

THE COLORIMETRIC DETERMINATION OF HYDROGEN-ION CONCENTRATION IN AQUEOUS SOLUTION

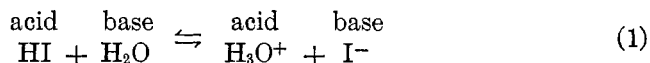
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The literature abounds with papers on the subject of the determination of pH, but even to-day there is a great deal of confusion as to the relative merits of the various methods available. A part of this confusion arises from the definition of the term pH, and another part arises from misunderstanding and neglect of salt effects (6). In many cases the worker talks and thinks in terms of concentration of hydrogen ion, but measures something approaching the activity of the hydrogen ion. In the use of the colorimetric method great care is often taken in making the measurements and all too little thought given to the calculation of the result. In order to avoid confusion, in the present paper results will be expressed not in terms of pH, but in actual hydrogen-ion concentrations in moles per liter.

The substances used for the colorimetric determination of hydrogen-ion concentration are acids and bases, of which the acid form or basic form (or both) is colored. In the case of a weak monobasic acid, HI, the double acid-base equilibrium with the solvent can be represented in the following manner



By increasing the concentration of the base I^- , the solution can be buffered in respect to the hydrogen ion H_3O^+ . If HI or I^- is colored, we have an indicator. The fact that the indicator establishes its own buffer equilibrium is of great importance in the determination of the hydrogen-ion concentration of unbuffered or poorly buffered solutions. For example, if we are determining the hydrogen-ion concentration of carbon dioxide-free water, with a hydrogen-ion concentration of $1 \times 10^{-7}M$, and we add an indicator, the hydrogen-ion concentration is no longer $1 \times 10^{-7}M$. This problem will be discussed in a later section of the paper. In the case of well-buffered solutions this problem does not arise, for here the constituents of the buffer system of the indicator are present at concentrations of

the order of $10^{-5}M$, while the constituents of the buffer system whose hydrogen-ion concentration we are measuring are usually present at concentrations of the order of 10^{-1} or $10^{-2}M$.

The equilibrium involved in equation 1 can be formulated by the mass law as follows

$$K_c = c_{H_3O^+}c_{I^-}/c_{HI} \quad (2)$$

where K_c represents the classical dissociation constant. When the concentration of HI is equal to that of I^- , that is, when the indicator is half transformed, we have

$$K_c = c_{H_3O^+} \quad (3)$$

Now K_c varies with electrolyte concentration so that the half-change point in one solution may not be the half-change point in another, even though the hydrogen-ion concentrations are the same. This means that equal color for equal indicator concentration does not always show equal hydrogen-ion concentration, and I might add that it does not always show equal hydrogen-ion activity. The fundamental equation for two solutions of equal indicator concentration and equal color is

$$(c_{H_3O^+}/K_c)_I = (c_{H_3O^+}/K_c)_{II} \quad (4)$$

Letting solution I be the known, there results for the hydrogen-ion concentration of the unknown solution

$$(c_{H_3O^+})_{II} = (c_{H_3O^+})_I(K_c)_{II}/(K_c)_I \quad (5)$$

If the ratio $(K_c)_{II}/(K_c)_I$ is known as well as $(c_{H_3O^+})_I$, $(c_{H_3O^+})_{II}$ can be calculated.¹

I. THE DETERMINATION OF HYDROGEN-ION CONCENTRATION BY COMPARISON WITH BUFFER STANDARDS

The standards for the determination of hydrogen-ion concentration are most conveniently prepared from monobasic acids and their salts, and potassium chloride. If the classical dissociation constant of the acid is known at the electrolyte concentration chosen, the standards can be made up from standard solutions of the weak acid and carbonate-free sodium hydroxide, and the neutral salt. For example, the classical dissociation constant of acetic acid in 0.1 M potassium chloride solution has been determined kinetically and electrometrically (9) and the values found are 2.90 and 2.84×10^{-5} , respectively. Both methods involve assumptions, but

¹ For the corresponding equations in terms of activity of hydrogen ion, see references 6 and 7.

the fact that the results agree within 3 per cent indicates the validity of the assumptions. If we take K_c for acetic acid as 2.90×10^{-5} , and prepare a solution 0.0100 M in sodium acetate, 0.0100 M in acetic acid, and 0.09 M in potassium chloride, we know its hydrogen-ion concentration within 3 per cent (0.01 pH unit) from equation 2. By varying the concentration of acetic acid from 0.05 to 0.002 M , a series of safely buffered standards can be prepared covering the range of hydrogen-ion concentration from (5) (2.90×10^{-5}) to (0.2) (2.90×10^{-5}) M .

There is given in table 1 the information necessary for the preparation of standard buffer solutions covering the range from 1×10^{-2} to 2×10^{-7} M in hydrogen-ion concentration. The second column of the table contains the thermodynamic dissociation constant, given for purposes of comparison; the third, the classical dissociation constant in 0.1 M potassium

TABLE 1

The classical dissociation constants of certain acids in 0.1 M potassium chloride solution at 25°C.*

ACID	$K_a(c = 0)$	$K_c(c = 0.1)$	INDICATOR	$K_c(c = 0.1)$
Monochloroacetic...	1.396×10^{-3}	2.42×10^{-3}	Thymol blue pink-yellow	2.04×10^{-2}
Formic.....	1.86×10^{-4}	3.00×10^{-4}	Methyl orange	4.27×10^{-4}
Glycolic.....	1.46×10^{-4}	2.38×10^{-4}		
Benzoic.....	6.312×10^{-5}	10.12×10^{-5}	Bromophenol blue	14.9×10^{-5}
Acetic.....	1.745×10^{-5}	2.90×10^{-5}	Bromocresol green	3.07×10^{-5}
			Methyl red	1.04×10^{-5}
Cacodylic.....	6.0×10^{-7}	8.49×10^{-7}	Chlorophenol red	1.10×10^{-6}
			Bromocresol purple	9.3×10^{-7}

* The total concentration of uni-univalent electrolyte, $c_{KCl} + c_{NaX}$ is 0.1 M . $c_{NaX} < c_{KCl}/5$.

chloride solution, as determined electrometrically or kinetically in this laboratory. In the fourth column are listed indicators suitable for use with the acid in question, and in the fifth is given the value of the classical dissociation constant of the indicator in 0.1 M potassium chloride solution.

Hydrogen-ion concentrations higher than 5×10^{-3} can be obtained by the use of hydrochloric acid or perchloric acid. For concentrations lower than 2×10^{-7} M , other buffer systems are available; for these data are to be found in the literature. Standards can be prepared at intervals of 5 per cent change in hydrogen-ion concentration. It is suggested that new standards be made up frequently from standard acid and base, since the indicator colors fade and the buffer solutions often decompose on standing.

Table 2 gives the $K_c/K_{c, 0.1}$ ratios for a number of indicators at various ionic strengths. The solvent salt is potassium chloride.

To determine the hydrogen-ion concentration of an unknown, the un-

known, containing indicator at the same concentration as the standards, is matched against the standards after the procedure of Clark (3). The hydrogen-ion concentration of the matching standard is then multiplied by the factor in table 2 corresponding to the ionic strength of the unknown.

TABLE 2
K_c/K_{c,0.1} ratios in potassium chloride solution at 25°C.

MOLES SALT PER LITER	THYMOL BLUE	BROMOPHENOL BLUE	CHLOROPHENOL RED	BROMOCRESOL GREEN	BROMOCRESOL PURPLE	METHYL RED	METHYL ORANGE
0.1	1.00	1.00	1.00	1.00	1.00	1.00	1.00
0.2		1.17					1.02
0.5	1.03	1.29	1.22	1.31	1.25	0.89	0.67
1.0		1.25	1.48	1.18	1.32	0.75	0.61
1.5		1.15	1.20	1.13	1.02	0.60	
2.0		1.06	1.20	0.95	0.91	0.51	0.33
2.5		0.95	0.86	0.83	0.82	0.35	
3.0		0.76	0.72	0.77	0.67	0.28	0.16

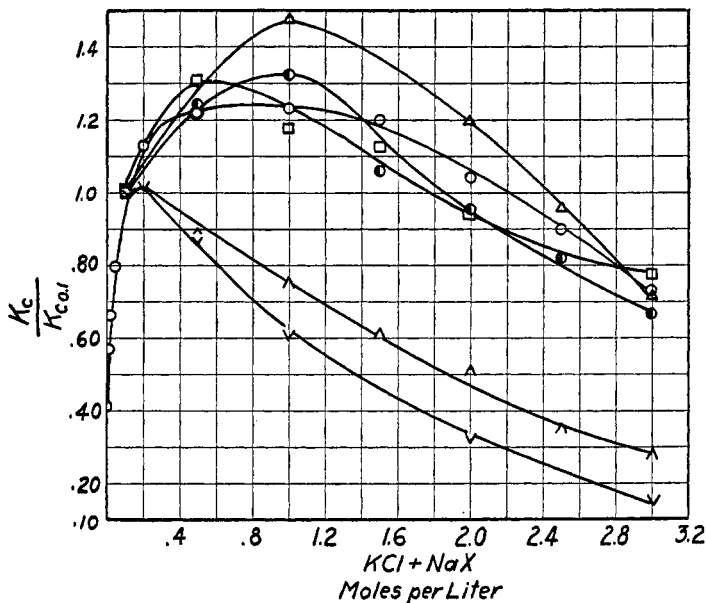


FIG. 1

For ionic strengths between 0.01 and 0.1, the values for bromophenol blue from table 3 can be used for the other sulfonphthaleins. For intermediate points the factor can be read from a plot similar to that shown in figure 1. The results are expressed in moles of hydrogen ion per liter and should be accurate to 5 per cent (0.02 pH unit).

Strictly speaking, the electrolyte in the unknown should be potassium chloride. At low ionic strengths (below 0.1) the error arising from the use of a different solvent salt is quite negligible. To show its magnitude at higher concentrations, in table 4 are given the values of the ratio $K_c/K_{c(0.1 \text{ KCl})}$ for the indicator bromophenol blue in solutions of four other uni-univalent salts, as well as in solutions of potassium chloride.

As pointed out elsewhere, no general method of expressing these second-order salt effects has as yet been found. Each salt has a specific effect on the dissociation constant of the indicator, and this becomes evident even

TABLE 3
 $K_c/K_{c(0.1 \text{ KCl})}$ ratios for bromophenol blue in dilute solution

MOLES ELECTROLYTE PER LITER	$K_c/K_{c(0.1 \text{ KCl})}$	MOLES ELECTROLYTE PER LITER	$K_c/K_{c(0.1 \text{ KCl})}$
0	0.41	0.01	0.57
0.0015	0.47	0.025	0.66
0.003	0.48	0.05	0.79
0.006	0.54	0.10	1.00

TABLE 4
 $K_c/K_{c(0.1 \text{ KCl})}$ ratios for bromophenol blue

MOLES SALT PER LITER	KCl	NaCl	LiCl	NaClO ₄	$p\text{-C}_6\text{H}_4\text{CH}_2\text{SO}_3\text{Na}$
0.1	1.00	1.05	1.07	1.01	1.01
0.2	1.17	1.19	1.24	1.07	1.04
0.4	1.31	1.22	1.34	1.07	0.99
0.6	1.31	1.25	1.37	1.04	0.89
0.8	1.30	1.27	1.33	1.00	0.74
1.0	1.25	1.26	1.32	0.91	0.64
1.5	1.15	1.10	1.13	0.76	
2.0	1.06	0.93	0.91	0.62	
2.5	0.95				
3.0	0.76	0.56	0.50	0.36	

at low concentrations when one is able to determine the differences accurately. The advantages of the method presented here are that it relates the salt error directly to the basic equation, that it makes the error immediately apparent, and that it offers a simple correction.

II. DETERMINATION OF HYDROGEN-ION CONCENTRATION WITHOUT BUFFER STANDARDS

It is possible to determine hydrogen-ion concentrations colorimetrically without the use of buffer solution standards. The method employed is the well-known Gillespie method (5) in which the reference solutions are

two solutions containing the indicator in its complete acid and basic form, respectively. A compensating colorimeter similar to that described by Clark (3) enables rapid determination of the ratio of acid to basic form of indicator in the unknown solution. It is important that the concentration of indicator be the same in the two standards and in the unknown. A microburet is a convenience in adding the indicator. At this point it seems desirable to mention that care must be taken in regard to the stability of the color, particularly the color of the basic form.

TABLE 5

Progressive change in colorimeter readings for alkaline solutions of bromophenol blue
Temperature, $25^{\circ} \pm 3^{\circ}\text{C}$. Bromophenol blue concentration, $2 \times 10^{-5} M$. Reference standard, freshly prepared basic form; reading, 20.0

DAYS	MOLES PER LITER								
	0.001* NaOH	0.001† NaOH 0.10 KCl	0.002 NaOH	0.003 NaOH	0.003 NaOH 0.10 KCl	0.005 NaOH	0.008 NaOH	0.009 NaOH	0.009 NaOH 0.10 KCl
1	19.6	19.2	18.6		16.9	16.6	14.6		11.3
2	19.0	18.1	17.6	16.8	14.1	14.0	10.6	11.1	8.4
3	18.4	16.9	16.7	15.4		11.4	7.8	7.9	
4	18.1	16.2		14.5	9.6			6.1	1.9
5	17.6	14.9	15.0	13.2		8.3	4.3	5.0	
6	16.8	14.0		11.9	6.4			3.3	0.9
7	16.2	13.1	13.0	10.7	5.0	5.5	2.3	2.4	0.6
8	15.8	12.0	12.0		4.3	4.4	1.8		
9	15.7	11.1	11.1	8.8	3.4	3.5	1.3	1.5	
10	15.1		10.4			3.1	1.1		Colorless
11	14.8			6.9				0.9	
12	14.4	9.0		6.2				0.6	
13	13.8	8.3		5.6	1.9		Colorless	Colorless	
14	12.7			5.0		1.8			
15			8.2						
16					Colorless				
18	11.9			3.5					

Solutions marked * represent the average of six experiments; those marked †, the average of three.

To show how rapidly the color of the standard may change, there are recorded in table 5 the results of a series of experiments on bromophenol blue in sodium hydroxide solution. These experiments were carried out with C. E. Gulezian in 1930. The data are presented graphically in figure 2.

The experiments were not carried out in a thermostat; nevertheless it is apparent from table 6 that the time required for the color to fade to one

half its original intensity is proportional to the concentration of sodium hydroxide. When potassium chloride is present the fading is much more rapid. From Gulezian's experiments it is evident that only enough alkali for conversion of the indicator to the basic form should be used.

A possible explanation of the fading has been given elsewhere (2). Calculation of the time of half-change, for lower hydroxyl-ion concentrations, indicates that a reaction with rate proportional to the hydroxyl-ion con-

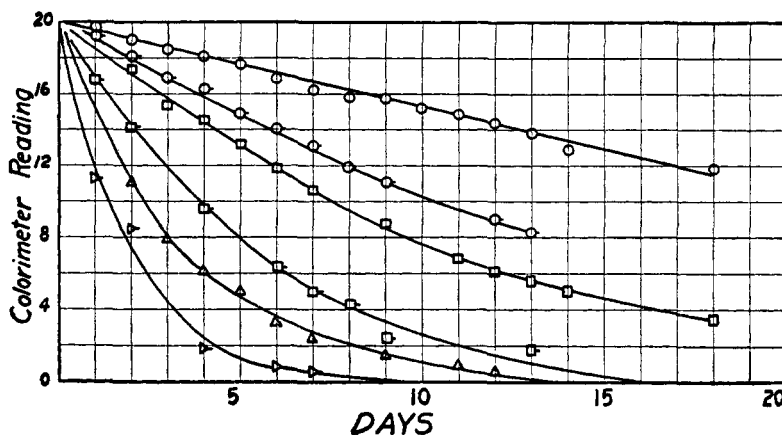


FIG. 2

TABLE 6
Fading of bromophenol blue in alkaline solution

MOLES NaOH PER LITER	APPROXIMATE TIME OF HALF-CHANGE
	<i>days</i>
0.001	20-22
0.002	10-11
0.003	7.5
0.005	4
0.009	2.3

centration is not the only one taking place. For we have observed, as have others (11), a fading of the color in solutions of much lower hydroxyl-ion concentration. The fading is not restricted to the halogen-containing sulfonphthaleins.

Having determined the acid-base ratio, one can calculate the hydrogen-ion concentration of the unknown from equation 2. As already pointed out, the classical dissociation constant of the indicator varies with the

nature and concentration of the electrolyte present, so that the proper value of K_c must be known. Table 7 gives the classical dissociation constants of a number of indicators in potassium chloride solutions of various ionic strengths. The values marked G were obtained by Güntelberg and Schiödt (6) at 18°C.; those marked K are computed from values compiled by Kolthoff (12), and the others are from this laboratory.

The dissociation constants of the indicators are most conveniently determined by the Gillespie method. The procedure is that just described, the only difference being that the hydrogen-ion concentration of the solution

TABLE 7

Classical dissociation constants in potassium chloride solution at 25° ± 3°C.

MOLES ELECTRO- LYTE PER LITER	THYMOL BLUE × 10 ²	BROMO- PHENOL BLUE × 10 ³	CHLORO- PHENOL RED × 10 ⁷	BROMOCRE- SOL GREEN × 10 ³	BROMOCRE- SOL PURPLE × 10 ⁷	METHYL RED × 10 ⁵	METHYL ORANGE × 10 ⁴
0	2.04 (K)	6.0	5.4	1.15 (K)	3.0 3.8 (K)	10.0 (K)	3.23 (G)
0.01		8.5	7.4	1.56 (K)	5.5 (K)		
0.025		9.9					
0.05	2.29 (K)	11.7	9.8	2.07 (K)	6.8 (K)		
0.1	2.32 (K)	14.9	11.0	3.07 2.33 (K)	9.3	10.4	4.27 (G)
0.2		17.4					4.34 (G)
0.3		17.9			11.2		
0.4		19.6					
0.5	2.38 (K)	19.2	13.4	4.03	11.6	9.21	3.71 (G)
0.6		19.5					
0.7		19.7			12.6		
0.9		19.3					
1.0		18.7	16.2	3.61	12.3	7.75	2.62 (G)
1.5		17.1	13.1	3.46	11.0	6.25	
2.0		15.8	13.2	2.93	8.9	5.33	1.40 (G)
2.5		14.1	9.45	2.55	7.6	3.61	
3.0		11.3	7.90	2.38	6.2	2.90	0.69 (G)

examined is known from previous electrometric or kinetic (8, 9) or even colorimetric (7, 9) measurements. In all cases the primary standard is a solution of a strong acid.

III. DETERMINATION OF THE HYDROGEN-ION CONCENTRATION IN UNBUFFERED SOLUTIONS OF LOW HYDROGEN-ION CONCENTRATION

In measuring the hydrogen-ion concentration of an unbuffered or weakly buffered solution it is necessary first of all to determine whether or not the addition of the indicator has changed the hydrogen-ion concentration. To

do this one must carry out a series of measurements at several indicator concentrations and several acid-base ratios of the indicator (1, 4, 11, 13). In principle the method of determining the hydrogen-ion concentration of the unknown consists in finding an indicator solution of such an acid-base ratio that its addition does not alter the hydrogen-ion concentration. Comparison can then be made with the standard buffer solutions and the correction for the salt error made from table 2 or 3, or, if complete acid and basic standards are employed, from table 7.

For unbuffered or very weakly buffered solutions Acree and Fawcett (1, 4) recommend the use of a series of standard solutions of the indicator, adjusted in steps of 0.2 pH unit (70 per cent in hydrogen-ion concentration). By matching against buffer standards, they determine which of their adjusted indicator solutions does not change color upon addition of the unknown, and call this indicator solution "isohydric" with the unknown. The pH as read off is corrected for salt error if necessary. Kolthoff and Kameda (13) state that it is not worth while to prepare a series of adjusted indicator solutions, since these solutions are not stable. They advocate approaching the correct acid-base ratio of indicator empirically. When the correct adjustment is found, comparison with buffer standards shows the same pH for different concentrations of indicator. Both Acree and Fawcett, and Kolthoff and Kameda, emphasize the necessity of using pure, carbon dioxide-free water, and of preventing the entrance of carbon dioxide during the test. To be consistent, it should be said that these investigators define the salt error as the difference between the colorimetric and electrometric pH values, and that the pH values as given by them are not equal to the negative logarithm of the hydrogen-ion concentration (10). For experimental details, and for references to other work on unbuffered solutions reported in the literature, the reader is referred to the papers of Acree and Fawcett and of Kolthoff and Kameda.

SUMMARY

1. The fundamental equation for the determination of hydrogen-ion concentration by the colorimetric method has been discussed.
2. A set of *hydrogen-ion concentration* standards is suggested, and the data necessary for the preparation of the standards furnished.
3. Indicators suitable for use with the standards have been listed, and their dissociation constants given.
4. A simple and direct method of correcting for salt error is presented, together with the data necessary for making the correction when measurements are made in the presence of certain of the more common uni-univalent solvent salts.

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