RADIOMETRIC MEASUREMENTS OF THE IONIZATION CONSTANTS OF INDICATORS.[1]

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The radiometric measurements recorded in this paper were made with a very sensitive radiomicrometer and a grating spectroscope. The spectroscope is well known to the chemist, but its use in connection with the radiomicrometer, has not, as yet, found an extensive application to the study of chemical problems. This is perhaps due in part to the difficulty in constructing a sensitive and easily controlled radiomicrometer. By means of the grating spectroscope and radiomicrometer, it is possible to study quantitatively chemical reactions involving color changes, and even those not involving such changes, if there are absorption bands in the invisible regions of the spectrum. It will be seen that accurate determinations of very small concentrations of colored components in solutions, can be made very rapidly even when two or more such components are present. The structure of the solvent bands, and time reactions, are a few of the many other important chemical problems which may be investigated by means of this radiometric apparatus.

Purpose of this Investigation.—In connection with some problems now under investigation in this laboratory, it was desired to secure accurate measurements of the hydrolysis constants of certain salts. The spectroscope and radiomicrometer suggested the indicator method, which is based on the changes in the transmission of light by solutions of indicators when varying amounts of hydrogen or hydroxyl ion are present. It will be shown that by means of these changes the concentrations of very small amounts of hydrogen and hydroxyl ions can be determined. The method obviously involves a knowledge of the ionization constant of the indicator as an acid or as a base. A comparison of the ionization constants of the indicators obtained by several investigators, showed that the recorded values varied widely, not only with different methods, but with the same method. The results for phenolphthalein in particular, show how inaccurate is our knowledge concerning the ionization constant of that important indicator. Salm[2] gives the value 8×10^{-10}; McCoy,[3] 0.8×10^{-10}. In many cases the results of an individual investigation vary as much as 300 to 400 per cent. A. A. Noyes[4] has applied the theory of indicators to volumetric analysis, making use of the ionization constants of the various indicators. He expresses the opinion that our knowledge of the ionization constants of the indicators is for the most part inexact,

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[1] This investigation was carried out with the aid of a Grant from the Carnegie Institution of Washington generously awarded to H. C. Jones.

[2] *Z. phys. Chem.*, **57**, 492 (1907).

[3] *Am. Chem. J.*, **31**, 503 (1904).

[4] THIS JOURNAL, **32**, 858 (1910).

and needs to be supplemented by further careful investigation. Stieglitz,[1] McCoy,[2] and Salm[2] have also recognized the importance of such a study. McCoy, Salm, and in particular Noyes and Bjerrum,[3] have already applied the indicator constants to some of the more important problems which the chemist must face in titrating weak acids and bases; and they have shown in certain cases the extent of the error involved in such titrations. It will then be readily seen, that it is important to know the ionization constants of the more important indicators, especially of methyl orange and phenolphthalein. In view of these facts, and the value of such ionization constants in many other lines of work involving the use of indicators, it was decided to make a radiometric investigation of this problem. Methyl orange was first studied, and a method was developed through the application of Beer's law, which readily gave the concentration of the yellow azo-base and that of the red quinoid ion. Knowing these values and the hydrogen ion concentration, the hydrolysis constant of methyl orange can be readily calculated. The method employed is different from, and was worked out independently of any other method thus far used in investigating this problem.

Historical.—The results of a number of preliminary investigations on the ionization constants of various indicators were published in 1904. McCoy,[4] like most of the other investigators who studied this problem, worked colorimetrically, the intensity of the color being judged by the eye. McCoy employed Nessler tubes for this purpose, while others made use of special colorimeters to determine the amount of indicator transformed into its salt by varying amounts of hydrogen or hydroxyl ions. Tables showing roughly the hydrogen ion concentration at which a large number of indicators undergo change in color, have been published by Friedenthal,[5] Salessky,[6] Fels,[7] and Salm.[8] Nearly all of the early investigators utilized the principle that the ionization constant of an indicator is equal to the hydrogen ion concentration at which it is one-half transformed into its salt. (See Salm[2] and A. A. Noyes.[2]) Salessky, and later Salm, determined the concentration of the hydrogen ions at this point by means of the hydrogen electrode. Criticisms showing how inexact most of these methods are will be found in the separate articles. Salm,[9] referring to the work previous to 1907, says that the investigations have been for the most

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[1] This Journal, **25**, 1126 (1903).

[2] *Loc. cit.*

[3] *Ahr. Versamm.*, **21**, 1 (1914).

[4] *Am. Chem. J.*, **31**, 503 (1904).

[5] *Z. Elektrochem.*, 10, 113 (1904).

[6] *Ibid.*, 10, 204 (1904).

[7] *Ibid.*, 10, 208 (1904).

[8] *Ibid.*, 10, 344 (1904).

[9] *Z. physik. Chem.*, **57**, 490 (1907).

part qualitative, and that with few exceptions, the dissociation constants of the indicators are still unknown. Salm made a more careful investigation, employing a satisfactory colorimeter to determine when the indicator was one-half transformed into its salt, and like Salessky obtained the hydrogen ion concentration at this point by means of the hydrogen electrode. The results which he obtained with phenolphthalein illustrate the uncertainty of the values found by his method. Wegscheider[1] proceeded in much the same manner as the others who have used the colorimetric method, and obtained constants for the ionization of phenolphthalein which seem to be in fair agreement with those found by Hildebrand.[2] Hildebrand's method, involving the use of the spectro-photometer for the estimation of color intensities, is the most exact of all the methods previously employed. His photometric method somewhat resembles the radiometric method which we employed. Rosenstein,[3] following essentially the procedure of McCoy, has carried out very carefully a colorimetric investigation of the ionization constant of phenolphthalein, and the effect upon it of neutral salts. He employed the Duboscq type of colorimeter to determine the fraction of the indicator transformed by a known hydrogen ion concentration. As he shows, the ionization constant is equal to the hydrogen ion concentration, times the fraction of the indicator transformed into its salt. When the indicator is a fairly strong electrolyte, *e. g.*, *p*-nitrophenol, its dissociation constant was determined by the conductivity method.

Before we can judge of the absolute value of the results obtained in any radiometric investigation, it is necessary that the radiometric instrument, and the other parts of the apparatus used in connection with it, fulfill several requirements. What these requirements are will be taken up in the discussion of the apparatus which follows. In view of the fact that radiometric apparatus has not been extensively used by chemists, it seems desirable that this be discussed in some detail.

The Radiomicrometer.—The methods employed in the construction of the radiomicrometer and especially of the thermo-junctions, we owe to Prof. A. H. Pfund.[4] By means of these methods we were able to build a very satisfactory instrument.

The radiomicrometer previously constructed by Guy[5] was found to be unsatisfactory for use with the grating spectroscope. Its sensibility, according to a recent test, was 2 per sq. mm. of exposed vane, candle and scale being at a meter's distance. The full period of this instrument was,

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[1] *Z. Electrochem.*, 14, 510 (1908).

[2] *Ibid.*, 14, 351 (1908).

[3] THIS JOURNAL, 34, 1117 (1912).

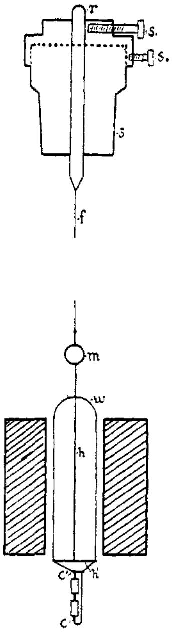
[4] *Phys. Rev.*, 34, 228 (1912); *Phys. Zeit.*, 13, 870 (1912).

[5] Publication of the Carnegie Institution of Washington, No. 190, 30 (1913).

however, very short, it being 8 seconds. His radiomicrometer could have been made about as sensitive as the one constructed for this work, by using a longer and finer quartz fiber, and making the full period about 20 seconds. However, due to the fact that this instrument was not equipped with a compensating junction, and that its drift, due to this cause, had proved so troublesome in the work of the previous year, it was decided to construct a new radiomicrometer.

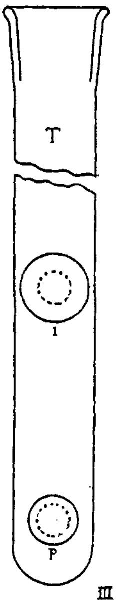
Briefly, the radiomicrometer consists of a thermo-electric junction attached to a loop of nonmagnetic wire. The whole system is suspended by a quartz fiber in a glass tube. A strong magnetic field surrounds that portion of the tube inclosing the loop of wire. Radiant energy falling upon the blackened junction is converted into electrical energy. In proportion to the amount of energy received by the junction, the suspended system turns through a definite angle in the magnetic field, the loop tending to set itself at right angles to the lines of force. The deflection or turn is given by means of a mirror attached to the suspended system.

The essential parts of the radiomicrometer are shown in the following sketch. Fig. I represents the type of compensating junction which was constructed and used. It is fastened to the loop of copper wire *w* at *c* and *c'*, as shown in Fig. II. To support the loop of wire small glass rods are placed at *h* and *h'*. A light mirror is attached to *h* at *m*. A quartz fiber, *f*, is fastened to the end of the glass rod *h*, and to the brass stopper S. The whole system is then set in the glass tube *T*, having two windows *l* and *p*. The lens *l* focuses the reflected light from the mirror *m*, on a glass scale. At *p* is inserted a plane glass window 1 mm. thick. The beam of light which is to be measured passes through this window before falling on the junction. The magnetic field is placed between *l* and *p*.



II

I



III

The wire loop was made of a very fine specimen of No. 36 copper wire, furnished by Leeds and Northrup. Pure nitric acid was used to dissolve the exterior surface of the wire, which was very likely to be contaminated with various magnetic materials. That this wire must have been very pure is shown by the behavior of the completed instrument. As regards purity, a still better specimen of silver wire was obtained from Weston; but unfortunately none of the junctions attached to this silver wire were sufficiently sensitive for our purpose.

The alloys used for the construction of the thermo-junction were of the composition recommended by Hutchins.[1] Fig. I of the sketch gives an enlarged view of the junction. It will be noticed that it consists of two thermo-electric junctions A and B, which compensate each other. When the same beam of light falls on both junctions, each sends equal amounts of electrical energy through the loop of nonmagnetic wire w, but in opposite directions. Hence, it follows that for exact compensation there should be no turn of the suspended system. In actual operation the beam of light energy which is to be measured is focused on one of the junctions. This arrangement of junctions is quite essential in any sensitive radiomicrometer where a constant zero point is required; and it is only in this way that the effects of temperature changes and stray sources of light can be eliminated.

The two arms represented by a and a' in Fig. I, have the composition 97 parts bismuth and 3 parts antimony. The composition of b is 95 parts bismuth and 5 parts tin. These metals are quite pure and the strips used are very thin. Junction A is formed by sealing strip a to strip b, and junction B is formed by sealing strip b to strip a'. R. and R′ are the receiving surfaces, or so-called vanes, cut from very thin tin foil, and soldered to junctions A and B, respectively. These vanes each have an area of four square millimeters, and are coated with lamp black to prevent radiation of light energy. It was found that the action of an acidified solution of antimony chloride on the tin foil produces a black receiving surface. Theoretically, it appears that such a metallic receiving surface should be more effective than lamp black. However, none of the junctions having the antimony receiving surface were sufficiently sensitive to determine whether or not its use is to be preferred to that of lamp black. Greater sensibility can be obtained with a single junction than with a compensating one, since in the former we have but one seal and two metal strips. This follows from the fact that the sensibility of the radiomicrometer is materially increased when the resistance of the junction is made more nearly equal to that of the wire loop. However, the advantages to be derived from the compensating type of junction are well worth the sacrifice in sensibility.

It is very important that the weight of the junction be kept as small as possible, not only to lessen the weight of the suspended system, but especially to reduce the heat capacity of the junction to a minimum. A small heat capacity insures a quick acting suspension, and one which will more rapidly return to the zero point. That the mass of material

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[1] *Sill. Journ.*, 48, 226 (1894).

in the junction is very small, can be seen from the fact that the actual weight of one of the completed compensating junctions was 2.9 milligrams.

The quartz fiber[1] was obtained from molten quartz by means of a bow and arrow arrangement. The total length of this fiber is nearly 30 cm. A long fiber materially aids in eliminating vibrations. This is most essential, especially when the work necessitates small deflections. The period and sensibility of the radiomicrometer depend in a large measure on the proper selection of the quartz fiber.

The plane mirror *m* (Fig. II) is very thin and has an area of about 20 sq. mm. Directly in front of it is the lens *l*, having a focal length of twelve feet. By means of this arrangement the image of a lamp filament could be sharply focused on a glass scale about twelve feet distant from the mirror; and it is on this scale that the deflections as given by the radiomicrometer are noted.

The torsion-head stopper *s*, made of brass and tightly ground into the glass tube T, serves the purpose of making adjustment. By means of it, the suspended system can be made to occupy any position in the magnetic field, and the whole system can be raised or lowered without danger of breaking the very fragile suspension. The torsion-head stopper contains a brass rod *r* and the two screws s_1 and s_{11} for making the above adjustments.

The glass tube T in which the whole system is suspended is about 45 cm. in length. To it is attached the lens *l* previously referred to, and the glass window *p*, through which the beam of light is directed either to junction A or to junction B.

The glass tube surrounding that portion of the suspended system to which the thermo-junction is attached was insulated from temperature changes and air drafts by a layer of fine lead shot and wool fiber. To prevent stray sources of light and air drafts from reaching the radiomicrometer, it was inclosed in a wooden box covered with painted canvas.

That the image on the scale should remain steady at a focal distance of twelve feet, it is necessary to shield the radiomicrometer very carefully from the usual vibrations of the building. The long quartz fiber aided materially in this respect. Between the leveling stand of the radiomicrometer and the base on which it rested, various insulating materials were introduced at six points to absorb vibrations.

The completed radiomicrometer, candle and scale being at a meter's distance, gave a deflection of 20 cm., the half-period being nearly 10 seconds. In making this determination of the sensibility of the instrument the radiation was passed through a glass window 1 mm. thick, and the tube containing the suspension was not evacuated. Evacuating the tube and passing the radiation through a rock salt window would increase the sensibility about six times, and the period would become somewhat shorter.

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[1] Dr. C. W. Hewlett has very kindly supplied us with several satisfactory fibers.

Since the receiving vane has an area of four square millimeters, the sensibility per square millimeter of exposed vane is 5, and the full period 20 seconds. When making this determination, owing to the difficulty of properly shielding the junction not in use but serving as compensator, it is thought that the value of 5 for the sensibility is somewhat low. Practically every junction that was tested showed that the sensibility was approximately one-fourth of the whole period in seconds. The sensibility value as given by the candle has but little meaning, owing to the varying intensity of the light emitted. The light from the Nernst glower burning at 0.8 ampere and 120 volts, dispersed into the visible first order spectrum six inches long at slit s_1 of the spectroscope, gave at $\lambda = 0.95\mu$, a deflection of 250 mm. when focused on the junction of the radiomicrometer. Both slits are 1 mm. in width, and the scale twelve feet from the mirror. Considering the high resolving power of the grating, it will be seen that our radiomicrometer is very satisfactory both as regards sensibility and period. It enabled us to make quantitative measurements of radiant energy from $\lambda = 0.4\mu$ to $\lambda = 2.0\mu$.

For the same source of light energy, the radiomicrometer always gave the same deflection and returned quickly to zero; showing that our efforts to eliminate magnetic materials from the wire loop had been very successful. The conduct of the completed instrument has demonstrated that the suspended system is very free from paramagnetic disturbances. The diamagnetic materials composing the junction were all arranged at right angles to the lines of force of the magnetic field, and in this way diamagnetic disturbances were reduced to a minimum. The use of the radiomicrometer has shown that the heat capacity of the junction is sufficiently low to be within the desired limit. The compensating junction and its insulation from temperature changes practically removed any drift of the zero point. The zero point for weeks at a time would not drift more than 10 cm. on either side of the zero. In case there was any drift during the measurements, it was always very slight and the proper correction could easily be applied. The insulation from vibrations made the reflected beam upon the scale fairly steady, even when there were rather violent disturbances in the building. There is every reason to suppose that the scale could be read to about one-quarter of a millimeter when the building was quiet. Duplicate readings under ordinary conditions nearly always agreed to within 0.5 mm.

The Spectroscope.—The grating spectroscope was designed and built in the Physical Laboratory under the direction of Prof. John A. Anderson. The use of such a spectroscope presents two especially desirable advantages. First, the position of regions of absorption can be very accurately determined; second, due to its high resolving power, the structure of even the very narrow absorption bands and some absorption lines can be studied in detail. The spectroscope is so constructed that either the photographic plate or any of the radiometric instruments can be used with it. The use of the radiomicrometer enables us to determine not only the actual positions of regions of absorption, but also to make quantitative measurements of the light transmitted by a solution, for a wide range of wave lengths. The deflections of the radiomicrometer give an accurate measure of the relative intensities of the different absorption bands, and of the different parts of the same bands. It will thus be seen that the radiometric method has distinct advantages over the photographic method, which is chiefly useful in determining the positions of regions of absorption and the general characteristics of the visible spectrum as transmitted by the solutions. Moreover, the photographic plate is only sensitive from $\lambda = 0.2\mu$ to $\lambda = 0.76\mu$, whereas, with the radiomicrometer and the apparatus used in this work, quantitative measurements of absorption could be made from $\lambda = 0.4\mu$ to $\lambda = 2.0\mu$, using slits only 1 mm. in width. Considering the high dispersion that could be obtained with the four inch grating, this width of slit gives a very pure spectrum.

The plane four inch grating with which the spectroscope is equipped, was ruled by Anderson; and the ruling is of such a character that a very bright first order spectrum is produced. This is quite essential for radiometric measurements in the visible region of the spectrum. Energy measurements were made in both first order spectra, one being on each side of the central image. The spectrum on one side was found to be somewhat more intense, and therefore this brighter side was used.

If either the intensity of the light source, or the sensitiveness of the radiomicrometer exceeds certain limits, it is possible that light energy from the second order spectrum will vitiate the energy measurements made in the first order spectrum. This will be readily seen if we consider that wave length of light $\lambda = 0.35\mu$ of the second order overlaps wave length of light $\lambda = 0.7\mu$ of the first order, etc. Therefore, it was desired to know if, with a Nernst glower burning at 0.8 amperes and 120 volts, the second order spectrum had sufficient energy to be detected by the radiomicrometer. If such proved to be the case, it would be found necessary to introduce color screens to eliminate the light energy from the second order spectrum. That the first order spectrum can be regarded as pure is shown by the following considerations.

Glass cuts off all wave lengths of light beyond $\lambda = 0.35\mu$. Since the glass in the path of the light is of considerable thickness, the first order spectrum is not contaminated with any light from the second order spectrum as far out as $\lambda = 0.7\mu$ of the first order. A solution of copper sulfate is entirely transparent to all wave lengths of light shorter than $\lambda = 0.6\mu$. A 10 mm. depth of a saturated solution of copper sulfate shows complete absorption beyond $\lambda = 0.6\mu$. Using the above solution of copper sulfate, radiometric measurements were made from $\lambda = 0.4\mu$ to $\lambda = 1.3\mu$. Beyond $\lambda = 0.6\mu$ the solution of copper sulfate is entirely opaque, and therefore no evidence of light energy from the second order was obtained as far out as $\lambda = 1.3\mu$. It has already been shown that the first order spectrum is pure up to $\lambda = 0.7\mu$, and the above shows that the light from the overlapping second order spectrum does not contain a sufficient amount of energy to be detected by the radiomicrometer as far out in the infra-red as $\lambda = 1.2\mu$ of the first order spectrum. The radiometric measurements of the dissociation constants of the indicators were all made between $\lambda = 0.5\mu$ and $\lambda = 0.6\mu$, and in this region the first order spectrum is absolutely pure.

The drum head which rotated the grating through definite angles is a large one, its diameter being four inches. It is attached to a very carefully constructed screw, so designed that each complete revolution changes the wave length of light falling on the slit by approximately 500 Ångstrom units. The drum contains five hundred divisions, and, all things considered, it is quite probable that the wave length settings are accurate to within one or two Ångstrom units.

The spectroscope is of the Littrow mounting, the same lens serving both as telescope and collimator. It is provided with two four inch lenses made by Brashear. One lens has a focal length of 72 inches and is intended for photographic work. The other, and the one which was used in this work, has a focal length of 30 inches. With this lens, the visible first order spectrum at slit s_2, has a length of over six inches. Provision has also been made for the mounting of a large glass prism on the grating table, and it is purposed to use this prism when an intense first order spectrum is desired, rather than a spectrum which is widely dispersed. Had we not been successful in constructing a very sensitive radiomicrometer, it would have been necessary to make frequent use of the glass prism.

The spectroscope was placed in a brass box, blackened on the inside, which prevented stray sources of light from reaching the grating. The slits were of the bilateral type.

The calibration curve for the grating and drum head was calculated from the known grating space, by means of the equation:

$$\lambda = 33{,}866.7 \sin \frac{3000T + 6R}{3500}$$

where T is the number of complete turns of the screw which rotates the grating, and R is the reading on the drum. The calibration was also effected by observing the positions of various mercury, sodium and lithium lines. It was decided that the calculated values are more accurate than the observed; and, accordingly, the dispersion curve based on the calculated values was used.

Source of Light.—A Nernst glower served as the source of light, the electrical energy being supplied by a series of storage batteries. By means of a rheostat, the light intensity could be kept quite uniform. The glower was protected from air drafts by means of a box of asbestos wood. Provision was also made for the mounting of a nitrogen lamp,[1] when it was desired to secure large deflections of the radiomicrometer for wave lengths of light shorter than $\lambda = 0.5\mu$.

The Cells.—A very important part of the equipment is the cells which contain the solutions to be investigated. There are two cells both made as nearly alike as possible. The cell consists of two brass cylinders which closely telescope into one another. One end of each cylinder is closed by a glass plate held in position by Wood's fusible metal. The four glass ends used in the cells are all of the same thickness, *i. e.*, 2 mm. Their surfaces are plane, and are parallel to within five wave lengths of light. It is a difficult problem to set these plates in the brass cylinder with Wood's fusible metal, without warping them and destroying their plane-parallelism. The character of the interference fringes which the plates gave with the mercury arc determined when they were correctly adjusted. A fine thread was "chased" on the outer cylinder. This thread carried a nut which, when turned, raised or lowered the inner cylinder a definite amount. Each complete revolution of this nut changed the distance between the plates by 1 mm. The nut contained 100 divisions, and by means of this arrangement we could readily adjust the depth of the solutions to within less than 0.01 mm. Each cell was then filled with a layer of water 5 mm. in depth, and the deflections given by the radiomicrometer were noted for a light source of uniform intensity throughout the whole region of the spectrum under investigation, namely, from $\lambda = 0.4\mu$ to $\lambda = 2.0\mu$. The deflections should agree with each other very closely for all wave lengths of light, if the cells are optically identical. Having made sure that the cells are optically identical, they were heavily plated with gold to remove any possibility of the solutions attacking the metals of the cell. It is very important to keep the solutions perfectly clear when measurements are being made, and the glass ends must be maintained absolutely clean. The following table shows the optical identity of the two cells. Under Cell A and Cell B are given the actual radiomicrometer deflections for various wave lengths of light (Table I).

Having discussed the principal parts of the apparatus, *viz.*, the radiomicrometer, spectroscope, source of light, and the cells; and having shown how they meet the requirements demanded by work of this character, it is desirable to consider next the general arrangement of the various parts.

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[1] Dr. W. R. Whitney of the General Electric Co. very kindly supplied us with two lamps of special design to be used for this purpose.

TABLE I.

λ = Å. U.	Cell A.	Cell B.	λ = Å. U.	Cell A.	Cell B.
4546	4	4	8029	125.0	125.0
4797	8.2	8.2	8275	127.0	127.5
5047	14.2	14.5	8520	129.0	129.0
5298	22.0	22.5	9009	129.5	130.0
5548	31.5	31.5	9497	115.5	115.0
5797	41.5	41.7	9982	105.5	106.0
6046	50.5	50.5	10465	113.5	114.0
6295	60.7	60.5	10946	108.5	108.0
6543	70.5	71.2	11424	69.0	69.0
6792	86.7	86.5	11900	51.5	52.0
7041	100.5	100.0	12373	56.0	56.0
7290	107.7	107.7	12843	53.5	54.0
7536	114.0	114.5	13314	34.0	34.0
7784	120.5	120.5	13775	11.0	10.7

Arrangement of Apparatus.—The Nernst glower, lenses, prisms and carriage for the cells were mounted on an upright steel standard placed by the side and near the end of the spectroscope next to the radiomicrometer. Parallel light from the Nernst glower was made to pass, by means of a carefully adjusted sliding carriage, first through one cell and then through the other. The two cells could thus be made to occupy the same position in the path of the light. The light transmitted by the solutions contained in the cells was then deflected by means of a right angle prism and focused on the slit of the spectroscope s_1. Inside of the box inclosing the spectroscope and directly in the rear of slit s_1, was placed another right angle prism which reflected the light through a four inch lens to the grating. The dispersed light was reflected back through this same lens and focused on the slit of the spectroscope s_2. The light which emerged through slit s_2 was again brought to a focus on the junction of the radiomicrometer. By turning the drum head of the spectroscope to the proper points, we could then determine quantitatively the light transmitted by any solution for all wave lengths of light between $\lambda = 0.4\mu$ and $\lambda = 2.0\mu$.

The Differential Method.—It was desired to measure the absolute percentage transmission of 20 mm. of solution. This was done by a differential method which eliminated corrections for reflection from the glass ends, and differences in the refractive index of the glass and the solutions. The method of procedure is as follows: Cell A is filled with 21 mm. of solution; cell B with 1 mm. of solution. Light of unvarying intensity I_o, was then passed through cell A, and the intensity of the transmitted light I_I measured by means of the radiomicrometer. As soon as possible cell B was made to occupy the same position formerly occupied by cell A, and the intensity of its transmitted light I_{II} determined. The deflection produced when cell A was in the path of light, divided by that given when cell B occupied the same position, determines the absolute percentage transmission for 20 mm. of solution; or, in other words, I_I/I_{II} is the value desired. The justification for this procedure is seen from what follows.

If the depth of solution under investigation is l, the intensity of the incident light I_0, and that of the transmitted light I, we have the following relations for depths of solution l' and l''.

$$I_I = I_0 \, e^{-kl'} \qquad (a)$$

$$I_{II} = I_0 \, e^{-kl''}. \qquad (b)$$

Dividing a by b we get

$$I_I/I_{II} = e^{k(l''-l')}. \qquad (c)$$

But the actual percentage transmission of the same solution of depth $l' - l'' = l$ is given by

$$I/I_0 = e^{-k(l'-l'')} = e^{-k(l''-l')}, \quad \text{or} \quad I_I/I_{II} = I/I_0. \qquad (d)$$

Theoretical Discussion.—The Ostwald[1] theory of indicators, explaining first the cause of color, and second, the difference in sensitiveness of various indicators towards different acids and bases, has been found to be inadequate. Concerning the latter, which is by far the most important side of the indicator question, the Ostwald interpretation is substantially correct. But in consideration of well known relations between the color and structure of organic compounds, and of the researches of Bernthsen,[2] Nietzi and Burckhart,[3] Hantzsch[4] and others, it has been found necessary to modify the Ostwald view as to the cause of color. The facts and relations brought out by these investigations have been correlated and interpreted by Stieglitz[5] in the so-called chromophoric theory of color. A. A. Noyes,[6] in a quantitative application of the theory of indicators to volumetric analysis, has also fully explained the significance of the chromophoric theory. According to this theory it is necessary to consider an indicator solution as containing a mixture of two tautomeric substances of different structural types. The ionization constants of the two forms and the equilibrium relations between them are such that when the indicator exists as a slightly ionized acid or base, one form is present in greatly predominating quantity. The other form largely predominates when the indicator exists as a highly ionized salt.

Considering phenolphthalein, the ionization constant K_i, according to the Ostwald conception is expressed by the simple equilibrium equation:

$$\overset{+}{H} \times \overset{-}{P} = K_i \times PH \qquad (1)$$

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[1] *Lehrbuch der all. Chem.*, **1**, 799 (1891).

[2] *Chem. Zeit.*, 1956 (1892); also Friedländer, *Ber.*, **26**, 172, 2258 (1893).

[3] *Ber.*, **30**, 175 (1897).

[4] *Ibid.*, **32**, 583, 3085 (1899).

[5] THIS JOURNAL, **25**, 1112 (1903).

[6] *Ibid.*, **32**, 815 (1910).

The chromophoric theory, as Stieglitz[1] has shown, requires two such equations, (*a*) and (*b*).

$$LH \times k = QH \qquad (a)$$

$$\overset{-}{Q} \times \overset{+}{H} = K' \times QH \qquad (b)$$

where *k* is the stability constant expressing the equilibrium relation between the two tautomeric acids. The acid represented by LH is assumed to be a pseudo- or an extremely weak acid; and that by QH is the true acid. Its ionization constant K′ is of such a magnitude that the quinoid salt is formed in greatly predominating quantity in the presence of alkalies, the stability constant *k* acting so as to maintain the equilibrium relation between the two tautomeric acids. The ionization constant for phenolphthalein is the product of the stability constant *k*, and the ionization constant K′ of the acid QH; or combining *a* and *b* and incorporating *k* and K′ into K_i we have:

$$\overset{-}{Q} \times \overset{+}{H} = K_i \times LH \qquad (2)$$

The above equations illustrate the fundamental differences between the two color theories; and accepting the Stieglitz interpretation of K_i according to Equation 2, the theory underlying the calculation of the dissociation constant of methyl orange from radiometric measurements will be discussed.

Methyl orange is in reality a weak base. Noyes[2] has deduced a general expression for the equilibrium relations of any pair of tautomeric bases and their ions. This deduction involves three fundamental equations. Expressing the equilibrium relation *k*, between the quinoid and azo-base, it being understood that the symbols represent gram-molecular or gram-ionic concentrations, we have:

$$\frac{QOH}{AzOH} = k. \qquad (3)$$

The quinoid base and the azo-base are also in equilibrium with their ions according to 4 and 5 —

$$\frac{\overset{+}{Q} \times \overset{-}{OH}}{QOH} = K_{QOH}, \qquad (4)$$

$$\frac{\overset{+}{Az} \times \overset{-}{OH}}{AzOH} = K_{AzOH}. \qquad (5)$$

Multiplying 3 by 4 and adding 5 to the product, we obtain:

$$\frac{\overset{+}{Q} \times \overset{-}{OH} + \overset{+}{Az} \times \overset{-}{OH}}{AzOH} = k \times K_{QOH} + K_{AzOH}, \qquad (6)$$

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[1] *Loc. cit.*

[2] THIS JOURNAL, **32,** 818 (1910).

and substituting in the denominator for AzOH its value $\frac{\text{AzOH} + \text{QOH}}{1 + k}$, it follows that—

$$\frac{\overset{+}{\text{Q}} \times \overset{-}{\text{OH}} + \overset{+}{\text{Az}} \times \overset{-}{\text{OH}}}{\text{AzOH} + \text{QOH}} = \frac{k \times \text{K}_{\text{QOH}} + \text{K}_{\text{AzOH}}}{1 + k}. \tag{7}$$

Letting the above equal K_i, we have:

$$\frac{\overset{-}{\text{OH}}(\overset{+}{\text{Az}} + \overset{+}{\text{Q}})}{\text{AzOH} + \text{QOH}} = \text{K}_i. \tag{8}$$

Noyes has called attention to the fact that for a satisfactory two-color indicator such as methyl orange, the sum of the two tautomeric bases (AzOH + QOH), must be substantially equal to AzOH; and that the sum of the two ions $(\overset{+}{\text{Q}} + \overset{+}{\text{Az}})$ must be substantially identical with $\overset{+}{\text{Q}}$. It therefore follows:

$$\frac{\overset{-}{\text{OH}} \times \overset{+}{\text{Q}}}{\text{AzOH}} = \text{K}_i, \tag{9}$$

where K_i expresses the equilibrium relations of the two tautomeric bases and their ions, and is substantially the equation derived by Stieglitz.[1]

Combining Equation 9 with that of the ion product of water $\overset{+}{\text{H}} \times \overset{-}{\text{OH}} = \text{K}_w$, we get:

$$\frac{\overset{+}{\text{H}} \times \text{AzOH}}{\text{Q}^{+}} = \frac{\text{K}_w}{\text{K}_i} = \text{K}_{(\text{hydrolysis})} \tag{10}$$

which is in reality the familiar equation of Walker[2] $\left(\frac{\text{acid} \times \text{base}}{\text{salt}} = k\right)$.

Having determined the hydrolysis constant according to Equation 10, the ionization constant K_i of methyl orange as a base can readily be obtained. The procedure, then, is to determine by radiometric measurements, the concentrations of $\overset{+}{\text{Q}}$, $\overset{+}{\text{H}}$ and AzOH in solutions of methyl orange containing varying amounts of these constituents. A method was developed whereby the concentration of the quinoid ions $\overset{+}{\text{Q}}$ in Equation 10 could be determined from the light transmitted by the indicator solutions. The percentage transmissions for these solutions were given by the radiomicrometer deflections. The method will be made clear by the following theoretical considerations applied to methyl orange.

If we consider light to pass through an absorbing solution of depth l, the solvent itself having no absorption, the rate of change of intensity $d\text{I}$ is given by

$$d\text{I} = -k\text{I}dl. \tag{11}$$

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[1] THIS JOURNAL, **25**, 1112 (1903).

[2] *Z. physik. Chem.*, **4**, 324 (1889).

The constant k depends only on the wave length of light and the nature of the absorbing medium. If I_0 denotes the intensity of the incident light, then, when $l = 0$, $I_0 = I =$ constant. Integrating, the intensity of the transmitted light I given by an absorbing solution of depth l and concentration c is—

$$I = I_0 \, e^{-klc}. \qquad (12)$$

If the solution has a second absorbing component, the light transmitted by it will be:

$$I_1 = I_0 \, e^{-k'l'c'}. \qquad (13)$$

Since the total transmission is the product of the separate transmissions, we have for the actual percentage transmission of a solution containing two absorbing components such as methyl orange:

$$I/I_0 = e^{-klc - k'l'c'}; \text{ or } \ln (I/I_0) = -klc - k'l'c'. \qquad (14)$$

Since the depth of solution was maintained constant (20 mm.), the above equation becomes—

$$\ln (I/I_0) = -Kc - K'c'. \qquad (15)$$

Applying this equation to methyl orange, let c represent the concentration of the quinoid salt or Q in Equation 10, and c' that of the azo-base. If T is the total quantity of methyl orange in solution, then $c' = (T - c)$; or since a dibasic acid was used, *viz.*, sulfuric acid, $c' = (T - 2c)$. When a pure solution of methyl orange is slightly acidified with sulfuric acid, and not all of the azo-base converted into the quinoid salt, both c and c' are present. The light transmitted by such a solution will be:

$$\ln (I/I_0) = -Kc - K'(T - 2c). \qquad (16)$$

In a pure aqueous solution of methyl orange, or one containing an excess of alkali, $c = 0$, therefore, Equation 15 reduces to:

$$\ln (I/I_0)' = -K'c' = -K'T. \qquad (17)$$

If to a solution of methyl orange sufficient sulfuric acid is added to convert all of the azo-base into the quinoid salt and completely suppress hydrolysis, $c' = 0$, and Equation 15 becomes:

$$\ln (I/I_0)'' = -Kc = -K\,T/2. \qquad (18)$$

From Equations 16, 17 and 18, K and K′ can be eliminated, and solving for c we obtain:

$$c = \frac{T[\ln (I/I_0) - \ln (I/I_0)']}{2[\ln (I/I_0)'' - \ln (I/I_0)']}. \qquad (19)$$

In the above equation $(I/I_0)'$ is the percentage transmission for the solution of pure methyl orange for some given wave length of light; $(I/I_0)''$ the percentage transmission of the solution containing an excess of acid for the same wave length, and (I/I_0) the percentage transmission for the same wave length of the solution whose quinoid salt concentration c, is to be determined.

Returning now to the fundamental hydrolysis equation for methyl orange previously derived:

$$\frac{\overset{+}{\mathrm{H}} \times \mathrm{AzOH}}{\mathrm{Q}^{+}} = \frac{\mathrm{K}_w}{\mathrm{K}_i},$$

we can readily insert the proper values knowing the total concentration of methyl orange T, and having determined by radiometric means the quinoid salt concentration c. Q is equal to $2c$. AzOH $= c' = \mathrm{T} - 2c$. $\overset{+}{\mathrm{H}}$ is given by $2(\mathrm{T}' - c)$, where T′ represents the total quantity of acid added. It is assumed that the dissociation of these extremely dilute solutions is practically complete. The sulfonic acid group can have but little effect upon the hydrogen ion concentration, since benzenesulfonic acid[1] is as strong as sulfuric acid, being dissociated at 25° to the extent of 90% for a dilution $v = 32$. As Stieglitz[2] has pointed out the whole behavior of methyl orange is that of a very weak base, and the elimination of the sodium sulfonate group from it leaves dimethylaniline azobenzene, which shows all the characteristics of methyl orange as an indicator.

It will be noticed from Equation 10 that it is necessary to know the ionization constant for water, before the constant for the indicator can be calculated from its hydrolysis constant. The generally accepted value of K_w at 25° is 1.2×10^{-14}. It was desired to know the value of the constant at 20°, since, unless otherwise stated, it was at this temperature that all measurements were made. Owing to the large value of the heat of ionization of water, the value of its ionization constant is much less at 20° than at 25°. Just what this change is may be calculated from the well known Van't Hoff formula:

$$\ln \frac{\mathrm{K}_1}{\mathrm{K}_2} = \frac{q\,(\mathrm{T}_2 - \mathrm{T}_1)}{\mathrm{R}(\mathrm{T}_2 \times \mathrm{T}_1)} \qquad (20)$$

where K_1 and K_2 represent the ionization constants for water at temperatures T_1 and T_2. R_1 is the gas constant which equals 1.986 calories per degree, and q is the heat of ionization of water or 13,700 calories. Inserting these values in Equation 20, $\mathrm{K}_w = 0.81 \times 10^{-14}$ at 20°. This value was used for the calculation of the ionization constants of both methyl orange and phenolphthalein.

Experimental Work on Methyl Orange.—Before discussing the tables showing the results of the calculations based on the above deductions, it will perhaps be of interest to consider a few of the more important results of the preliminary work on methyl orange. Two mother solutions of known concentrations were prepared, the one being methyl orange and the other sulfuric acid. All solutions were made up at 20°, and carefully

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[1] Publication of the Carnegie Institution of Washington, No. **170**, 128 (1912).

[2] THIS JOURNAL, **25**, 1117 (1903).

purified substances dissolved in conductivity water, were employed in all cases. A number of test solutions were prepared from the mother solutions, all of which contain equal amounts of methyl orange but different amounts of sulfuric acid. The volume of each solution was 100 cc. The solutions thus presented a series of color shades, ranging from yellow to deep red. The percentage transmissions I/I_0, were taken with a 20 mm. depth of each solution for the same four or five wave lengths of light. The region of the spectrum to be studied is given by the ascending arm of the transmission curve for methyl orange. This region for the above named indicator is between $\lambda = 0.56\mu$ and $\lambda = 0.59\mu$. The radiomicrometer deflections in this region are necessarily small, and certain variations which appear in the data can be explained in a large measure as due to the vibrations of the building, which often prevented accurate readings.

Special attention is called to a solution of methyl orange containing an excess of alkali, and another solution containing an excess of acid. Equation 19 shows that the calculation of c depends not only on the percentage transmission of the solution in question, but also on the percentage transmission for a solution in which all of the methyl orange exists as the azo-base, and one in which all of the indicator has been converted into the quinoid salt. It is thus necessary to know if any alkali must be added to convert all of the methyl orange into the azo-base and to prevent hydrolysis; and also how much acid is required to form the quinoid salt and to completely suppress hydrolysis. Furthermore, the stability of these solutions must be considered.

Table II shows that in a pure aqueous solution of methyl orange, there is no appreciable hydrolysis, and that practically all of the indicator exists as the azo-base. It is, therefore, not necessary to add alkali in determining the value of $(I/I_0)'$ in Equation 19. The volume of all solutions used in Table II was 100 cc. and each solution contained the same amount of methyl orange.

I Methyl orange in pure water.
II Methyl orange plus 1 cc. *N* sodium hydroxide.
III Methyl orange plus 2.5 cc. *N* sodium hydroxide.

TABLE II.

I/I_0 for depth of solution = 20 mm.

λ = Å. U.	I.	II.	III.
5648	70.3	71.2	70.5
5698	79.3	78.8	79.0
5748	84.6	86.0	84.8
5797	90.0	90.0	88.5
5847	91.4	92.2	90.0

Table III gives results for three solutions of methyl orange, each containing an excess of acid and the same amount of indicator diluted to 100 cc.

I Methyl orange plus 0.2 cc. concentrated sulfuric acid.
II Methyl orange plus 0.5 cc. concentrated sulfuric acid.
III Methyl orange plus 1.0 cc. concentrated sulfuric acid.

TABLE III.

I/I_0 for depth of solution = 20 mm.

λ = Å. U	I.	II.	III.
5698	15.2	15.2	16.6
5723	20.2	20.1	20.1
5748	30.7	31.2	31.9
5773	39.5	39.2	38.8
5797	48.7	49.2	48.1
5823	55.0	53.8	55.3
5847	61.4	62.6	63.2

It is obvious from Table III, that 0.2 cc. of the acid is sufficient to convert all of the azo-base into the quinoid salt and to suppress hydrolysis completely.

Stable solutions of methyl orange are given only when the concentration is less than 2×10^{-4} gram molecules per liter. Considerable difficulty was encountered during the preliminary work, owing to the fact that the indicator solutions were more concentrated than the above named limit. Such solutions of methyl orange, especially those containing a large excess of acid and also those with enough acid to give an intense red color, gradually become more transparent on standing. The action of light very greatly accelerates this bleaching process. The solutions most susceptible to the action of light and of time are those containing the greatest amounts of acid. It was found that these solutions could be kept in the dark for four or five hours unchanged, and that as soon as they were exposed to the light, bleaching again took place. Experiments were made which showed that light of the shorter wave lengths was more actinic in increasing the transparency of the solutions than light of longer wave lengths. The addition of ten per cent of ethyl alcohol rendered these solutions fairly stable against the action of light and time After standing for a day or two, solutions containing an excess of acid often showed the presence of fine crystals. Large amounts of these crystals could be obtained by strongly acidifying a saturated solution of methyl orange. It is thought that the formation of these crystals, very probably helianthine itself, causes the instability of the solutions in question. The obvious procedure to follow was to use more dilute solutions, which were found to be quite stable, and even the solution containing the excess of acid would remain practically unchanged when exposed to the action of light for a short time. However, when the concentration of methyl orange approximated 2×10^{-4} gram-molecules per liter, as is the case for the solutions given in Table IV, the solution containing an excess of acid was prepared last and its percentage transmission measured immediately. The remaining solutions were kept in the dark until used. It is certain that when such precautions are taken, no appreciable change in transparency could occur before the radiometric measurements were completed. Table III, the concentration of the methyl orange being 1.98×10^{-4} gram-molecules per liter, shows that even the solutions containing an excess of acid can be safely used in this way.

The following shows how accurately small concentrations of hydrogen and hydroxyl ions can be estimated by radiometric measurements. If the percentage transmission for the various solutions be plotted as curves, the abscissas being wave lengths and the ordinates percentage transmissions, it will be noted that with increasing amounts of acid the transmission curve for pure methyl orange is widely displaced towards the red end of the spectrum. The solution curve corresponding to the excess of acid is displaced about 400 Ångstrom units from the curve corresponding to a pure aqueous solution of methyl orange. From the displacements produced by solutions containing known amounts of acid, and the displacement given by a solution containing an unknown amount, the concentration of the unknown amount of acid can be quite accurately and quickly determined. In one case a solution was prepared containing an amount of sulfuric acid unknown to us. The concentration of the acid was determined by the above method, and the value found was 0.00000216 gram per cc. The amount actually present was 0.00000210 gram per cc. Several similar attempts were made and they were quite as successful.

Results with Methyl Orange.—The hydrolysis and ionization constants for methyl orange, recorded in Tables V and VII, are to be regarded as part of the preliminary work. Table IV contains the percentage transmissions for nine solutions of methyl orange prepared in accordance with the scheme given below. The concentration of the mother solutions of methyl orange was 3.973×10^{-4}; that of the mother solution of sulfuric acid 3.0885×10^{-4} gram-molecules per liter.

SOLUTIONS.

I 50 cc. methyl orange, diluted to 100 cc.
II 50 cc. methyl orange, 5 cc. sulfuric acid, diluted to 100 cc.
III 50 cc. methyl orange, 10 cc. sulfuric acid, diluted to 100 cc.
IV 50 cc. methyl orange, 15 cc. sulfuric acid, diluted to 100 cc.
V 50 cc. methyl orange, 20 cc. sulfuric acid, diluted to 100 cc.
VI 50 cc. methyl orange, 30.9 cc. sulfuric acid, diluted to 100 cc.
VII 50 cc. methyl orange, 35 cc. sulfuric acid, diluted to 100 cc.
VIII 50 cc. methyl orange, 1.0 cc. conc. sulfuric acid, diluted to 100 cc.
IX 50 cc. methyl orange, 2.0 cc. conc. sulfuric acid, diluted to 100 cc.

TABLE IV.

I/I_0 for depth of solution = 20 mm.

λ = Å. U.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	Average of VIII and IX.
5748	84.6	..	71.9	65.1	57.7	49.1	46.7	9.5	8.4	8.95
5798	90.0	85.6	79.3	73.3	70.0	62.2	61.0	22.1	22.1	22.1
5847	91.4	..	84.6	81.4	77.9	70.3	..	35.7	35.7	35.7

Attention is called to the blank spaces appearing in some of the tables. For some solutions and certain wave lengths of light no transmission values were obtained. It was known at the time the measurements were made that certain transmission values were erroneous, due either to variations in the current intensity or to vibrational disturbances. The action of light, as has been previously explained, renders these solutions of methyl orange more transparent, and for this reason it was necessary to complete the reading as soon as possible. This excluded the possibility of remeasuring the percentage transmissions made when conditions were unfavorable for accurate readings.

Table V gives the quinoid salt and azo-base concentrations of each of the above solutions, the hydrolysis constant (K_w/K_i), and the ionization constant K_i of methyl orange as a base.

TABLE V.

Solution.	λ = Å. U.	Azo-base $c' \times 10^4$.	Quinoid salt. $c \times 10^5$.	$K_w/K_i \times 10^4$.	$K_i \times 10^{11}$.
II.......	5798	1.91	0.353	6.5	1.3
III.......	5748	1.84	0.716	6.1	1.3
	5797	1.80	0.897	4.4	1.8
	5847	1.82	0.813	5.1	1.6
IV.......	5748	1.75	1.16	5.2	1.6
	5797	1.69	1.46	3.7	2.2
	5847	1.74	1.23	4.8	1.7
V.......	5748	1.64	1.69	4.4	1.9
	5797	1.63	1.78	4.0	2.0
	5847	1.65	1.68	4.4	1.8
VI.......	5748	1.50	2.41	4.5	1.8
	5797	1.46	2.61	3.9	2.0
	5847	1.43	2.76	3.5	2.3
VII.......	5847	1.46	2.62	4.6	1.8
	5797	1.46	2.65	4.5	1.8
				Av., 4.5×10^{-4}	Av., 1.8×10^{-11}

The calculations of the hydrolysis and ionization constants are based on logarithmic functions; and where the transmission of the solution is nearly complete, a slight variation from the actual percentage transmission will cause a great change in the calculated hydrolysis and ionization constants. If we consider an experimental case where the amount of absorption to be measured is slight, the above can be made quite clear. Solution II in Table IV for wave length of light λ = 5798 Å. U. actually gave a percentage transmission of 85.6. Changing the percentage transmission by small amounts, and calculating the value of the hydrolysis and ionization constants from these values, we obtain:

I/I_0.	K_w/K_i.	K_i.	
85.6	6.46×10^{-4}	1.25×10^{-11}	found experimentally
86.0	7.21×10^{-4}	1.12×10^{-11}	
86.6	8.59×10^{-4}	0.94×10^{-11}	

It will thus be seen that changing the percentage transmission by about 1% will cause a variation in the ionization constant of about 25%. When conditions are not satisfactory, it is quite possible that the error in some of the percentage transmissions may be greater than one per cent. Considering these facts, the constants show that the efforts which were made to eliminate errors arising from variations of the current intensity and vibrational disturbances, were fairly successful.

The transmission values given in Table VI are for a much more dilute solution of methyl orange. The concentration of the mother solution of methyl orange was 1.9865×10^{-4} gram-molecules per liter; that of the mother solution of sulfuric acid being 3.0885×10^{-4} gram-molecules per liter.

SOLUTIONS.

I 50 cc. methyl orange, diluted to 100 cc.
II 50 cc. methyl orange, 10 cc. sulfuric acid, diluted to 100 cc.
III 50 cc. methyl orange, 15 cc. sulfuric acid, diluted to 100 cc.
IV 50 cc. methyl orange, 20 cc. sulfuric acid, diluted to 100 cc.
V 50 cc. methyl orange, 1 cc. conc. sulfuric acid, diluted to 100 cc.
VI 50 cc. methyl orange, 0.5 cc. conc. sulfuric acid, diluted to 100 cc.
VII 50 cc. methyl orange, 0.2 cc. conc. sulfuric acid, diluted to 100 cc.
VIII 50 cc. methyl orange, 0.5 cc. conc. sulfuric acid, diluted to 100 cc.

TABLE VI.

I/I_0 for depth of solution = 20 mm.

λ = Å. U.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	Average V, VI, VII and VIII.
5698	87.7	75.3	67.6	66.3	16.6	15.2	15.2	17.1	16.0
5723	88.9	80.7	74.2	72.3	20.1	20.1	20.2	..	20.1
5748	90.3	83.7	79.8	76.6	31.9	31.2	30.7	30.3	31.3
5773	91.6	..	81.7	81.3	38.8	39.0	39.5	41.1	39.9
5797	93.5	88.9	85.1	84.4	48.1	49.2	48.7	47.5	48.4
5823	94.5	91.3	87.0	86.2	55.3	53.8	55.0	56.4	55.1
5847	95.6	91.7	..	88.2	63.2	62.6	61.4	61.7	62.2

The constants given in Table VII are calculated from the values in Table VI.

The ionization constants for methyl orange, recorded in Tables V and VII, do not by any means represent the most accurate values that can be obtained by this radiometric method. It is necessary that the measurements be made in a region of the spectrum where the light energy is not intense, and, consequently, the deflections of the radiomicrometer are small. The largest deflection that could be obtained for wave lengths of light $\lambda = 0.58\mu$ was 60 mm. It is for this reason that vibrations, and variations in the intensity of the Nernst glower, seriously interfere with the accuracy of the percentage transmissions. The temperature which prevailed at the time these measurements were made was not accurately known. However, it is certain that it was between 20° and 23°. The constants were calculated for 20°; therefore, there is good reason to suppose that the real constants are somewhat higher (See Table IX).

TABLE VII.

Solution.	λ = Å. U.	Azo-base $c' \times 10^5$.	Quinoid salt $c \times 10^6$.	$K_w/K_i \times 10^4$.	$K_i \times 10^{11}$.
IV............	5698	8.30	8.14	5.5	1.5
	5723	8.55	6.88	6.8	1.2
	5748	8.41	7.62	6.0	1.4
	5773	8.49	7.18	6.4	1.3
	5797	8.42	7.56	6.0	1.4
	5823	8.22	8.56	5.1	1.6
	5847	8.06	9.36	4.5	1.8
III............	5698	8.42	7.58	4.3	1.9
	5723	8.72	6.03	5.8	1.4
	5748	8.78	5.76	6.2	1.3
	5773	8.55	6.88	4.9	1.7
	5797	8.54	6.95	4.8	1.7
	5823	8.40	7.63	4.3	1.9
II............	5698	9.04	4.47	5.3	1.5
	5723	9.28	3.24	7.9	1.0
	5748	9.22	3.53	7.1	1.1
	5797	9.20	3.62	6.9	1.2
	5823	9.28	3.22	8.0	1.0
	5847	8.96	4.84	4.8	1.7
				Av., 5.8×10^{-4}	Av., 1.5×10^{-11}

The transmission values given in Table VIII, were obtained when the temperature at the time of measurement was known to be 20°. The measurements were made at night when the building was fairly free from vibrations. Under these conditions, the scale could be read accurately to 0.25 mm. Except for Solutions II and VI, the current intensity remained very constant. A different mother solution of methyl orange was used, its concentration being 3.054×10^{-4} gram-molecules per liter. The concentration of the mother solution of sulfuric acid was 3.089×10^{-4} gram molecules per liter.

SOLUTIONS.

I 50 cc. methyl orange, diluted to 100 cc.
II 50 cc. methyl orange, 10 cc. sulfuric acid, diluted to 100 cc.
III 50 cc. methyl orange, 15 cc. sulfuric acid, diluted to 100 cc.
IV 50 cc. methyl orange, 20 cc. sulfuric acid, diluted to 100 cc.
V 50 cc. methyl orange, 25 cc. sulfuric acid, diluted to 100 cc.
VI 50 cc. methyl orange, 40 cc. sulfuric acid, diluted to 100 cc.
VII 50 cc. methyl orange, 0.7 cc. conc. sulfuric acid, diluted to 100 cc.
VIII 50 cc. methyl orange, 0.8 cc. conc. sulfuric acid, diluted to 100 cc.

TABLE VIII.

I/I_0 for depth of solution = 20 mm. Temperature = 20°.

λ = Å. U.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	Average VII and VIII.
5723	88.2	71.8	63.7	58.0	51.6	..	11.8	11.6	11.7
5748	90.0	77.6	68.6	64.0	59.8	..	17.1	17.6	17.4
5773	91.6	..	75.2	71.0	67.4	..	24.8	24.9	24.9
5797	93.4	..	78.7	76.2	72.6	63.8	32.5	33.2	32.4
5848	95.4	89.6	86.6	84.5	..	75.2	49.0	49.8	49.4
5898	97.2	..	91.4	89.8	88.7	..	63.5	63.5	63.5

The values calculated from Table VIII are recorded in Table IX.

TABLE IX.

Solution.	λ = Å. U.	Azo-base $c' \times 10^4$.	Quinoid salt. $c \times 10^5$.	$K_w/K_i \times 10^4$.	$K_i \times 10^{11}$.
VI......	5797	0.975	2.76	3.4	2.4
	5848	0.975	2.76	3.4	2.4
V......	5723	1.193	1.67	4.3	1.9
	5748	1.147	1.99	3.5	2.3
	5773	1.167	1.80	3.8	2.1
	5797	1.203	1.62	4.5	1.8
	5898	1.197	1.65	4.4	1.8
IV......	5723	1.211	1.58	3.5	2.3
	5748	1.211	1.58	3.5	2.3
	5773	1.227	1.50	3.8	2.1
	5798	1.235	1.46	4.0	2.0
	5848	1.315	1.36	4.7	1.8
	5898	1.245	1.42	4.2	1.9
III......	5723	1.281	1.23	3.5	2.3
	5748	1.277	1.25	3.5	2.3
	5773	1.295	1.16	3.9	2.1
	5798	1.269	1.24	3.5	2.3
	5848	1.309	1.09	4.3	1.9
	5898	1.301	1.13	4.0	2.0
II......	5723	1.372	0.773	4.1	2.0
	5748	1.390	0.687	4.9	1.7
	5848	1.383	0.718	4.6	1.8
				Av., 4.0×10^{-4}	Av., 2.1×10^{-11}

The greatest variation from the mean is less than 20%. It has already been shown in one experimental case, that an error of 1 per cent. in the percentage transmission would cause a variation of 25 per cent. in the ionization constant. The determination of the percentage transmissions from which the constants recorded in Table IX are calculated was made under the most favorable conditions. These constants, therefore, more likely represent the true constants of the indicator.

Phenolphthalein.—Regarding phenolphthalein as a monobasic acid, we have from Equation 2:

$$\frac{\overset{-}{Q} \times \overset{+}{H}}{LH} = K_i.$$

Dividing this by the ion product of water, it follows that:

$$\frac{\mathrm{LH} \times \overset{-}{\mathrm{OH}}}{\mathrm{Q}^{+}} = \frac{\mathrm{K}_w}{\mathrm{K}_i}. \qquad (21)$$

Phenolphthalein has but one component of absorption, and the application of Beer's Law is much simpler than for methyl orange where there are two components of absorption. A solution of phenolphthalein in pure water is perfectly transparent. The addition of an excess of sodium hydroxide converts all the colorless lactoid molecules into the red quinoid salt, the concentration of which we will represent by c'. Let c be the concentration of the quinoid salt in the phenolphthalein solutions containing ammonium hydroxide and ammonium chloride. Since the depth of solution was maintained constant, we have the two fundamental equations given below:

$$\ln\ (\mathrm{I}/\mathrm{I}_0) = -\mathrm{K}c \qquad (22)$$

$$\ln\ (\mathrm{I}/\mathrm{I}_0)' = -\mathrm{K}c' \qquad (23)$$

The constant K is the same in both cases. Dividing 22 by 23 we obtain:

$$\frac{\ln\ (\mathrm{I}/\mathrm{I}_0)}{\ln\ (\mathrm{I}/\mathrm{I}_0)'} = c/c' \text{ or } c = \frac{c' \times \ln\ (\mathrm{I}/\mathrm{I}_0)}{\ln\ (\mathrm{I}/\mathrm{I}_0)'} \qquad (24)$$

Where $(\mathrm{I}/\mathrm{I}_0)'$ is the percentage transmission of a solution of phenolphthalein containing an excess of alkali, for some given wave length of light; $(\mathrm{I}/\mathrm{I}_0)$ that for the solution in which the concentration of the quinoid salt c, is to be determined for the same wave length of light. Knowing then, the amount of phenolphthalein converted into the quinoid salt, LH in Equation 21 is given by $\mathrm{T} - c$, where T represents the total amount of phenolphthalein. The hydroxyl ion concentration was varied by the addition of ammonium chloride to ammonium hydroxide.

The value of OH to be substituted in the hydrolysis equation for phenolphthalein was obtained from the following equation:

$$\frac{\overset{+}{\mathrm{NH}_4} \times \overset{-}{\mathrm{OH}}}{(\mathrm{NH}_4\mathrm{OH} + \mathrm{NH}_3)} = \mathrm{K}_b.$$

If ammonium chloride and ammonium hydroxide are present in the same solution, the concentration of the NH_4 ions is furnished almost entirely by the ammonium chloride. Let S equal the concentration of the salt and B the concentration of the base. We then have for dilute solutions:

$$\frac{\mathrm{S} \times \overset{-}{\mathrm{OH}}}{\mathrm{B}} = \mathrm{K}_b \qquad (25)$$

or

$$\overset{-}{\mathrm{OH}} = \frac{\mathrm{K}_b \times \mathrm{B}}{\mathrm{S}} \qquad (26)$$

The ionization constant for ammonium hydroxide[1] at 25° is given as 18×10^{-6}. All of the work on phenolphthalein was done at 20°, and reducing the above value to 20°, we obtain from Equation 20, q being equal to 1400 calories, $K_b = 17.4 \times 10^{-6}$.

A pure sample of phenolphthalein was recrystallized from absolute methyl alcohol. A weighed amount of purified phenolphthalein was dissolved in 50 cc. of absolute ethyl alcohol. By means of a small pipet, carefully calibrated, a small volume of this alcoholic solution, say 1.25 cc., could be quite accurately measured. This volume was diluted with conductivity water to 2000 cc. Experiments were made which showed that the effect of this small trace of alcohol was negligible. (See McCoy.[2]) The ammonia employed for the solution of ammonium hydroxide, was distilled from barium hydroxide to eliminate carbon dioxide. All solutions were prepared with conductivity water at 20°. Special care was taken to prevent carbon dioxide from coming in contact with any of the solutions.

It is well known that an excess of alkali causes a rather rapid fading of solutions of phenolphthalein. Experiments were made which showed that a very slight error would be introduced, if the solutions of phenolphthalein containing an excess of alkali were used directly after being prepared. Filling the cells with the solution, and taking radiometric measurements for five wave lengths of light, required about eight minutes, and during this short space of time, the change in transparency was found to be very slight.

A few of the experiments made with solutions of phenolphthalein containing an excess of alkali are recorded in Table X. All solutions were diluted to 100 cc., and each contained equal amounts of phenolphthalein. A normal solution of sodium hydroxide was used for these experiments. The percentage transmissions given by Solutions I and II are for 0.8 cc. and 1 cc., respectively, of the alkali. The interval which elapsed between the time the solutions were prepared and the last measurement made, was between seven and eight minutes. Measurements were again made with Solution II, fifteen minutes later. The results are recorded under III. By comparing the transmission values, the effect of the bleaching for an interval of fifteen minutes can be noted. Solution IV contained 0.5 cc. alkali, and was kept in the dark nearly a half-hour before being used. Solution V containing 1 cc. of alkali, was used about four hours after being prepared.

Similar experiments were made with solutions of phenolphthalein, partially converted into the quinoid salt, and it was found that such solutions are fairly stable. Very little change in transparency could be detected during the first four or five hours after the solutions were prepared.

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[1] Publication of the Carnegie Institution of Washington, No. 63, 298 (1907).

[2] *Loc. cit.*

TABLE X.

I/I_0 for depth of solution = 20 mm.

λ = Å. U.	I.	II.	III.	IV.	V.
5773	10.5	10.1	12.1	10.1	24.9
5798	15.2	15.4	16.5	15.2	31.0
5823	20.8	20.2	22.6	21.4	37.8
5848	28.7	27.4	30.3	28.4	45.6
5947	59.4	57.7	61.2	60.3	71.1

Results with Phenolphthalein.—The six solutions recorded below were prepared from the following mother solutions: The concentration of the phenolphthalein was 6.697×10^{-5} gram-molecules per liter; that of the ammonium hydroxide 0.1448 gram-molecules per liter, and that of the ammonium chloride 0.1 gram-molecules per liter.

SOLUTIONS.

I 75 cc. phenolphthalein, diluted to 100 cc.
II 75 cc. phenolphthalein, 2 cc. NH_4OH, 1 cc. NH_4Cl, diluted to 100 cc.
III 75 cc. phenolphthalein, 2 cc. NH_4OH, 2 cc. NH_4Cl, diluted to 100 cc.
IV 75 cc. phenolphthalein, 2 cc. NH_4OH, 5 cc. NH_4Cl, diluted to 100 cc.
V 75 cc. phenolphthalein, 2 cc. NH_4OH, 10 cc. NH_4Cl, diluted to 100 cc.
VI 75 cc. phenolphthalein, 1 cc. *N* NaOH, diluted to 100 cc.

TABLE XI.

I/I_0 for depth of solution = 20 mm. Temperature = 20°.

λ = Å. U.	I.	II.	III.	IV.	V.	VI.
5773	100.0	30.8	46.3	70.7	..	10.1
5798	100.0	37.8	53.4	76.3	86.7	14.3
5823	100.0	45.3	58.9	78.5	89.3	20.2
5848	100.0	51.7	66.2	83.0	91.3	27.4
5948	100.0	..	83.7	..	..	57.7

TABLE XII.

Solutions.	λ = Å. U.	Lactoid form $c \times 10^5$.	Quinoid salt $c \times 10^5$.	$OH \times 10^5$.	$K_w/K_i \times 10^5$.	$K_i \times 10^{10}$.	Average $K_i \times 10^{10}$.
II..........	5773	2.44	2.58	5.039	4.77	1.70	..
	5798	2.51	2.51	5.039	5.05	1.60	1.63
	5823	2.54	2.48	5.039	5.17	1.57	..
	5848	2.46	2.56	5.039	4.85	1.67	..
III..........	5773	3.33	1.69	2.519	4.96	1.64	..
	5798	3.40	1.62	2.519	5.27	1.54	..
	5823	3.35	1.67	2.519	5.06	1.60	1.56
	5848	3.42	1.60	2.519	5.38	1.51	..
	5948	3.40	1.62	2.519	5.28	1.53	..
IV..........	5773	4.26	0.757	1.007	5.68	1.43	..
	5798	4.32	0.696	1.007	6.27	1.29	1.38
	5823	4.26	0.761	1.007	5.63	1.44	..
	5848	4.30	0.720	1.007	6.02	1.35	..
V..........	5798	4.65	0.369	0.503	6.37	1.27	..
	5823	4.67	0.356	0.503	6.63	1.22	1.23
	5848	4.67	0.352	0.503	6.68	1.21	..

The percentage transmissions for these solutions are given in Table XI. The concentrations of the two tautomeric forms, and the hydrolysis and ionization constants calculated from Table XI, are recorded in Table XII.

The series of solutions, the results of which are recorded in Table XIII, were prepared from another solution of phenolphthalein. Its concentration was 4.603 × 10^{-5} gram-molecules per liter. The concentrations of the ammonium hydroxide and ammonium chloride solutions were the same as for the previous series. It will be noticed that 1 cc. of a solution of ammonium hydroxide was used instead of 2 cc. as in the former case.

SOLUTIONS.

I 75 cc. phenolphthalein, 1 cc. NH_4OH, 0.5 cc. NH_4Cl, diluted to 100 cc.
II 75 cc. phenolphthalein, 1 cc. NH_4OH, 1 cc. NH_4Cl, diluted to 100 cc.
III 75 cc. phenolphthalein, 1 cc. NH_4OH, 2 cc. NH_4Cl, diluted to 100 cc.
IV 75 cc. phenolphthalein, 1 cc. NH_4OH, 2.5 cc. NH_4Cl, diluted to 100 cc.
V 75 cc. phenolphthalein, 0.8 cc. *N* NaOH, diluted to 100 cc.

TABLE XIII.

I/I_0 for depth of solution = 20 mm. Temperature 20°.

λ=Å. U.	I.	II.	III.	IV.	V.
5773	48.2	62.2	73.0	81.3	15.7
5798	54.2	66.3	78.7	83.0	22.7
5823	59.6	70.7	83.9	86.0	30.5
5848	66.4	74.6	85.1	89.0	37.9
5948	84.8	87.7	..	94.8	62.2

TABLE XIV.

Solution.	λ=Å. U.	Lactoid form $c \times 10^5$.	Quinoid salt $c \times 10^5$.	OH × 10^5.	K_w/K_i × 10^5.	$K_i \times 10^{10}$.	Average $K_i \times 10^{10}$.
I..........	5773	2.09	1.36	5.039	7.79	1.04	..
	5798	2.03	1.42	5.039	7.24	1.12	1.14
	5823	1.95	1.50	5.039	6.56	1.23	..
	5848	1.99	1.46	5.039	6.92	1.17	..
II..........	5773	2.56	0.884	2.519	7.31	1.11	..
	5798	2.49	0.953	2.519	6.61	1.23	..
	5823	2.44	1.006	2.519	6.13	1.32	1.25
	5848	2.41	1.040	2.519	5.83	1.39	..
	5948	2.49	0.951	2.519	6.61	1.23	..
III............	5773	2.86	0.587	1.259	6.15	1.32	..
	5798	2.89	0.557	1.259	6.53	1.24	1.21
	5823	2.94	0.508	1.259	7.96	1.02	..
	5848	2.87	0.573	1.259	6.37	1.27	..
IV..........	5773	3.05	0.386	1.007	8.03	1.01	..
	5798	3.01	0.433	1.007	7.01	1.15	..
	5823	3.01	0.436	1.007	7.01	1.15	1.06
	5848	3.03	0.413	1.007	7.42	1.09	..
	5948	3.06	0.385	1.007	8.04	1.01	..

The concentrations of the mother solutions used in the preparation of the solutions for the following series of measurements, were the same as those employed for Table XI. The results are recorded in Tables XV and XVI.

SOLUTIONS.

I 75 cc. phenolphthalein, 0.5 cc. NH_4OH, 0.5 cc. NH_4Cl, diluted to 100 cc.
II 75 cc. phenolphthalein, 0.5 cc. NH_4OH, 1 cc. NH_4Cl, diluted to 100 cc.
III 75 cc. phenolphthalein, 0.5 cc. NH_4OH, 2 cc. NH_4Cl, diluted to 100 cc.
IV 75 cc. phenolphthalein, 0.8 cc. *N* NaOH, diluted to 100 cc.

TABLE XV.

I/I_0 for depth of solution = 20 mm. Temperature = 20°.

λ = Å. U.	I.	II.	III.	IV.
5773	63.2	76.2	87.3	9.9
5798	65.8	80.3	89.2	14.7
5823	72.0	82.8	91.5	20.4
5848	74.3	..	..	27.4
5948	88.8	93.3	..	57.6

TABLE XVI.

Solution.	λ = Å. U.	Lactoid form $c \times 10^5$.	Quinoid salt $c \times 10^5$.	OH × 10^5.	K_w/K_i × 10^5.	$K_i \times 10^{10}$.	Average $K_i \times 10^{10}$.
I.........	5773	4.026	0.99	2.519	10.16	0.80	..
	5798	3.935	1.09	2.519	9.07	0.99	..
	5823	3.985	1.04	2.519	9.65	0.83	0.89
	5848	3.875	1.15	2.519	8.47	0.97	..
	5948	3.955	1.07	2.519	9.28	0.87	..
II.........	5773	4.43	0.59	1.26	9.46	0.86	..
	5798	4.45	0.57	1.26	9.77	0.83	0.87
	5823	4.42	0.60	1.26	9.24	0.88	..
	5948	4.39	0.62	1.26	8.82	0.92	..
III.........	5773	4.73	0.30	0.63	10.07	0.81	..
	5798	4.73	0.30	0.63	10.00	0.81	0.79
	5823	4.74	0.28	0.63	10.65	0.75	..

The concentration of phenolphthalein is not a factor in the variations of the constants in the different tables. The following shows that it is possible to determine K_i without knowing the concentration of the indicator.

If we consider Equation 21—

$$\frac{LH \times \overline{OH}}{Q^+} = \frac{K_w}{K_i}$$

and represent the total concentration of phenolphthalein by T, and that of the quinoid salt by Q, we have from Equation 24:

$$\frac{\ln (I/I_0) \times T}{\ln (I/I_0)'} = Q.$$

LH is then equal to (T — Q) or,

$$LH = (T - Q) = T - \frac{\ln (I/I_0) \times T}{\ln (I/I_0)'}. \qquad (27)$$

Substituting these values in the hydrolysis equation, we have:

$$\frac{\left[T - \frac{\ln (I/I_0) \times T}{\ln (I/I_0)'}\right] \times \overline{OH}}{\frac{\ln (I/I_0) \times T}{\ln (I/I_0)'}} = \frac{K_w}{K_i} \qquad (28)$$

Simplifying, T, the concentration of the phenolphthalein disappears, and we have:

$$\frac{\overline{OH}[\ln (I/I_0)' - \ln (I/I_0)]}{\ln (I/I_0)} = \frac{K_w}{K_i}. \qquad (29)$$

K_i, calculated from Equation 29, gives the same value as when calculated from the equations previously derived.

Since it is not necessary to know the concentration of the indicator to determine its ionization constant, the variation of K_i, shown by the different tables, must be due to other causes. It will be noticed from the separate tables that K_i decreases with the hydroxyl ion concentration. This is in accordance with the results of previous investigators. When the hydroxyl ion concentration, or the ratio of ammonium chloride to ammonium hydroxide remains the same, K_i shows a marked decrease with decreasing amounts of neutral salts. If we consider Solutions III and I in Tables XII and XVI, respectively, it will be seen that decreasing the concentration of the neutral salt four times, changes K_i from 1.6×10^{-10} to 0.9×10^{-10}. This is in accord with the results of Rosenstein,[1] who has made a very careful study of the effect of neutral salts on the ionization constant of phenolphthalein. It will, therefore, be seen that the discrepancies in the value of K_i are due in part at least to the effect of the neutral salt. From this it might be concluded that K_i would be largest for those solutions containing the greatest amount of neutral salt. A study of the separate Tables, Table XII for instance, shows that just the reverse is true. The solution which contains the largest amount of neutral salt always gives the smallest concentration of hydroxyl ions, and the K_i value for such a solution is much lower than for a solution containing less neutral salt but a greater concentration of hydroxyl ions. It is thus evident that K_i varies not only with the concentration of the neutral salt, but also with the concentration of the hydroxyl ions. From the above, it will be seen that if the neutral salt had no effect, the variation of K_i in the separate tables would be much greater than it actually is. It is therefore obvious that the equilibrium equations, based on the assumption that phenolphthalein acts as a monobasic acid, do not hold.

[1] *Loc. cit.*

Wegscheider[1] concludes that these variations may be accounted for by regarding phenolphthalein as a dibasic acid. The results of Rosenstein[1] make it appear very probable that this indicator does act as a dibasic acid. The limitations of his method and the presence of neutral salts made it impossible for him to determine satisfactorily the ionization constant for phenolphthalein and the question must therefore be regarded as still open.

The radiometric method has thus far been applied for determining the hydrolysis and ionization constants of indicators. Knowing these values, it is possible, by radiometric means, to determine from them the hydrolysis constants of many salts. The calculation of the ionization constants of weak acids and bases formed by the hydrolysis of these salts is then a simple matter.

This method has been applied in a preliminary way to aluminum sulfate, using methyl orange as the indicator. It is assumed that the secondary and tertiary hydrolysis of this salt can be neglected, and, on this assumption, the ionization constant of the base formed by the primary hydrolysis has been calculated.

The calculations of the constants are based on two fundamental equilibrium equations, the symbols representing gram-ions per liter. Expressing the equilibrium relation for the primary hydrolysis of aluminum sulfate, we have:

$$\frac{\overset{++}{\mathrm{AlOH}} \times \overset{+}{\mathrm{H}}}{\overset{+++}{\mathrm{Al}}} = \frac{K_w}{K_b}. \qquad (30)$$

In the hydrolysis equation for methyl orange,—

$$\frac{\mathrm{AzOH} \times \overset{+}{\mathrm{H}}}{Q^+} = \frac{K_w}{K_i}.$$

K_i has been determined and K_w is known. The concentration of the quinoid ions $\overset{+}{Q}$ is given by:

$$\overset{+}{Q} = \frac{T[\ln (I/I_o) - \ln (I/I_o)']}{\ln (I/I_o)'' - \ln (I/I_o)'} \qquad (31)$$

as explained in Equation 19. If the total amount of indicator is T, $\mathrm{AzOH} = T - \overset{+}{Q}$. We then have all the data necessary for the calculation of the hydrogen ion concentration in Equation 30. The concentration of the ion $\overset{++}{\mathrm{AlOH}}$ in the same equation is given by $\overset{+}{H} + \overset{+}{Q}$, both of which have been determined. If T′ represents the total salt added and α its dissociation, $\overset{+++}{\mathrm{Al}}$ is $(T' - \overset{++}{\mathrm{AlOH}})\ \alpha$.

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[1] *Loc. cit.*

The following solutions were prepared from mother solutions of methyl orange and aluminium sulfate, the concentrations being 1.9865×10^{-4} and 0.391 gram-molecules per liter, respectively.

SOLUTIONS.

I 50 cc. methyl orange, diluted to 100 cc.
II 50 cc. methyl orange, 5 cc. $Al_2(SO_4)_3$, diluted to 100 cc.
III 50 cc. methyl orange, 7 cc. $Al_2(SO_4)_3$, diluted to 100 cc.
IV 50 cc. methyl orange, 10 cc. $Al_2(SO_4)_3$, diluted to 100 cc.
V 50 cc. methyl orange, 0.5 cc. conc. H_2SO_4, diluted to 100 cc.

The percentage transmissions given by these solutions are recorded in Table XVII.

TABLE XVII.

I/I_0 for depth of solution = 20 mm.

λ = Å. U.	I.	II.	III.	IV.	V.
5698	87.7	47.7	44.7	39.7	16.0
5723	88.9	56.7	53.1	..	20.1
5748	90.3	63.0	59.1	56.7	31.0
5773	91.6	70.2	66.8	63.6	39.9
5797	93.3	74.7	73.6	68.6	48.4
5823	94.5	78.4	78.1	75.5	55.1
5847	95.6	81.6	..	78.5	62.2

The constants calculated from these percentage transmissions are given in Table XVIII. It has been found[1] that the dissociation of the aluminium sulfate in Solutions II, III and IV, is approximately 35, 32 and 30%, respectively.

TABLE XVIII.

Solution.	λ = Å. U.	$\overset{+}{Q}$ 10^5.	Average AzOH 10^5.	Average $\overset{+}{H}$ 10^4.	Average $\overset{++}{AlOH}$ 10^4.	Average $\overset{+++}{Al}$ 10^8.	Average K_wK_b $\times 10^6$.	Average $K_b \times 10^9$.
II......	5698	3.56	..	..	...	...	..	..
	5723	3.01	..	..	...	...	..	..
	5748	3.35	..	..	...	...	..	..
	5773	3.20	6.56	1.97	2.307	6.76	6.75	1.2
	5797	3.37	..	..	...	...	..	..
	5823	3.44	..	..	...	...	..	..
	5847	3.65	..	..	...	...	..	..
III......	5698	3.94	..	..	...	...	..	..
	5723	3.44	..	..	...	...	..	..
	5748	3.94	6.24	2.24	2.609	8.66	6.75	1.2
	5773	3.79	..	..	...	...	..	..
	5797	3.50	..	..	...	...	..	..
	5823	3.51	..	..	...	...	..	..
IV......	5698	4.62	..	..	...	...	..	..
	5748	4.33	..	..	...	...	..	..
	5773	4.36	5.49	3.12	3.564	11.62	9.70	0.84
	5797	4.66	..	..	...	...	..	..
	5823	4.16	..	..	...	...	..	..
	5847	4.54	..	..	...	...	..	..

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[1] Publication of the Carnegie Institution of Washington, No. 170, 60 (1912).

Summary.

A satisfactory radiomicrometer, having a half-period of 10 seconds and a sensibility of 5 per square millimeter of exposed vane (candle and scale being at a meter's distance) was constructed.

Making use of the radiomicrometer and the grating spectroscope, a radiometric method was worked out for the determination of the ionization constants of indicators. This method is freer from objections and limitations than any method previously used. It serves as well for a two-colored indicator as for a one-colored indicator.

Very small concentrations of colored components were determined, and it has been shown that minute concentrations of hydrogen and hydroxyl ions can be quickly and accurately estimated by means of radiometric measurements.

Satisfactory constants were obtained for the ionization of methyl orange as a base. The value found is 2.1×10^{-11}.

The ionization and hydrolysis constants for phenolphthalein considered as a monobasic acid are far from being satisfactory.

From the known ionization constant of methyl orange and from radiometric measurements, the ionization constant of a very weak base and the hydrolysis constant of one of its salts have been roughly determined. The method can likewise be applied for the determination of the ionization constants of very weak acids, and the hydrolysis constants of the salts formed by these acids. Work is now in progress in this laboratory on other indicators, from this same standpoint, and the results will soon be published in THIS JOURNAL.

JOHNS HOPKINS UNIVERSITY, BALTIMORE, MD.,
February, 1915.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY.]

THE FRACTIONAL CRYSTALLIZATION OF THE PICRATES OF THE RARE EARTHS OF THE DIDYMIUM GROUP.

BY L. M. DENNIS AND F. H. RHODES.

Received February 13, 1913.

The salts of the rare earths with picric acid form well-defined crystals, are much more soluble in hot water than in cold, and crystallize very well from solution. For these reasons, the fractional crystallization of the picrates naturally suggests itself as a method for the separation of the rare earths. Holmberg[1] made a brief examination of this method in the attempt to separate the earths of the terbium group. By the fractional crystallization of the picrates of gadolinium and terbium containing 25 g. of the earths he obtained a rapid concentration of terbium in the first mother liquors and an accumulation of gadolinium in the crystals which

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[1] *Z. anorg. Chem.*, **53**, 80 (1907).