

CCLV.—*The Colour Changes of Methyl-Orange and Methyl-Red in Acid Solution.*

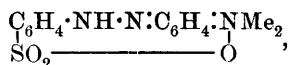
By HENRY THOMAS TIZARD.

It is well known that the colour of an indicator in solution depends, within certain limits, on the concentration of the hydrogen ion (or hydroxyl ion) in the solution. These limits, which vary greatly with the nature of the indicator, have been determined for a large number of indicators by Fels (*Zeitsch. Elektrochem.*, 1904, **10**, 208) and Salessky (*ibid.*, p. 205), and a knowledge of them enables us to choose, for any given volumetric operation, the indicator that will give the best results. Conversely, by testing a solution with a large number of indicators, we can arrive at an estimate of the concentration of hydrogen ions in it. Friedenthal (*Zeitsch. Elektrochem.*, 1904, **10**, 114) and Salm (*Zeitsch. physikal. Chem.*, 1906, **57**, 471) have measured in this way the degree of dissociation of weak acids and weak bases, and have obtained results agreeing often to within a few per cent. of those obtained by conductivity measurements; but it can hardly be seriously proposed to supersede the latter, more accurate, although more laborious, method by the former, except when the acid or base under investigation is extremely weak. On the other hand, the determination of the degree of hydrolysis of salts in aqueous solution is often both laborious and at the same time subject to large percentage errors; a simple colorimetric method would therefore be of considerable importance, provided that it could be made as accurate as, or more so than, the methods usually employed. Friedenthal's method cannot be considered accurate enough for this purpose; the difficulty of judging colours without employing a suitable apparatus is very great, and, moreover, it is impossible to keep weakly acidic standard solutions of indicators (for comparison) unchanged for any length of time. It is far better to determine once and for all the relation between depth of colour and the concentration of the hydrogen ion.

For this purpose only those indicators can be used that are either colourless in one form, or exist in two coloured forms which are practically alike in tint and only differ in depth of colour. For all practical purposes, methyl-orange sufficiently fulfils the latter condition; the complete change of colour of this indicator from alkaline to strongly acid solutions can be followed by matching it against a suitable standard solution in a tintometer. I have therefore examined this change of colour with as great care and accuracy as possible, and have applied the results obtained to the determination of the hydrolysis of aniline salts at different dilutions (see following paper). Veley, in a series of papers (*Zeitsch. physikal. Chem.*, 1906, **57**, 147; *Trans.*, 1907, and following years), has to a large extent opened up the field in this direction; but he worked only with extremely dilute solutions, where the total colour change is small, and the error of observation relatively large. Further, he based all his conclusions on empirical relations, which can be only approximately true. For these and other reasons, which will be mentioned later, his results can only be considered qualitative.

Theory of the Colour Change.

The simplest theory of the colour changes of an indicator is that of Ostwald. According to this, the ions of an indicator have a different colour from that of the undissociated molecule. For example, the undissociated molecule, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$, is red, whilst the ion, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3^-$, is light yellow. It has recently been proved in many cases, and is probably true in all, that this change in ionisation is accompanied by a change in the chemical structure of the molecule. According to Hewitt, the undissociated molecule of methyl-orange mainly consists of an internal compound,



to which the deep red colour is due. From this point of view, indicators are pseudo-acids, the pseudo-acidic form being always in equilibrium with the true acidic form, from which the ions are directly derived. It must, however, be emphasised that these considerations make no difference whatever to the theoretical treatment from the ionic point of view; for if the undissociated acid exists in solution in two or even more forms, these must always be present in strictly constant ratios, and hence, for all practical purposes, the acid behaves as if it existed in only one form. This will be assumed to be true for the sake of clearness in the following considerations, but it must be understood that the results obtained have no bearing

on the question as to what particular form of the undissociated molecule the deep red colour is due.

Now let the molecular colour of the ion be taken as unity, and let that of the undissociated acid be equal to c_1 . By this we mean that if the colour of a solution containing completely dissociated methyl-orange is balanced by a height " h " of a standard solution in a tintometer, the colour of the same solution when excess of acid (hydrochloric) is added, that is, when the indicator is entirely in the undissociated form, will be balanced by a height $= c_1 \times h$.

Then the molecular colour of a solution containing methyl-orange partly in the undissociated form, and partly in the form of ions, will be somewhere between c_1 and 1. Let y equal the fraction undissociated, and therefore $(1-y)$ the fraction dissociated. The molecular colour of the solution is then obviously given by the equation:

$$C = c_1 y + (1 - y) \quad . \quad . \quad . \quad (1).$$

Further, if K_a is the dissociation constant of the indicator acid, we have by Ostwald's law:

$$K_a y = (1 - y) \times \text{conc. H}^+ \quad . \quad . \quad . \quad (2).$$

Eliminating y from (1) and (2), we have:

$$\text{conc. H}^+ = K_a \frac{C - 1}{c_1 - C} \quad . \quad . \quad . \quad (3).$$

Hence, if we know K_a and c_1 , the relation between the molecular colour C of a solution and the concentration of hydrogen ions it contains is completely determined. K_a and c_1 can be determined by measuring the colour of solutions containing varying quantities of hydrochloric acid.

When $y = 1/2$, that is, when the indicator acid is 50 per cent. dissociated, the molecular colour:

$$C = \frac{c_1 + 1}{2},$$

that is, is just midway between the two extreme colours.

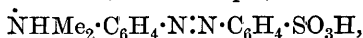
Further, equation (2) becomes:

$$K_a = \text{conc. H}^+.$$

In a solution, therefore, the colour of which is just midway between the two extreme colours, the concentration of the hydrogen ion is equal to the dissociation constant of the indicator acid. Salm (*loc. cit.*) has determined in this way the dissociation constant of a large number of indicators. He measured the concentration of the hydrogen ions by means of a hydrogen electrode. The method is of advantage when the two extreme colours of an indicator differ widely, but since only one solution can be conveniently examined,

the results are probably not very accurate, although of the right order of magnitude.

Now there is another point with regard to methyl-orange and allied indicators which has not been taken into account in the above considerations. All these compounds contain a substituted amino-group, and are therefore amphoteric electrolytes. Hence in an acid solution the basic ion, for example,



may be present, as well as the undissociated molecules. To this basic ion we must assign a molecular colour, say c_2 , and its presence to any considerable extent would greatly affect conclusions drawn from colour measurements. Lundén has, in fact, criticised Veley's results adversely from this point of view, but, as will be shown later, the basic dissociation constant K_b of methyl-orange is so small that no appreciable quantity of the $\dot{\text{N}}\text{HMe}_2\text{R}$ ion is formed even in $N/20$ -hydrochloric acid. On the other hand, that of methyl-red (which differs from methyl-orange in having an ortho-carboxyl instead of a para-sulphonic group) is larger, and in consequence we find that the basic properties of this indicator have a considerable influence on the colour in solutions which are greater than $N/5000$ with respect to hydrogen ions.

If we consider solutions which contain only the basic ion and the undissociated acid, and if the fraction of the former present is y' , and therefore that of the latter is $(1 - y')$, then as before:

$$C = c_2 y' + c_1(1 - y') \quad \dots \quad (1a).$$

Also, Ostwald's law gives:

$$K_b(1 - y') = y' \times \text{conc. OH}'.$$

Since

$$\text{conc. OH}' = \frac{K_w}{\text{conc. H}^+}$$

(K_w = dissociation constant of water), the last equation becomes:

$$\frac{K_w}{K_b} \cdot y' = (1 - y') \times \text{conc. H}^+ \quad \dots \quad (2a).$$

These two equations are precisely similar in form to equations (1) and (2), and it is evident that we cannot decide at once, without further evidence, whether the "dissociation constant," found colorimetrically, of an amphoteric indicator is really K_a or $\frac{K_w}{K_b}$.

This is especially true when the dissociation constant is found by Salm's method. When the whole course of the colour curve is examined, it is generally possible to see at a glance whether the change of colour must be attributed to the presence of three coloured molecules (basic ion, undissociated molecule, acid ion) in the solu-

tion, or only two (compare the curves for methyl-red and methyl-orange).

EXPERIMENTAL.

To test these equations, and to determine the values of K_a and c_1 , the depth of colour of methyl-orange solutions of known strength in presence of hydrochloric acid ranging from $N/20$ - to $N/100,000$ has been investigated. The apparatus employed was the Donnan tintometer, used as described, for example, by Sidgwick and Tizard (Trans., 1908, **93**, 188). The standard used for comparison was a faintly acid solution of methyl-orange. It was, of course, unnecessary to know its exact strength, as it was compared before any series of measurements against a neutral solution of methyl-orange of known strength. The colours were all referred to this dilution as unit. Veley (*loc. cit.*) found it impossible to measure the depth of colour of a strongly acid (red) solution of methyl-orange by comparing it to the same standard that he used in his colour measurements with weakly acidic (orange) solutions. I found comparatively little difficulty in doing so; the difference may be partly due to the fact that whilst Veley used daylight as his illuminant, I used the yellow light from a 50 c.p. electric lamp (carbon filament).

All the solutions used were made up carefully by weight with conductivity water. They were filtered to remove dust as far as possible, and kept in steamed-out Jena-glass flasks.

It was found impossible to prepare a clear solution of methyl-orange with a concentration greater than $N/1000$. In fact, solutions of this strength were slightly turbid, but immediately cleared on dilution. The effect of dilution is to cause a slight decrease in molecular colour, as the following measurements show.

Ten c.c. of a neutral solution, $N/2000$, were taken and diluted in the tintometer tube.

	V for methyl- orange.	Height of balancing column.
10 c.c. $N/2000$ solution	2000	4.6
" " " + 10 c.c. H_2O	4000	4.3
" " " + 20 c.c. H_2O	8000	4.0
" " " + 60 c.c. H_2O	20,000	4.0
" " " + a few drops $N/10$ -alkali	20,000	4.0

This decrease in colour may be due to increasing dissociation; the presence of even a small quantity of undissociated salt may have a considerable effect on the colour. In the experiments with hydrochloric acid, the methyl-orange was used at a dilution of $V=20,000$, high enough to avoid complications of this kind. The last colour measurement is important. Methyl-orange is a sodium salt; if its corresponding acid were very weak, the salt would be

considerably hydrolysed at high dilutions. This means that the solution would contain undissociated acid, which is of a much deeper colour than its ions. Addition of alkali would, in this case, diminish the colour by destroying hydrolysis. As a matter of fact, no such effect is observed, and this is strong evidence that the acid of methyl-orange cannot be very weak; on the contrary, it must be considerably stronger than acetic acid. We should therefore expect its basic dissociation constant, K_b , to be correspondingly small. These conclusions are confirmed by the colour measurements with hydrochloric acid. The latter measurements were carried out in the following way. Ten to 50 c.c. of an $N/10,000$ -solution of methyl-orange were placed in the tintometer tube, a suitable quantity of a standard solution of hydrochloric acid added, and then water added up to twice the original volume of methyl-orange. The concentration of the latter was then $N/20,000$. That of the hydrochloric acid varied from $N/20$ to $N/100,000$; or, if we denote the ratio (mols. HCl) \div (mols. methyl-orange) by " a ," " a " varied from $20,000 \div 100,000 = 0.2$ to $20,000 \div 20 = 1000$.

If the height of the balancing column is h' , and the height required to balance the same amount of methyl-orange in neutral solution is h , then the molecular colour of the acid solution is given by:

$$C = \frac{h'}{h},$$

that of the neutral solution being taken as unity.

Three series of measurements were taken on different days, and with entirely fresh solutions. The temperature was 25° . The greatest deviation in the molecular colour found for any particular strength of solution was 5 per cent., the usual error being 2 to 3 per cent. It was found impossible to reduce the error consistently beyond this point.

The curve for methyl-orange is drawn by plotting molecular colour against concentration of hydrogen ions, the latter being expressed in inverse powers of 10. There is very little change in colour between H^+ concentrations of 10^{-7} (neutral solution) and 10^{-5} ; after this point the rise in colour is rapid—the middle part of the curve being practically a straight line—until a maximum is reached somewhere about the point conc. $\text{H}^+ = 10^{-2}$, the colour only rising about 5 per cent. in more concentrated solutions. It is obvious from the curve that these changes can be explained if we assume the presence of two coloured substances in the solution. These must evidently be the anion and the undissociated acid, and equations (1) and (2), or (3) may therefore be applied.

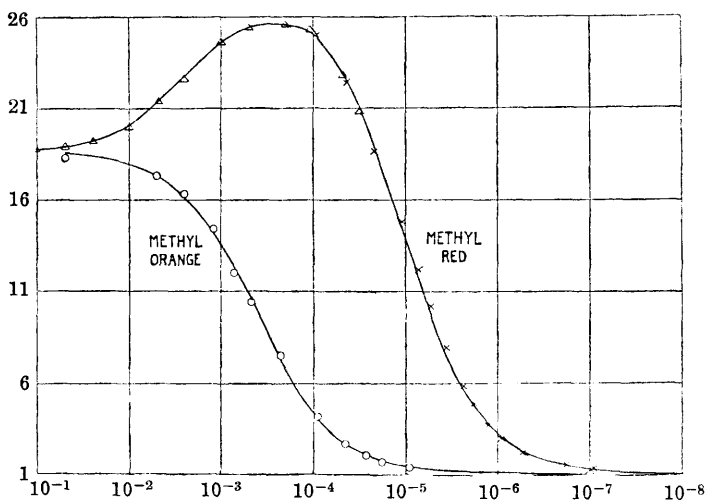
The concentration of hydrogen ions in the solutions examined is,

however, by no means the same as that of the hydrochloric acid added, as Veley assumed, since the undissociated indicator acid in the solution is formed by a combination of part of the anion of the salt with hydrogen ions derived from the added hydrochloric acid. In other words, the concentration of hydrogen ion in the solution is not a/V , where V is the dilution of methyl-orange, but

$$\frac{a-y}{V},$$

y being the fraction present in the form of undissociated indicator acid.

This correction is of considerable importance, especially at the



extreme dilutions with which Veley worked, and the fact that he did not take it into account may possibly explain some of his anomalous conclusions.

Equation (2) may therefore be written in the form:

$$K_a V y = (1-y)(a-y),$$

where $V=20,000$.

From the results, the mean values for K_a and c_1 are found to be:

$$K_a = 4.25 \times 10^{-4} \text{ (at } 25^\circ\text{)}.$$

$$c_1 = 18.8.$$

The agreement between calculated and observed values is shown in the following table:

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$a = \frac{\text{mols. HCl}}{\text{mols. indicator}}$	Conc. $H^* = \frac{a-y}{20,000}$	y	Colour (calc.).	Colour (obs.).
0.0	10^{-7} *	0.00	(1.00)	(1.00)
0.2	$10^{-5.048}$	0.021	1.37	1.38
0.4	$10^{-4.746}$	0.041	1.73	1.68
0.6	$10^{-4.568}$	0.060	2.07	2.04
0.8	$10^{-4.443}$	0.078	2.39	2.39
1.0	$10^{-4.344}$	0.096	2.71	2.65
2.0	$10^{-4.040}$	0.177	4.15	4.18
5.0	$10^{-3.634}$	0.353	7.28	7.48
10.0	$10^{-3.324}$	0.527	10.4	10.7
15.0	$10^{-3.144}$	0.63	12.2	12.0
25.0	$10^{-2.916}$	0.74	14.2	14.4
50.0	$10^{-2.609}$	0.85	16.1	16.3
100.0	$10^{-2.305}$	0.92	17.4	17.3
1000.0	$10^{-1.300}$	0.99	18.6	18.3

* Neutral point.

Salm found $K_a = 4.6 \times 10^{-4}$ as a mean of several values ranging from 4.0 to 5.5.

The greatest deviation between the observed molecular colours and those calculated by means of the above equations is 3 per cent. It appears therefore that there is no appreciable quantity of the positive ion NMe_2R formed even when the concentration of the hydrogen ion is as high as $N/20$, for it is unlikely that the colour of this ion is the same as that of the undissociated molecule. In the parallel case of methyl-red, it is distinctly lower, as will be shown later. If we assume that not more than 1 per cent. of the methyl-orange is present in the form of the basic ion when the concentration of the hydrogen ion in the solution is 10^{-2} , we can deduce an upper limit for the basic dissociation constant from equation (2a), which gives:

$$\frac{K_w}{K_b} \times 0.01 = 0.99 \times 10^{-2},$$

or $K_b = K_w = 10^{-14}$ (at 25°).

K_b is therefore probably $< 10^{-14}$.

When a is greater than 1, the increase in colour is approximately proportional to the increase in the amount of hydrochloric acid in the solution. Thus, with each successive 0.2 molecule, the increase in colour (calculated) is 0.37, 0.36, 0.34, 0.32, 0.32. This agrees with the observations of Veley, who found that by plotting increase in colour against concentration of acid added, a straight line was obtained. The relation is, however, evidently only approximately true.

At the theoretical neutral point the concentration of hydrogen ions is 10^{-7} . Since methyl-orange does not appreciably lighten in colour below a concentration of $H^* = 10^{-5}$, it must be considered a bad indicator for accurate volumetric analysis, apart from the fact that, since the change of colour takes place only gradually, it is

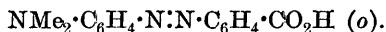
difficult to get a sharp end-point. On the other hand, the closeness of the results obtained with those required by the simple theory expressed by equations (1) and (2) shows that methyl-orange is a very good indicator to use for the quantitative colorimetric estimation of the concentration of hydrogen ions between 10^{-3} and 10^{-5} , that is, between $N/1000$ and $N/100,000$.

Substituting the values found for K_a and c_1 in (3), we get for the relation between concentration of hydrogen ions and molecular colour of methyl-orange the expression:

$$\text{conc. H}^+ = 4.25 \times 10^{-4} \cdot \frac{C-1}{18.8-C}.$$

Methyl-red.

In order to throw further light on the colour changes of indicators which are amphoteric electrolytes, a series of similar colour measurements were made with methyl-red, an indicator discovered by Rupp and Loose (*Ber.*, 1908, **41**, 3905). Its constitution is expressed by the formula:



The method of preparation given by these authors is not satisfactory, only small yields being obtainable. The following method is recommended by Mr. T. F. Winmill, who kindly supplied me with the indicator in the first place.

Five grams of anthranilic acid are dissolved in 150 c.c. of water and 15 c.c. of concentrated hydrochloric acid. To this, 2.5 grams of solid sodium nitrite are added, and the solution kept for half an hour. It is then poured into a solution of 4.65 grams of dimethylaniline in a mixture of 5 c.c. of concentrated hydrochloric acid and 50 c.c. of water. Fifty grams of sodium acetate are added. On warming to 40° , the red product quickly separates, but the reaction does not appear to be complete for about three hours. The substance is then collected, and can be crystallised from glacial acetic acid. The yield is almost quantitative.

Methyl-red is very insoluble in water; its saturated solution at the ordinary temperature is only about $N/100,000$. Since it contains a carboxyl instead of a sulphonic group, we should expect it to be a weaker acid than methyl-orange, and a correspondingly stronger base. In accordance with this, methyl-red is easily soluble both in acids and in alkalis. Its alkali salts are surprisingly soluble; the potassium salt can only be obtained by evaporating an alcoholic solution to dryness, since it is soluble to a considerable extent in ether, and deliquescent in air. Since the sodium salt of helianthin (methyl-orange) is somewhat insoluble in water, the difference in behaviour is striking.

The pure potassium salt appears to dissolve completely in a very small quantity of water, forming a very deep red solution; on diluting further, the acid separates out. The hydrolysis appears to be excessive if we accept the value for the dissociation constant of the acid (10^{-5}), found from the colour measurements, but since the solubility of the acid is so small, the appearance may be deceptive. It would probably be interesting to investigate further the behaviour of the alkaline salts of this indicator, but this does not come within the scope of the present paper.

Since a clear neutral solution of the salt could not be obtained, the saturated solution of the acid was used in the colour measurements. Its strength was found approximately in the following way. A known quantity of the potassium salt was dissolved in a slight excess of alkali, so as to make an $N/1000$ -solution; 10 c.c. of this were then diluted to 1 litre. This $N/100,000$ -solution contained, of course, a slight, but only a slight, excess of alkali. Ten c.c. were placed in the tintometer tube, the same volume of $N/1000$ -hydrochloric acid added, and the colour was measured. Ten c.c. of the saturated solution of the acid + 10 c.c. of $N/1000$ -hydrochloric acid were then measured in the same way. It makes no difference if the concentration of hydrogen ions in this solution was slightly greater than that in the salt solution, for, as will be shown later, the molecular colour is at a maximum at this point, and does not change appreciably between H^+ concentrations of $N/5000$ and $N/2000$ (see the curve for methyl-red).

Since the depth of colour of the two solutions was approximately the same, the strength of the acid solution was taken to be roughly the same as that of the salt solution, namely, $N/100,000$. The saturated solution was usually diluted in the tube up to about four times its original volume.

It has already been pointed out in discussing the results with methyl-orange, that the concentration of the hydrogen ions in a very dilute solution of hydrochloric acid containing an indicator, is not the same as that of the hydrochloric acid itself, but is less or greater, as the case may be. In order to allow properly for this, we must, of course, know exactly the quantity of indicator present. The uncertainty of the actual dilution of the methyl-red used makes, therefore, experiments with hydrochloric acid untrustworthy when the concentration of the latter falls below a certain amount. For this reason, the most dilute solution of hydrochloric acid used was about $N/30,000$, and the concentration of the hydrogen ion in this and more concentrated solutions was taken to be the same as that of the hydrochloric acid present. The remainder of the curve was determined by measuring the colour in solutions of

sodium acetate containing varying amounts of acetic acid. The concentration of the sodium acetate was $N/500$; that of the hydrogen ions, when a certain amount of acetic acid, equal to n times that of the sodium acetate, is added, may then be easily calculated by means of Ostwald's law, the dissociation constant of acetic acid at 18° (the temperature of measurement) being taken as 1.8×10^{-5} . Hence:

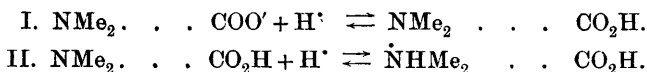
$$1.8 \times 10^{-5} \times \text{conc. HA} = \text{conc. A}' \times \text{conc. H}'.$$

Since we may assume the sodium acetate to be completely dissociated, the equation becomes:

$$\begin{aligned} \text{conc. H}' &= 1.8 \times 10^{-5} \times \frac{\text{HA}}{\text{NaA}}. \\ &= n \times 1.8 \times 10^{-5}. \end{aligned}$$

Since the amounts of acetic acid and sodium acetate in the solution are always large compared to that of the indicator, the correction that must be made when strong acids, such as hydrochloric acid, are used is unnecessary.

The colour curve obtained in this way is shown on p. 2483. The lower part of the curve is similar to that of methyl-orange, but the colour falls again when the concentration of hydrogen ions is greater than $N/2000$ or thereabouts. We must therefore assume that two changes take place:



The colours of the acid ion, undissociated molecule, and basic ion are taken, as before, as 1, c_1 , and c_2 respectively. Since the maximum is very flat, the first change must be nearly complete before the second begins. Disregarding the latter for the present, then, we may apply the equations:

$$\begin{aligned} C' &= c_1 y + (1 - y), \\ K'_a y &= (1 - y) \times \text{conc. H}', \end{aligned}$$

to the lower part of the curve, the concentration of hydrogen ions being calculated in the ways already indicated. For the mean values of K'_a and c_1 , we find:

$$\begin{aligned} K'_a &= 1.05 \times 10^{-5}. \\ c_1 &= 27.6. \end{aligned}$$

The temperature was in this case 18° .

The following table contains the results so obtained:

*Molecular Colour of Methyl-red.*1.—*Experiments with Mixtures of Sodium Acetate and Acetic Acid.*

$n = \frac{HA}{NaA}$	Conc. H ⁺	Colour (obs.).	Colour (calc.).
0.0	10 ^{-8.272}	1.10	1.02
0.005	10 ^{-7.046}	1.26	1.22
0.01	10 ^{-6.745}	1.46	1.46
0.03	10 ^{-6.268}	2.24	2.30
0.05	10 ^{-6.046}	3.00	3.10
0.07	10 ^{-5.900}	3.68	3.84
0.1	10 ^{-5.745}	4.86	4.88
0.13	10 ^{-5.631}	5.86	5.84
0.2	10 ^{-5.444}	7.84	7.78
0.3	10 ^{-5.268}	10.2	10.2
0.4	10 ^{-5.143}	12.2	11.8
0.6	10 ^{-4.967}	14.8	14.5
1.2	10 ^{-4.666}	18.6	18.9
2.4	10 ^{-4.365}	22.0	22.4
5.0	10 ^{-4.046}	25.2	24.8

2.—*Experiments with Hydrochloric Acid up to N/2000.*

V_{HCl}	Conc. H ⁺	Colour (obs.).	Colour (calc.).
31,000	10 ^{-4.491}	19.9	21.0
21,000	10 ^{-4.322}	22.3	22.8
11,000	10 ^{-4.041}	24.9	24.8
9000	10 ^{-3.954}	25.4	25.3
[5000	10 ^{-3.689}	25.6	26.2]
[2000	10 ^{-3.301}	25.6	27.0]

The observed and calculated values closely agree; in particular the two series of measurements agree well where they overlap. The last colour measurement (in $N/2000$ -hydrochloric acid) is considerably below the calculated value; this is due to the formation of the basic ion. In still higher concentrations of hydrogen ions, the colour sinks further, until it again becomes practically constant when conc. H⁺ is greater than $N/20$. Equations (1a) and (2a) apply to this case. If we assume that no acid dissociation takes place, we get:

$$C = y_2 c_2 + (1 - y_2) c_1,$$

where y_2 is the fraction of the indicator present in the basic form, and c_2 is the molecular colour of the basic ion; c_1 has already been found to be 27.6.

Also, if K_b is the basic dissociation constant of the indicator:

$$\frac{K_w}{K_b} y_2 = (1 - y_2) \text{conc. H}^+.$$

From the colour measurements, we find:

$$\frac{K_w}{K_b} = 2.0 \times 10^{-3},$$

$$c_2 = 18.6.$$

Molecular Colour of Methyl-red in Solutions of Hydrochloric Acid greater than N/5000.

V_{HCl} .	Conc. H^+ .	Colour (obs.).	Colour (calc.).
2	$10^{-0.3}$	18.4	18.6
10	$10^{-1.0}$	18.8	18.8
20	$10^{-1.3}$	18.8	18.9
30	$10^{-1.5}$	18.9	19.1
40	$10^{-1.60}$	19.2	19.2
100	$10^{-2.00}$	19.9	20.0
210	$10^{-2.322}$	21.6	21.4
410	$10^{-2.613}$	23.0	22.6
1000	$10^{-3.00}$	24.8	24.6
[2000	$10^{-3.301}$	25.6	25.8]
[5000	$10^{-3.699}$	25.6	26.7]

The dilutions $V_{\text{HCl}}=2000$ and 5000 require further consideration; it is evident that the molecular colours at and between these dilutions cannot strictly be calculated on either of the assumptions: (1) that no basic ion is present, (2) that no acid ion is present. Both these ions as well as the undissociated molecule must be present to an appreciable extent. By using the dissociation constants given above, we can calculate the amount of these ions present, and thus arrive at the following results:

V_{HCl} .	Acid ion. ($1 - y_1 - y_2$)	Undiss. mol. y_1	Basic ion. y_2	Col. (calc.).	Col. (obs.).
2000	0.015	0.788	0.197	25.4	25.6
5000	0.045	0.868	0.087	25.6	25.6

Hence the whole course of the colour curve is satisfactorily accounted for.

Since

$$K_w = 0.6 \times 10^{-14} \text{ at } 18^\circ,$$

we have

$$K_b = \frac{0.6 \times 10^{-14}}{2 \times 10^{-3}} = 3 \times 10^{-12}.$$

It must not, of course, be assumed that the colours of methyl-orange and methyl-red are the same in equivalent alkaline solution, because the molecular colours of both the acid ions have been taken as unity. As a matter of interest, however, it may be mentioned that, as far as could be judged, the difference between the two depths of colour of the two acid ions is but small.

As an indicator methyl-red is greatly superior to methyl-orange, as the colour curves show. The visible change, red to yellow, takes place between $10^{-5.7}$ and 10^{-7} , that is, between H^+ concentrations of $N/200,000$ and $N/10,000,000$. Not only therefore is the end-point very much sharper than when methyl-orange is used, but the neutral point so found is very much nearer the theoretical neutral point. Methyl-red is, in fact, an extremely sensitive indicator, and should come into extended use; it is especially valuable for the

exact titration of moderately weak bases (such as ammonia) by strong acids.

As a means for measuring colorimetrically the concentration of hydrogen ions in a solution, methyl-red would probably be found valuable when such concentration lies between 10^{-5} and 10^{-6} . Methyl-orange cannot be used when conc. H^+ is greater than 10^{-5} . If methyl-red is used for this purpose, it would be advisable to refer all molecular colours to the maximum colour found when conc. H^+ lies between $N/2000$ and $N/5000$; this maximum colour can be measured very accurately, whilst the extreme yellow colour of the ion is somewhat difficult to measure. Taking the maximum colour as 25.6, the theoretical colour of the undissociated molecule is 27.6, and the relation between concentration of hydrogen ions (between $10^{-4.5}$ and $10^{-6.5}$, say) and the molecular colour of the solution can be expressed by the equation:

$$\text{conc. } H^+ = \frac{1.05 \times 10^{-5}(C - 1)}{27.6 - C}.$$

Summary.

The depths of colour of methyl-orange and methyl-red in solutions of varying concentrations of hydrogen ions have been measured.

From the results, the following constants have been deduced:

	K_a .	K_b .
Methyl-orange (at 25°): $NMe_2 \cdot C_6H_4 \cdot N:N \cdot C_6H_4 \cdot SO_3H$	4.25×10^{-4}	$< 10^{-14}$
Methyl-red (at 18°): $NMe_2 \cdot C_6H_4 \cdot N:N \cdot C_6H_4 \cdot CO_2H$ (o)	1.05×10^{-5}	3×10^{-13}

The value of methyl-red as an indicator is discussed.

Expressions are given connecting the depths of colour of methyl-orange and methyl-red solutions with the concentrations of hydrogen ion in the solutions.

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