

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

THE MEASUREMENT OF THE HYDROGEN-ION CONCENTRATION IN UNBUFFERED SOLUTIONS. III. THE COLORIMETRIC METHOD

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I. Acid-base indicators are substances with a weak acidic or basic character and therefore they have a tendency to change the P_{H} when added to a slightly buffered or unbuffered solution. As the molecular concentration of indicators in colorimetric work is of the order of 10^{-5} or smaller, the "acid" or "base" error will only be noticeable in solutions with extremely slight buffer action. Large errors, however, may occur when the P_{H} of pure water or solutions of neutral salts in water or extremely dilute solutions of acids and bases have to be measured. I. M. Kolthoff,² for example, found that 0.1 cc. of a 0.04% solution of methyl red added to 10 cc. of water (P_{H} 7.0) gave a color corresponding to a P_{H} of 5.1. He has already pointed out that in the measurement of P_{H} in slightly buffered solutions, reliable results can only be obtained if the indicator solution added has the same P_{H} as the unknown. Edna H. Fawcett and S. F. Acree,³ who recently published extensive papers on the colorimetric measurement of P_{H} in unbuffered solutions, call these indicator solutions adjusted or isohydric.

In unknown cases mixtures of the two forms of the indicator in different ratio must be used. If different amounts of the mixture added to the unknown give the same P_{H} , it is isohydric with the latter. This has been pointed out already by W. H. Pierre and J. F. Fudge,⁴ and especially emphasized by Fawcett and Acree.³

The color of the indicator in the unbuffered solution is compared with that of the same mixture in an ordinary buffer solution. As the ionic strength of the two may be quite different, a correction must be applied for the difference in activity of the indicator ions in both solutions.⁵

II. Preparation of Adjusted Indicator Solutions.—For the preparation of adjusted solutions, H. T. Stern⁶ titrated the indicators with sodium hydroxide and determined the P_{H} with the quinhydrone electrode. It is

¹ From the experimental part of a thesis submitted by T. Kameda to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² I. M. Kolthoff, *Biochem. Z.*, **168**, 110 (1926).

³ E. H. Fawcett and S. F. Acree, *J. Bact.*, **17**, 163 (1929); *Ind. Eng. Chem., Anal. Ed.*, **2**, 78 (1930).

⁴ W. H. Pierre and J. F. Fudge, *THIS JOURNAL*, **50**, 1254 (1928).

⁵ Cf. I. M. Kolthoff, *J. Phys. Chem.*, **32**, 1820 (1928).

⁶ H. T. Stern, *J. Biol. Chem.*, **65**, 675 (1925).

claimed that the readings are accurate to within about 0.2 in P_H . Pierre and Fudge⁴ used a similar technique; however, the results described by these authors are not very convincing. In their table⁷ a close agreement between the reading with the hydrogen electrode and the colorimetric "varying drop method" is shown. This agreement, however, is more or less illusory as they neglect the difference in ionic strength between the unknown and the buffer. The correction may amount to 0.2–0.3 in P_H .

Fawcett and Acree³ prepared series of adjusted indicators of known P_H more in an empirical way, by noticing the change in color upon addition of an equal volume of a very dilute buffer solution. As a matter of fact, it is not very important to know the P_H of the indicator mixture with a high degree of accuracy. As the P_H of the solution to be tested is not known, different indicator mixtures must be tried, until one is found which gives the same reading after addition of different amounts of indicator. The color is then compared with that of the same amount of indicator in buffer solutions of known P_H . More important is the use of pure indicators in this type of work. Most commercial products show quite a variation in their composition. Therefore, the authors have tried to prepare pure samples of indicators; their purity was tested by a conductimetric titration with sodium hydroxide. If a solution of a sulfonephthalein is titrated, the conductivity drops as in the titration of any strong acid. After the neutralization of the sulfonic group, the conductivity increases and a second break in the conductivity line occurs after the neutralization of the phenol group. Upon further addition of sodium hydroxide, there is a much stronger increase in conductivity. In the titration of phenolphthalein only one break in the conductivity line occurs after addition of two equivalents of sodium hydroxide (neutralization of carboxyl and phenolic group). In the neutralization of methyl red only one break can occur after addition of one equivalent of base.

If pure indicators are available, the composition of mixtures of a definite P_H can be calculated by means of the equation

$$\frac{[HI^-]}{[I^-]} = \frac{(H^+)}{K_1}$$

The most reliable data of the ionization constant K_1 of the indicators have been collected by Kolthoff⁸ and the authors have used these figures in their computation.

Indicators Used

Brom Thymol Blue.—A product of Schering-Kahlbaum was recrystallized from benzene: 1.5% was insoluble; this residue was sodium chloride. The crystals were dried at 190° to remove all water. The conductimetric titration showed that this product was quite pure. The data obtained are summarized in the table.

⁷ Ref. 4, p. 1260.

⁸ I. M. Kolthoff, *J. Phys. Chem.*, **34**, 1466 (1930).

Phenol Red.—Commercial products are usually impure. According to W. R. Orndorff and F. W. Sherwood,⁹ phenol red is usually contaminated by a dyestuff with weak acid character, which is insoluble in sodium bicarbonate. Therefore, the crude product can be purified by dissolving it in sodium bicarbonate solution and acidifying the filtrate with hydrochloric acid. The phenol red is collected and dried at 130°. A product of Schering-Kahlbaum was still impure after this treatment. Further crystallization from acetic acid is necessary to obtain it in a pure state. The authors are obliged to Hynson, Westcott and Dunning,¹⁰ Baltimore, Maryland, for supplying them with samples of pure phenol red, thymol blue and brom thymol blue.

Phenolphthalein.—A product obtained from J. T. Baker Company was recrystallized from methyl alcohol. According to the melting point and the result of the conductimetric titration it was quite pure.

Methyl Red.—A commercial product recrystallized from methyl alcohol took after drying the theoretical amount of sodium hydroxide.

A summary of the results obtained in the conductimetric titration of different samples of indicators is given in Table I.

TABLE I
CONDUCTIMETRIC TITRATION OF INDICATORS

Indicator	Origin	Alcohol concn. of soln. titrated, %	1st equiv. point		2d equiv. point	
			Theoret- ical	M. moles, found	Theoret- ical	M. moles, found
Brom thymol blue	Schering-Kahlbaum	20	0.160	0.153	0.321	0.330
Brom thymol blue	Same, purified	20	.160	.159	.321	.322
Brom thymol blue	National Aniline Co.	20	.160	.148	.321	.323
Phenol red	Schering-Kahlbaum	40	.283	.253	.567	.580
Phenol red	Same, purified	40	.283	.263	.567	.588
Phenol red	Same, recryst. from alc.	40	.283	.264	.567	.576
Phenol red	Hynson, Westcott and Dunning	40	.283	.260	.567	.571
Thymol blue	National Aniline Co.	40	.214	.179	.429	.412
Thymol blue	Hynson, Westcott and Dunning	80	.214	.197	.429	.424
Phenolphthalein	Purified	40			.629	.632
Methyl red	Purified	70	.372	.373		
Methyl red	National Aniline Co.	70	.372	.377		

The indicator solutions were prepared from the purified products. As a rule 100 mg. of a sulfonephthalein was dissolved in an equivalent amount of sodium hydroxide, in order to neutralize the sulfonic group. The solution was diluted with water to 100 cc. (solution of monovalent salt). To another 100 mg. of indicator double the amount of sodium hydroxide was added and the solution diluted to 100 cc. (solution of divalent salt). From these two standard solutions indicator mixtures of known P_H were prepared

⁹ W. R. Orndorff and F. W. Sherwood, THIS JOURNAL, 45, 486 (1923).

¹⁰ According to our experience the indicators marketed by this company are of the purest obtainable in any country. It is peculiar that in the titration of pure phenol red the first break in conductivity appears before the complete neutralization of the sulfonic acid group.

in the way described above. With phenolphthalein as an indicator it is hard to prepare mixtures of known P_H , as the first and second ionization constants are not known exactly and are of the same order of magnitude. Two 0.1% stock solutions of phenolphthalein in 50% alcohol were prepared: one with one equivalent sodium hydroxide (mono-), the other with two equivalents (di-). The right mixture was found empirically. From methyl red a 0.1% solution in 70% alcohol was prepared, and another in 50% alcohol with the same amount of indicator to which one equivalent of sodium hydroxide had been added.

Stability of Indicator Mixtures.—In agreement with the statement of other authors (especially Stern⁶) it was found that partly neutralized indicator solutions cannot be kept for a long time without changing their P_H . This, of course, is especially the case with phenolphthalein, as the red quinoid is transformed into the carbonium salt. However, with partly neutralized brom thymol blue, thymol blue and phenol red solutions the authors had a similar experience. Usually the P_H decreases after a few days' standing. This behavior, of course, has only to be considered in the determination of P_H in pure water or solutions of neutral salts in pure water. If the solution to be tested has a distinct buffer action, it is immaterial whether the indicator solution used is exactly isohydric with the former.

For the measurement of P_H in pure water or any other unbuffered solution, it is recommended that freshly prepared indicator mixtures be used and that these be made up fresh every two or three days. According to the authors' experience, there is no special advantage in keeping a complete series of solutions of an adjusted indicator, each differing 0.2 in P_H from the other, as Fawcett and Acree recommend. The right mixture must be found in any case by empirical testing, and the series of adjusted solutions is not stable.

III. Technique of the Colorimetric P_H Determination in Unbuffered Solutions.—In the P_H measurement of pure water, neutral salt solutions in pure water and dilute solutions of sodium hydroxide, the liquid has to be protected from contamination by carbon dioxide (and other impurities of acid or basic nature) in the atmosphere. For the measurements described in this paper, the authors used a cell such as is shown in Fig. 1.

A sample of pure water is introduced into the Pyrex glass cell and made carbon dioxide free by passing through purified air which has been thoroughly washed by passing through soda lime, dilute sulfuric acid and several wash-bottles of pure water. After the water is carbon dioxide free (tests must be made after different times of passage of air, until the P_H does not change further), a measured amount of the indicator mixture is added quickly from a pipet, by removing the glass stopper of the cell. During the addition of indicator the air is kept flowing through the cell.

Then after the solution is homogeneous, the taps A and B are closed and the color is compared with that of the same amount of indicator in a buffer solution kept in a cell of similar shape (glass stopcocks are not necessary here). After the reading the carbon dioxide-free air is again passed through the sample, and more indicator is added. After the color comparison a third portion of indicator is added. *If the correct indicator mixture is used, the same P_H readings are found with different amounts of indicator.* If the P_H found decreases with increasing amounts of indicator, the mixture is too acid, and if the P_H increases, the indicator mixture has too alkaline a reaction.

In the P_H measurements of solutions of neutral salts in pure water, a measured volume of pure water was introduced into the cell and made carbon dioxide free, whereupon a weighed amount of salt was quickly added. The comparison was then made as described above. Several P_H measurements have been made in extremely dilute sodium hydroxide solutions. It is one of the hardest problems to measure the P_H of such solutions with any degree of accuracy. The hydrogen electrode is easily poisoned in such an unbuffered solution. The colorimetric method if properly applied gives excellent results, as will be shown in the experimental part.

The water used was carefully prepared by distilling conductivity water over extremely dilute sulfuric acid to remove traces of volatile bases. The distillation was twice repeated without any addition and finally in a quartz apparatus with a quartz condenser. The first and last quarters of the distillate were discarded. The quartz receiver was protected by means of soda-lime tubes and wash-bottles containing very dilute sulfuric acid from atmospheric contamination. As a rule the water was used on the same day that the final distillation was made. It was siphoned from the quartz receiver into the pyrex cells. At least ten samples of water have been prepared, which after having been made carbon dioxide free showed a P_H of 7.0 to 7.05. All measurements have been made at a temperature of $25 \pm 1.0^\circ$. Clark and Lubs buffer solutions were used for comparison, the P_H of these being determined with the hydrogen electrode in a thermostat at 25° .

The P_H value found with the isohydric indicator mixture must be corrected for the difference in ionic strength between the sample and the

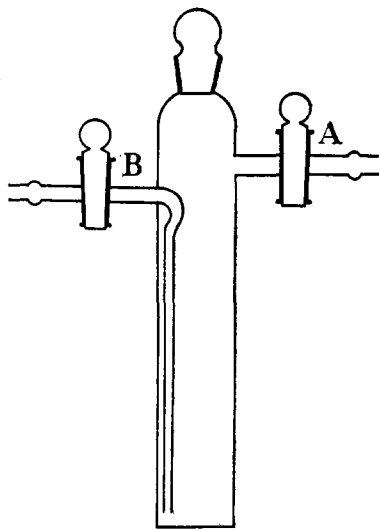


Fig. 1.

buffer solution. According to I. M. Kolthoff⁵ a correction of 0.25 to 0.30 should be added to the P_H found under the conditions mentioned in measurements in solutions with an ionic strength smaller than 0.0001 (water, and extremely dilute sodium hydroxide solutions) with brom thymol blue, phenol red, thymol blue and phenolphthalein as indicators. For methyl red the salt error is negligibly small.

IV. Experimental Results.—Fifteen cc. of water to which the indicated amounts of 0.1% indicator mixtures were added was used. The water was practically carbon dioxide free when introduced into the cell; the P_H was constant after passing through carbon dioxide-free air for thirty minutes. Some of the results obtained with mixtures of brom thymol blue and phenol red, respectively, are given in the following table.

TABLE II
COLORIMETRIC DETERMINATION OF P_H IN 15 CC. OF PURE WATER AT 25°

Indicator	Ratio [HI ⁻]/[I ⁻]	P_H for various volumes of indicator ^a		
		0.1 cc.	0.3 cc.	0.5 cc.
Brom thymol blue	96 : 4	6.62	6.50	6.20
Brom thymol blue	100 : 55	7.03	7.00	7.01
Brom thymol blue	4 : 96	7.93	8.05	8.25
Phenol red	99 : 1	6.70	6.60	6.50
Phenol red	100 : 10	7.03	7.05	7.07
Phenol red	1 : 99	8.55	8.85	9.00

^a The observed P_H has been increased by 0.25 to correct for the salt error.⁵

It appears that the mixtures of brom thymol blue, 100:55, and of phenol red, 100:10, are isohydric with the water. The corrected value of P_H found in ten different experiments with different samples of water varied between 7.00 and 7.05. The pure water is very sensitive to traces of carbon dioxide. After the water had been made carbon dioxide free the stopper of the cell was removed for one minute. The P_H (corrected) dropped from 7.00 to 6.85. Upon transferring this water-indicator mixture to another cell, the P_H fell to 6.35.

TABLE III
COLORIMETRIC DETERMINATION OF P_H IN 15 CC. OF POTASSIUM CHLORIDE SOLUTION (AT 25°)

Indicator	Ratio [HI ⁻]/[I ⁻]	Concentration of		
		0.1 m.	0.25 m.	0.5 m.
Brom thymol blue ^a	100 : 55	6.77	6.77	6.77
Phenol red ^a	100 : 10	6.78	6.75	6.75
Hydrogen electrode ^b		6.70-6.77		

^a No correction for salt error has been made. ^b Adapted for unbuffered solution, THIS JOURNAL, 53, 821 (1931).

The following table gives values found in extremely dilute sodium hydroxide solutions. From the known hydroxyl ion concentration P_H (theoretical) was calculated: $P_H = 14.00 - p_{OH}$ (25°). Measurements

have been made with phenolphthalein and thymol blue, respectively, as indicators.

TABLE IV
COLORIMETRIC DETERMINATION OF P_H IN (15 CC. OF) DILUTE SODIUM HYDROXIDE SOLUTION (AT 25°)

Indicator	Ratio [HI ⁻]/[I ⁻]	P_H for various volumes of indicator ^a			Theoretical
		0.1 cc.	0.3 cc.	0.5 cc.	
Phenolphthalein	99 : 1	9.30	9.30	9.30	9.22
Phenolphthalein	70 : 30	9.32	9.42	9.50	9.22
Phenolphthalein	60 : 40	9.40	9.50	9.60	9.22
Thymol blue	30 : 70	9.25	9.25	9.25	9.22
Thymol blue	50 : 50	9.25	9.15	9.10	9.22
Phenolphthalein	...	9.30	9.28	..	9.22
Phenolphthalein	...	9.45	9.47
Phenolphthalein	...	9.73	9.82
Phenolphthalein	...	9.87	10.00
Phenolphthalein	...	10.05	10.12

^a The observed P_H has been increased by 0.25 to correct for the salt error.⁵

From these experiments it may be inferred that the P_H of extremely dilute sodium hydroxide solutions can be determined with an accuracy of at least 0.1 if isohydric solutions of phenolphthalein or thymol blue are used as indicators and the proper correction for the salt error is added to the experimental figure. Recently J. W. McBain, O. E. Dubois and K. G. Hay, and J. W. McBain, M. E. Laing and O. E. Clark¹¹ have given data showing that phenol red, *o*-cresol red, phenolphthalein and thymol blue cannot be used for the colorimetric determination of P_H in extremely dilute sodium hydroxide solutions, as the experimental figures differ by more than one to two units from the theoretical ones. From the above it is quite evident that this conclusion is unwarranted if precautions are taken against contaminations by carbon dioxide and if isohydric buffer solutions are used and the proper salt correction is applied.

Finally, it may be mentioned that the P_H of pure zinc sulfate solutions has been measured with adjusted methyl red as indicator. At concentrations of zinc sulfate below 0.1 molar the colorimetric readings agreed within 0.01 in P_H with the figures obtained with the hydrogen electrode. Details will be given in a paper on the hydrolysis of zinc sulfate.

Summary

1. Commercial indicators were purified by recrystallization and the purity tested by conductimetric titrations with sodium hydroxide.
2. A technique has been described for the colorimetric measurement of P_H in pure water, of neutral salts in pure water and of extremely dilute sodium hydroxide solutions.

¹¹ J. W. McBain, O. E. Dubois and K. G. Hay, *J. Gen. Phys.*, 9, 461 (1926); J. W. McBain, M. E. Laing and O. E. Clark, *ibid.*, 12, 695 (1929).

3. In using isohydric indicator solutions and applying the proper salt corrections, the P_H of pure water has been determined with brom thymol blue and phenol red at 25° with an accuracy of 0.05 in P_H . With isohydric phenolphthalein or thymol blue solutions, the P_H of extremely dilute sodium hydroxide solutions has been measured with an accuracy of 0.1 in P_H .

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE HYDROLYSIS OF ZINC SULFATE SOLUTIONS, SOLUBILITY PRODUCT OF HYDROUS ZINC OXIDE AND THE COMPOSITION OF THE LATTER PRECIPITATED FROM ZINC SULFATE SOLUTIONS

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1. **Hydrolysis of Zinc Sulfate.**—For two reasons no reliable data on the hydrolysis of solutions of zinc sulfate are given in the literature; in the first place, no careful attention has been paid to the preparation of pure zinc sulfate, and in the second place the accurate measurement of the hydrogen-ion activity in zinc sulfate solutions is relatively difficult. The latter solutions have an extremely small buffer capacity, and on account of the hydrolytic adsorption by platinized platinum described in a former paper,² the ordinary type of platinized hydrogen electrode does not give reliable or reproducible results. The use of the quinhydrone electrode too is rather precarious in slightly buffered solutions. The authors have applied this electrode in all measurements described in this paper, but the readings were reproducible no better than to within 0.04 to 0.05 in P_H , which was not considered sufficiently accurate for this type of work. Finally, the colorimetric method involves some complications on account of the salt influence upon the color of an indicator at constant activity of the hydrogen ions. In the present work the P_H has been determined with a hydrogen electrode adapted to measurements in unbuffered solutions and described in a former paper.³ The platinum wire was coated with a bright layer of platinum; after each set of measurements it was cleaned with aqua regia, ignited and replated. For details regarding manipulation the reader is referred to the former paper.³

The measurements were reproducible to within 0.01 to 0.02 of P_H . In a former study⁴ it had been found that the salt error of methyl red is negli-

¹ From the experimental part of a thesis submitted by T. Kameda to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² I. M. Kolthoff and T. Kameda, *THIS JOURNAL*, 51, 2888 (1929).

³ I. M. Kolthoff and T. Kameda, *ibid.*, 53, 821 (1931).

⁴ I. M. Kolthoff, *J. Phys. Chem.*, 32, 1820 (1928).