

On the Determination of pH in Seawater at Different Temperatures.

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In determining the pH of sea-water, sufficient regard has hitherto not been paid to the influence exercised by temperature.

As a rule, the temperature factor has been ignored entirely; in certain special investigations corrections have been made in a few instances, having been obtained by colorimetric determination of the changes in colour undergone by buffer indicator solutions during temperature changes.

If determinations are carried out — as at present is almost invariably the case — by the indicator method, the influence of temperature is of rather a complex character. Both buffer solutions, where such are used, and the fluid under examination may change their indicator colour with changes of temperature, but such changes of colour need not necessarily be in the same direction. If, for example, a sample of seawater and a borax buffer solution at a low temperature receive an admixture of phenol red and are afterwards heated, it will be found that the colour of the buffer changes in an alkaline direction, while that of the water has changed in an acid direction. But whether and to what extent pH changes have taken place in the respective solutions it is impossible for us to judge. Borax buffer solutions, with an admixture of cresol red, even show, as described later, the peculiarity that the colour of an alkaline mixture (pH about 8.5) fades with rising temperatures, whereas that of an acid mixture ($pH = 7$) is intensified. Between these limits, at about $pH = 8.20$ the colour remains perfectly unchanged. During the seasonal expeditions it may happen that samples of water taken from different depths at one and the same position, show differences in temperature of up to $25^{\circ}C$. It is obvious that if these samples are colorimetrically determined by one and the same buffer at a constant temperature, the values obtained cannot be exactly comparable with

each other. A quantitative investigation of the temperature error must embrace every factor in regard to which temperature plays a rôle. Such an investigation has been carried out by the author and described in an earlier work¹). This consisted of spectrophotometric investigation of the absorption of light by different colour indicators in buffer solutions and in sea-water of varying temperatures. This question was dealt with theoretically on the assumption that the indicators examined are weak acids, which become ionized on the addition of a base. The ion differs in colour from the undissociated acid. By applying the mass action law, it is possible to deduce a simple formula for calculation of the *pH* of the water at the time of collection, if once the temperature at that moment, as well as the *pH* and the temperature of the standard buffer solution with which the water sample has shown itself identical in colour on colorimetric determination, be known. If the two latter temperatures are indicated by t_w and t_b respectively, the *pH* of the comparison standard at the temperature t_b by pH_{t_b} , and that of the water by pH_{t_w} , one arrives at the *pH* of the water by means of the equation

$$pH_{t_w} = pH_{t_b} + \alpha (t_w - t_b)$$

α is a constant, individual for each indicator, showing the amount by which the dissociation exponent of the indicator varies for a temperature change of one degree. If the sample of water and the buffer solution used are of identical temperature, as is almost always the case in laboratory research, the term $\alpha (t_w - t_b)$ falls away, and the water should be allotted the same *pH* as that possessed by the buffer solution at the prevailing temperature. Should the latter deviate greatly from the temperature at which the *pH* of the buffer series has been fixed (generally 18° C.) a correction has to be made. WALBUM's²) investigations on the *pH* of a number of S. P. L. SÖRENSEN's standard buffer solutions have been of utmost value for fixing such a correction. The solutions used in the examination of sea-water are SÖRENSEN's phosphate solutions and especially PALITZSCH's³) boric acid-borax

¹) KURT BUCH: Über den Einfluss der Temperatur auf die *pH*-Bestimmung des Meerwassers; Merentutkimuslaitoksen julkaisu Havsforskningsinstitutets skrift N:o 61. Helsinki (Helsingfors) 1929.

²) WALBUM, L. E. Über die Wasserstoffionenkonzentration einiger Standardlösungen bei verschiedenen Temperaturen; Biochem. Ztschr. 107, 219. 1920. Ref.: W. MANSFIELD CLARK: The Determination of Hydrogen Ions. Third Edition, Baltimore 1928. Page 209.

³) SVEN PALITZSCH: Om Anvendelsen af Boraks- og Borsyreopløsninger ved den kolorimetrisk Maaling af Havvandets Brintionkoncentration. Meddelelser fra Carlsberg Laboratoriet 11te Bd. 5te Hefte 1916. Ref. CLARK's manual, page 213. Se foot note ²).

mixtures. According to WALBUM the *pH* of the former do not alter with the temperature. The latter have not been examined, but one has valid grounds for assuming that their sensitiveness to temperature will be similar to that of SÖRENSEN'S borate + HCl solutions, which were investigated by WALBUM. By the aid of WALBUM'S last-mentioned measurements, the author has made up an interpolation table (Table 1), showing

Table 1.

	<i>pH</i>	Temp. Coeff.	<i>t</i> =10°	<i>t</i> =12°	<i>t</i> =14°	<i>t</i> =16°	<i>t</i> =18°	<i>t</i> =20°	<i>t</i> =22°	<i>t</i> =24°	<i>t</i> =26°	<i>t</i> =28°	<i>t</i> =30°
Extrapolated	6.7	0.0021	+0.02	+0.01	+0.01	±0.00	±0.00	±0.00	-0.01	-0.01	-0.02	-0.02	-0.03
	6.8	21	2	1	1	0	0	0	1	1	2	2	3
	6.9	22	2	1	1	0	0	0	1	1	2	2	3
	7.0	22	2	1	1	0	0	0	1	1	2	2	3
	7.1	23	2	1	1	0	0	0	1	1	2	2	3
	7.2	24	2	1	1	0	0	0	1	1	2	2	3
	7.3	25	2	1	1	0	0	0	1	1	2	2	3
	7.4	27	2	2	1	+0.01	0	-0.01	1	2	2	3	3
7.5	28	2	2	1	1	0	1	1	2	2	3	3	
Interpolated	7.6	30	2	2	1	1	0	1	1	2	2	3	4
	7.7	31	2	2	1	1	0	1	1	2	2	3	4
	7.8	33	3	2	1	1	0	1	1	2	3	3	4
	7.9	35	3	2	1	1	0	1	1	2	3	3	4
	8.0	37	3	2	1	1	0	1	1	2	3	4	4
	8.1	39	3	2	2	1	0	1	2	2	3	4	5
	8.2	42	3	3	2	1	0	1	2	3	3	4	5
	8.3	45	4	3	2	1	0	1	2	3	4	5	5
	8.4	48	4	3	2	1	0	1	2	3	4	5	6
	8.5	50	4	3	2	1	0	1	2	3	4	5	6
	8.6	54	4	3	2	1	0	1	2	3	4	5	6
	8.7	58	5	3	2	1	0	1	2	3	5	6	7
8.8	62	5	4	2	1	0	1	2	4	5	6	7	
8.9	66	5	4	3	1	0	1	3	4	5	7	8	
9.0	70	6	4	3	1	0	1	3	4	6	7	8	

by how many *pH* units the inscription on the buffer solution container, referring to a temperature of 18° C., will need to be corrected to indicate the *pH* at the actual temperature of the buffer. The lowest temperature shown in the table is 10° C., which was the lowest limit of WALBUM'S temperature investigations. Extrapolation below this temperature cannot be considered advisable, as WALBUM himself had already made use of an extrapolated value for a constant needed in the calculations for

the electrometric determination at 10° C. Furthermore, the *pH*-range of the borate + HCl buffers investigated by WALBUM does not exactly coincide with PALITZSCH's boric acid-borax series, so that extrapolation was already partly necessary when calculating the temperature correction in the latter series. However, this extrapolated range of the borax series will but seldom come into question as far as ocean-water is concerned.

The necessity of observing the second term $\alpha(t_w - t_p)$ obviously depends on the value of α and the difference in temperature between the sample of water and the buffer¹). In the indicators examined by the author, α varies between the values 0.010 and 0.005, so that, with a difference of 20° C. between water and buffer, we may reach an error of up to 0.20 *pH*-units, i.e. a value considerably in excess of the usual run of experimental errors. The experiments should consequently be carried out so as to have the smallest possible difference $t_w - t_b$. This is, however, possible only to a very limited extent. We have already pointed out above, that the comparison series should not go below 10° C. ATKINS²) among others, has proposed that water of low temperature should not be measured immediately, but that the sample water should first be brought to approximately the same temperature as that of the buffer mixtures. This is, however, not altogether advisable, since equilibrium may be disturbed by the loss of carbonic acid (which is, however, of minor importance as regards sea-water and can be avoided by taking suitable precautions³), and further the indicator colouring of the water may change considerably with the temperature, as pointed out in the aforementioned work of the author, and as will also appear from the investigations here described. It is desirable, on the contrary, that the temperature of the water when measured should approximate as nearly as possible, to the temperature at the moment of collection. Should there be even some slight deviation, the original temperature of the water *in situ* ought to be assigned as the value for t_w in calculation.

The use of the aforementioned equation postulates satisfactory knowledge of the temperature coefficient of the dissociation constant

¹) Even in those instances where measurements are made by means of a colorimetric apparatus, so that comparison buffers are unnecessary, the influence of temperature on the buffers can nevertheless not be disregarded. The *pH* scale of the apparatus is generally calibrated with a buffer series at 18° C. and the calculation must then be worked as if this buffer had been used and its temperature were 18° C.

²) W. R. G. ATKINS: The Hydrogen Ion Concentration of Sea Water etc. Part II: Journ. Marine Biol. Assoc. Vol. XIII No. 1. 1923. Page 94.

³) See K. BUCH: Die *pH*-Bestimmung des Meerwassers etc.; Merentutkimuslaitoksen julkaisu Havsforskningsinstitutets skrift N:o 53. 1928. Page 22.

of the indicator used in measuring. By means of a series of spectrophotometric measurements at different temperatures this coefficient has previously been determined by the author as regards the indicators — α -naphtholphthalein, phenolphthalein and phenol red, which are all used in sea-water investigations, especially for water of low salinity. In examining ocean-water o-cresol-sulfon-phthalein or cresol red has now come into general use, and consequently this indicator has also been made the subject of a similar investigation, the results arrived at being described more particularly below. The investigation comprises 1) Spectrophotometric measurement of the absorption of light by cresol red in both alkaline and acid mixtures with varying wave-lengths, whereby the absorption spectrum of the indicator has been determined, together with the optimal wave-length for the following *pH* investigations. 2) Spectrophotometric measurement of the absorption of light of a series of boric acid-borax solutions mixed with cresol red at room temperature, whence the indicator's transformation curve and dissociation exponent have been calculated for 18° C. 3) Spectrophotometric investigation of some buffer solutions, and variations of their temperature, whence the temperature coefficient of the dissociation exponent has been calculated. 4) Spectrophotometric determination of sea-water, with an admixture of cresol red, at varying temperatures, rendering it possible to determine the extent to which the *pH* of the water is influenced by temperature.

1. Determination of the Absorption Spectrum of Cresol red.

A sample of cresol red from Schering-Kahlbaum A.-G., Berlin, was at first used in a 0.04 % alcoholic solution as a stock solution. Afterwards it was found that the indicator treated in this manner did not keep well. Spectrophotometric control determinations showed that after a few days had elapsed the colour strength had already faded several units per cent. After various measurements had been rejected for this reason, a preparation of the same strength dissolved in water, with the addition of NaOH in the proportion given in CLARK'S manual¹⁾ was used in later experiments with buffer solutions and has proved to keep well. For purposes of spectrophotometric determination 1 cm³ of this solution was added to 50 cm³ of the fluid under examination. This strength, (0.008 g/l), was afterwards used for all indicator investigations. The absorption spectrum of the indicator was fixed both in acid 0.001*n*

¹⁾ 3 Ed. Page 94.

HCl and in basic 0.001*n* NaOH solution. For spectrophotometric determination a KÖNIG-MARTENS spectrophotometer, supplied by Schmidt & Haensch¹⁾, Berlin, was used. The measurements were always carried out with the light passing simultaneously through two parallel solution tubes of equal length, the one tube containing the fluid under examination + indicator, the other the same fluid with no admixture of indicator, thus eliminating the light absorption of the fluid under examination. Fig. 1 below and Table 2 show the results of these investigations. The absorption of light is shown as the extinction coefficient ϵ , defined by the equation

$$\frac{J'}{J} = 10^{-\epsilon d}$$

in which J is the quantity of light entering the fluid, J' the quantity penetrating through it and d the thickness of the layer penetrated.

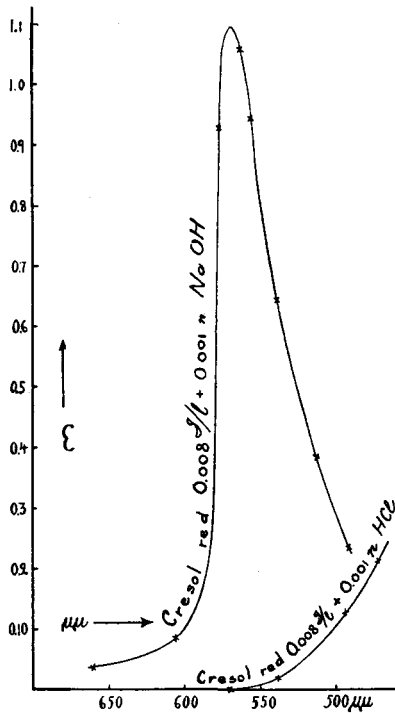


Fig. 1.

¹⁾ F. F. MARTENS und F. GRÜNBAUM: Ueber eine Neukonstruktion des König-schen Spektralphotometers. Ann. d. Phys. (4) 12 pp. 984—1003 (1903).

Table 2.

Wave length $\mu\mu$	Extinct coeff. ϵ	Wave length $\mu\mu$	Extinct coeff. ϵ
0.001 n NaOH		0.001 n NaOH	
660	0.032	513	0.387
604.5	0.084	492	0.238
577.5	0.929	0.001 n HCl	
570	1.078	570	0.0025
	1.097	539	0.0169
	1.108	513	0.0721
563.5	1.060	492	0.1311
557	0.946	474	0.2154
539	0.643	—	—

The maximum absorption of the indicator is found at the wave-length 570 $\mu\mu$. All later measurements of buffer solutions and sea-waters were made solely at this wave-length. The mean value of absorption at this wave-length was 1.094, which was used in calculating the indicator's dissociation constant. We may further point out that the absorption of the indicator in an acid solution at the same wave-length is practically 0, so that all absorption values mentioned hereafter are derived solely from the indicator ion, the application of BEER'S law rendering it possible to calculate the concentration of the latter directly from the absorption.

2. Cresol red and Boric acid-borax Buffer Solutions at room temperature.

In order to obtain suitable boric acid-borax buffer mixtures recourse was had to PALITZSCH's¹⁾ boric acid-borax solutions, which were mixed so that the solutions received the *pH* values valid at 18° C., given in Table 2, col. 1. Col. 2 indicates the temperature at which the measurements were carried out. Col. 3 shows the extinction values arrived at, col. 4 the value of the dissociation exponent *pK* (the negative logarithm of the dissociation constant), which was calculated by the application of the mass action law to the transformation equilibrium of the indicator by means of the equation

¹⁾ SVEN PALITZSCH: Om Anvendelsen af Boraks- og Borsyreopløsninger ved den kolorimetrisk Maaling af Havvandets Brintionkoncentration. Meddelelser fra Carlsberg Laboratoriet 11te Bd. 5te Hefte, 1916. S. 193.

$$pH - \text{Log} \frac{\epsilon}{1.094 - \epsilon} = pK$$

thus making use of the fact that the absorption coefficient ϵ can be regarded as a directly proportional to the concentration of the indicator ion.

Table 3.

N:o	1	2	3	4
	Boric acid- borax buffer. <i>pH</i> at 18°	<i>t</i> °	Extinct. coeff. 770 $\mu\mu$	<i>pK</i>
1	6.80	19.0	0.049	8.13
2	7.15	21.0	0.106	8.12
3	7.45	17.4	0.195	8.11
4	7.75	21.0	0.332	8.11
5	8.05	19.0	0.495	8.13
6	8.35	21.0	0.679	8.14
7	8.65	19.5	0.838	8.13
8	9.24	19.0	1.016	(7.32)

Mean (1—7): 8.124.

The results of the different measurements show a satisfactory coincidence, except in the case of the most alkaline buffer. This result coincides with the results of earlier investigations of other colour indicators, which correspond with the theoretic course only as far as the linear part of the transformation curve is concerned. A theoretic transformation curve, calculated in the reverse manner from the *pK*-value 8.124 and the absorption value in alkaline solution 1.094, coincides in the *pH* range — within which the indicator can be used — almost completely with a curve drawn through the experimental points. In CLARK'S¹⁾ manual, we find for the same indicator *pK* = 8.3, but it is not stated with the aid of which buffer series this determination has been made. The value of the constant varies with the quality and character of the electrolyte. A graphic representation of the course of the transformation of the indicator will be found in fig. 2 (right of figure, curve at 20° C.). The curve has been slightly corrected, so as to correspond exactly to the temperature indicated.

¹⁾ 3 Ed. Tabl. 23. P. 102.

3. Cresol red + borax Buffers at varying Temperatures.

The measurements at other than room temperature were made by the spectrophotometer tube, already filled with the fluid under examination, being placed for 15 to 20 minutes in a temperature bath and then rapidly dried, whereupon the spectrophotometric determination was carried out. The change in temperature during the spectrophotometric determination was checked by means of another tube, which was simultaneously subjected to the same treatment, the temperature of the latter tube meanwhile being measured both before and after the spectrophotometric determination. The temperature figures thus obtained can be regarded as accurate to ca. 1° C. The results are shown in Table 4 and in Fig. 2, on the left. We note the fact already mentioned, — and further verified by several experiments not recorded here — that the indicator ionization (proportional to ϵ) in the case of acid solutions increases and in that of alkaline solutions decreases with rising temperature. By graphic interpolation from the left hand system and by using WALBUM'S pH temperature coefficients as given in Table 1, the system shown on the right was set up, and shows the displacement of the indicator transformation curve with temperature. In theory such a parallel displacement implies a change in the value of pK , rendering it possible to calculate the temperature coefficient (alteration of pK per 1° C.) of the latter. In the case of cresol red a mean value of 0.0053¹⁾ was found. Consequently, when use is made of cresol red, the equation for calculation of the pH of the water is

$$pH_{t_w} = pH_{t_b} - 0.0053 (t_w - t_b)$$

Example. A sample of water, the temperature of which at the moment of collection is $t_w = 2^\circ$, is colorimetrically determined by a buffer series, with a temperature of $t_b = 25^\circ$. It is found to be identical in colour with a buffer tube inscribed $pH = 8.0$. By the aid of Table 1 we find that $pH_{t_b} = 7.98$

$$pH_{t_w} = 7.98 - 0.0053 (2 - 25) = 8.10.$$

The influence of temperature ought in theory to consist solely in a parallel displacement of the transformation curve. From fig. 2 it is nevertheless apparent that the alteration for temperature changes of equal degree is not the same at every part of the curve, being greater in the more acid portion. In this respect cresol red differs from the indicators previously tested by the author. This circumstance finds no explanation

¹⁾ Negative sign, as pK declines with rising temperature.

Table 4.

t	pH	Extinct. coeff ϵ	Degree of Trans-form. %	t	pH	Extinct. coeff ϵ	Degree of Trans-form. %	t
12.5	8.68	0.846	77.3	11	8.07	0.489	44.7	12
19.5	8.65	0.838	76.7	19	8.05	0.495	45.3	19.5
36	8.56	0.825	75.4	36.5	7.99	0.514	47.0	32

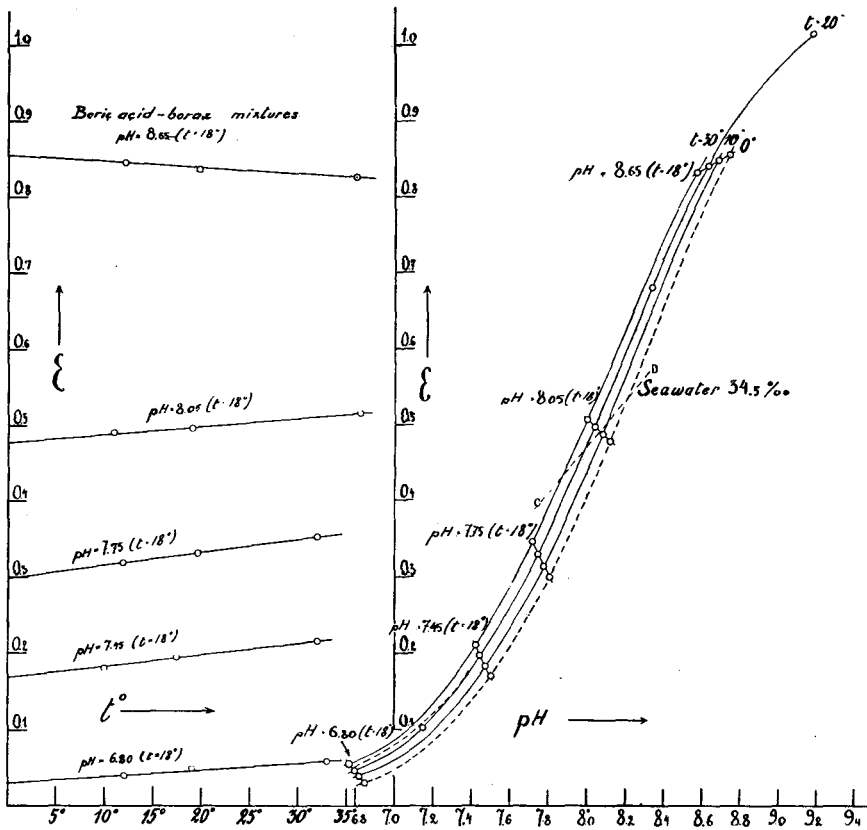


Fig. 2.

in the theory in its simplest form. In practice this deviation is of minor importance. The indicator should be used only within the pH range in which the curve is almost linear, and which coincides fairly closely with the pH range of sea-water; within this range the errors arising

Table 4 (continued).

t.	Degree of Transform. %	t	pH	Extinct. coeff. ϵ	Degree of Transform. %	t	pH	Extinct. coeff. ϵ	Degree of Transform. %
17	29.0	10	7.47	0.181	16.5	12	6.81	0.040	3.7
32	30.3	17.5	7.45	0.195	17.8	19	6.80	0.049	4.5
52	32.2	32	7.42	0.215	19.6	33	6.78	0.058	5.3

from the differences in question lie within the other experimental errors. The value assumed, 0.0053, is an average of the values at the limits of this indicator's range.

4. Cresol red and Sea-water at different Temperatures.

With the determination of the temperature coefficients of the pH of the buffer solutions and of the pK of the indicators, the data necessary for correct determination of the pH of the water, are known. To enable us to judge correctly the conditions, in which work with pH measurements in the open air should be undertaken in order to assure the most accurate results, it is necessary to know how the water alters its colour and pH in changing temperatures. The latter question has already been solved by the author¹⁾ by a series of spectrophotometric pH determinations, in which different indicators were used at varying temperatures, and by some measurements referring to different buffer series (borax and phosphate). Independently of the conditions under which the measurements were carried out, they led, in agreement with the theory, to practically identical results, *viz.*, that the pH of sea-water decreases by 0.012 units when the temperature rises 1° C. The result arrived at was the mean value of 10 determinations carried out in various ways and differing from one another within the limits ± 0.002 units. If the temperature of the water rises by, for example, 10° C. without its composition being altered through any loss of CO_2 , the acidity of the water increases by 0.12 pH units. From this it appears that temperature is by no means negligible with regard to the formation of pH conditions in nature.

In order to check the colour change of cresol red in sea-water, the pH was determined at two different temperatures with this

¹⁾ K. Buch: Loc. cit. Merentutkimuslaitoksen julkaisu Havsforskningsinstitutets skrift N:o 61. P. 19. 1929.

indicator also, the mode of procedure being as follows. A sample of sea-water, 34.5 ‰, received an admixture of indicator and was first spectrophotometrically examined at ordinary temperature. Thereupon the same tube was cooled and heated several times in succession, being spectrophotometrically examined after each change of temperature. The temperature was checked by means of parallel tubes. By taking the mean variation of heating and cooling, the result indicated by the line C—D fig. 2 (the system on the right) was obtained. If the temperature rises 30° C. the *pH* value declines by 0.36 units, or 0.012 units per 1° C., in agreement with the earlier mean value given above. With such an alteration of 30° C. in temperature, the light absorption value declines by 0.105 ϵ -units. If the corresponding *pH* alteration is read from the curve for 20° C., one arrives at not more than 0.18 *pH*-units, or merely the half of the actual figure. If a sample of water is taken for purposes of colorimetric determination and rises say 10° C. before the measurement is taken, the indicator colouring is lessened by an amount which would correspond to 0.06 *pH*-units on reading the buffer scale. We should thus obtain a value which would be this much too low.

An instance may be given of the *pH* values obtained by colorimetric determination according to the different methods in use. For the sake of simplicity we may assume that the temperature of the buffer series is 18° C., the temperature of the water on collection being $t_w = 2^\circ$. On immediate colorimetric determination the water is found to be identical in colour with a buffer tube inscribed 8.00, a value which consequently, if the temperature factor were to be neglected, would be regarded as correct. On heating the water to 18° C. and on the assumption that no CO₂-alteration takes place, the colour alters in an acid direction, in agreement with the tests already mentioned, the buffer scale showing a *pH* value of 8.00—0.006 \times 16 = 7.90. The correct value is obtained from the value arrived at on immediate colorimetric determination in accordance with the equation

$$pH_{t_w} = 8.00 - 0.0053(2-18) = 8.085.$$

The water may also be heated, however, to the same temperature as the buffer. Should this be done, the calculated value of *pH* must be corrected with the amount by which the indicator colour has changed in an acid direction during the heating process. The resulting equation is

$$pH_{t_w} = 7.90 + 0.0053 \times 16 + 0.006 \times 16 = 8.085.$$

The carrying out of pH Determinations in practice.

The indicator theory and the tests carried out show that in order to arrive at the greatest possible accuracy in taking measurements of *pH in situ*, heed must be paid to certain circumstances, which may be summarized as follows:—

1) In determining *pH* by the aid of indicators and standard solutions, effort should as a rule be made to keep the fluid under examination and the standard solution at one and the same temperature, *viz.*, that of the fluid *in situ*.

2) As the principle mentioned in 1) cannot always be adhered to, a note should always be made of t_b , the temperature of the standard solution, as well as of t_w , the temperature *in situ* of the fluid under examination. Should it be found impossible to avoid changes of several degrees in the temperature of the sample during the measurements, the temperature of the sample at the moment of measurement should also be noted.

3) The standard solutions should never be kept at a temperature of less than 10°.

4) The *pH* of the water sample *in situ* should be calculated according to the equation

$$pH_{t_w} = pH_{t_b} + \alpha (t_b - t_w)^1).$$

Here for pH_{t_b} is inserted the *pH* value found on colorimetric determination, corrected according to Table 1³⁾, and for α , depending on which indicator has been used, one of the following values:

cresol red	$\alpha = + 0.0053$
phenol red	$\alpha = + 0.010$
α -naphtholphthalein ²⁾	$\alpha = + 0.0084$
phenolphthalein	$\alpha = + 0.010$

¹⁾ For the sake of simplicity we have here, in contrast to our earlier procedure, changed the signs in the second term, in order to allow the α -values to be used with a positive sign, instead of a negative, as for reasons already pointed out should properly be the case.

²⁾ α -naphtholphthalein should not be used at temperatures approaching 0° C., as the colour fades at this temperature for reasons as yet impossible to explain by the theory now put forward.

³⁾ It should be remembered that Table 1 applies to borate buffer solutions only.

5) If the temperature of the sample under examination is several degrees higher at the time of measurement ($= t'_w$) than when collected, ($= t_w$) the correction $\beta (t'_w - t_w)$, should be added to the above equation in which β has one of the following values:—

cresol red	$\beta = 0.006$
phenol red	$\beta = 0.004$
naphtholphthalein	$\beta = 0.004$

Phenolphthalein needs no correction in the above respect. And in most instances this correction will probably not be needed for the other indicators also.
