed this study and directed the first part of the work, to W. H. Thurston and R. Leonard for their aid in assembling the apparatus and in observing, to Professor L. B. Loeb for his help in preparing this report, and to many other members of the physics department for their interest and suggestions.

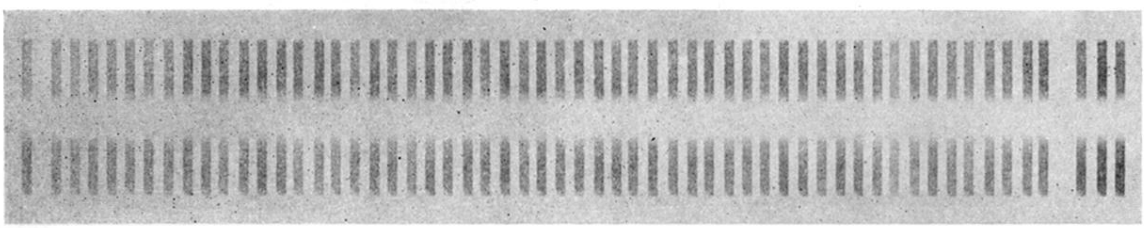

FIG. 5. A photographic plate used in intensity measurements. Microphotometer measurements of this plate gave the intensity curve II, Fig. 6.