

The Hydrogen Ion Concentration of Sea Water in its Biological Relations.

By

W. R. G. Atkins, O.B.E., Sc.D., F.I.C.,

Head of the Department of General Physiology at the Plymouth Laboratory.

With 1 Chart.

CONTENTS.

	PAGE
INTRODUCTION	718
HYDROGEN ION CONCENTRATION AND ACIDITY	718
BUFFER ACTION	720
THE DETERMINATION OF HYDROGEN ION CONCENTRATIONS	720
NEUTRALITY	721
THE HYDROGEN ION CONCENTRATION OF PURE WATER	722
THE COLORIMETRIC METHOD OF DETERMINING HYDROGEN ION CONCENTRATIONS	724
HYDROGEN ION CONCENTRATION OF SEA AND ESTUARINE WATERS	725
HYDROGEN ION CONCENTRATION PRODUCED BY CONSTITUENTS OF SEA WATER .	732
VARIATIONS IN HYDROGEN ION CONCENTRATION IN REGARD TO HEALTH AND MOVEMENTS OF FISHES	734
RELATION OF SOME PHYSICAL AND CHEMICAL FACTORS TO ALGAL DISTRIBUTION	735
LINES OF RESEARCH INDICATED	735
COLORIMETRIC AND TITRIMETRIC DETERMINATIONS OF THE HYDROGEN ION CON- CENTRATION AND THE LIMITS OF ACCURACY	736
THE HYDROGEN ION CONCENTRATION OF THE WATER OF THE AQUARIUM TANKS .	742
THE WATER OF THE SOUND AT VARIOUS TIMES COMPARED WITH THAT OF THE TIDE POOLS AND LAMINARIA BELTS	745
THE RELATION OF THE WATER OF THE SOUND TO THAT OF THE OPEN SEA	746
THE HYDROGEN ION CONCENTRATION OF OPEN SEA WATER AND ITS VARIATION WITH DEPTH AND SEASON IN RELATION TO THE PHOTOSYNTHETIC PRODUCTION OF CARBOHYDRATES	754
SUMMARY	766
BIBLIOGRAPHY	769

INTRODUCTION.

It has long been known that sea water is alkaline and numerous determinations of its alkalinity have been made. The method adopted was the usual one for mixtures of carbonates and bicarbonates, or some modification of it. Those waters which give no colour with phenolphthalein contain bicarbonate only, but for the most part ocean waters have a small amount of carbonate also. Owing to the presence of larger amounts of carbonates and bicarbonates the reaction of sea water is more stable than that of rain or river water, inasmuch as it has a greater alkaline reserve which acts as a "buffer." The significance of this has been pointed out by Moore, Prideaux, and Herdman (1915) and by other workers. The measurement of alkalinity was carried out by the above-named using N/100 hydrochloric acid and titrating to the end points with phenol phthalein and methyl orange. The results are recorded in cubic centimetres of centinormal acid per 100 c.c. of sea water; this is convenient as it is what is measured directly, but others adopt the perhaps more rational notation of milligram equivalents of hydroxyl per litre (Buch, 1914). One cubic centimetre of N/100 acid per 100 c.c. corresponds to 0.1 milligram equivalent per litre. Some workers on fresh waters, Birge and Juday (1911) for example, consider water as acid if it contains more carbon dioxide than that sufficient to convert the carbonate into bicarbonate, and titrate back to a pink with phenolphthalein. Their acid water is, however, still alkaline to methyl orange.

The advent of the methods of measuring the hydrogen ion concentration of water removed all such ambiguities, and it is very convenient to have one scale on which are measured all reactions, whether acid or alkaline. This may be done by giving the hydrogen ion concentration in grams per litre, symbolised as C_H or $[H^+]$, or by using the expression pH, which is defined as the logarithm of the reciprocal of the hydrogen ion concentration expressed in grams per litre. For a discussion of the advantages of this method of stating acidity reference may be made to Clark (1920). But to render what follows more intelligible to those biologists who are familiar neither with the methods by which hydrogen ion concentrations are determined nor with the terminology adopted, a brief account of the subject is given here.

HYDROGEN ION CONCENTRATION AND ACIDITY.

It has been found that the behaviour of enzymes and of living organisms towards acid or alkaline media is not correctly shown by titration, which gives a measure of the total replaceable hydrogen (or hydroxyl), not of

the concentration of the hydrogen ion effective at any instant. It is by the latter that the action on the organism is governed, as well as that on enzymes and the solubility of various salts. For example, equal volumes of N/100 hydrochloric and acetic acids require identical amounts of alkali for their neutralization, but the former solution has a far greater concentration of hydrogen ions than has the latter, since in dilute solution hydrochloric acid is almost completely ionized, whereas acetic is not; it is accordingly said to be a weaker acid. If it is assumed that the ionisation of hydrochloric acid is complete at this dilution, viz., N/100, its concentration in terms of gram ions is C_H or $[H^+] = 1 \times 10^{-2}$ grams per litre.

This may be written $[H^+] = \frac{1}{10^2}$ or $pH = \log \frac{1}{[H^+]} = -\log [H^+] = 2$.

It may at first sight appear to be both cumbersome and unnatural to use such an expression as pH, viz., $-\log [H^+]$, to denote hydrogen ion concentration, but in practice it is extremely convenient, and gives simple numerical values which are easily remembered. Moreover, since an increase of unity in a pH value denotes a decrease to one-tenth in the hydrogen ion concentration, it is obvious that for any graphical presentation of results difficulties arise when the changes are of the order of 10^{-3} or 10^{-6} , yet these are quite common in researches on enzyme action. For certain purposes, however, it is at times convenient to use C_H values. To convert the $-\log [H^+]$ or pH values into C_H or $[H^+]$ values use may be made of semi-logarithmic paper, as pointed out by Roaf (1920). The first decimal points of the pH values are marked off from right to left as abscissæ, the C_H values from 0.1 to 1.0 being ordinates against the logarithmic rulings. A diagonal being drawn, the C_H value of any pH value may be read off, the whole number of the latter being the negative power of ten, by which the C_H value must be multiplied. Thus, for example, with pH4.50 it is found that 0.50 on the abscissa corresponds to 0.32 on the ordinate; the C_H value is then 0.32×10^{-4} . Conversion tables are, however, given by Clark, also at shorter intervals by Schmidt and Hoagland (1919). A further reason for using $-\log [H^+]$ values will be given later on.

C_{OH} is used by Helland-Hansen (1914) and Gaarder (1917), but while it has perhaps some advantages of a local nature—if only sea water were being considered—its use is highly objectionable, as it necessitates the use of two scales and cuts off research on sea water from that on plant and animal tissues, which are often acid. It is true, of course, that as hydrogen ions increase, hydroxyl ions decrease, the product being constant, but for that very reason it is more convenient to adhere to the original use of pH values and C_H values, especially as the pH value of pure water is

not as yet known with any great precision. All C_{OH} values require recalculation for any alteration in the value accepted for pure water.

Thus while measurements of titratable alkalinity are of value as giving useful information and a measure of the buffer action of water between any selected hydrogen ion concentrations, yet the latter alone is capable of showing the reaction correctly, for a total alkalinity, equivalent say to one cubic centimetre of centi-normal acid, due to sodium hydroxide, is at a very different pH value from the same alkalinity due to a carbonate or bicarbonate. The titration value is, however, of much importance, as upon it the maintenance or otherwise of an approximately constant pH value depends.

BUFFER ACTION.

If alkali is added to acid, after a certain amount has been run in, a neutral solution is obtained. With a strong acid, such as hydrochloric, the addition of the alkali in successive portions results in a progressive diminution in the hydrogen ion concentration, as may be seen from the fact that the strong acid was largely ionised at the start. But with a weak acid the neutralization of the hydrogen ions existing at any instant results in a new equilibrium being attained by the remaining undissociated molecules of the acid, which become ionised to the same percentage as before. The alteration in the hydrogen ion concentration is therefore much less over a considerable range. If the results are plotted with pH values as ordinates and cubic centimetres of alkali as abscissæ, the slope of the curve will be less steep for the weak acid than for the strong, except near the neutral point. Curves illustrating this are given by Clark (1920), and in the older literature. A weak acid thus has a considerable "buffer action" in preventing rapid alterations in pH values, and the same is true of weak bases.

THE DETERMINATION OF HYDROGEN ION CONCENTRATIONS.

From theoretical considerations Nernst developed an equation connecting the electromotive force of a concentration cell with the concentration of its ions. Platinum black deposited on platinum and immersed in a solution through which pure hydrogen is bubbled constitutes a hydrogen electrode. On the assumption that in very dilute solutions the ions obey the gas laws, it has been shown that the potential of the hydrogen electrode changes with the concentration of hydrogen ions as follows:—

$$dE = \frac{RT}{nF} \frac{dP}{P}, \text{ which on integration becomes}$$

$$E = \frac{RT}{nF} \log_e P + A, \text{ where } A \text{ is an integration constant, } R$$

the gas constant, T the absolute temperature, n the valency of the ion, and F the faraday or quantity of electricity carried by one gram equivalent of the ion, and $\log_e P$ is the natural logarithm of the partial pressure due to hydrogen ions. Now if two such hydrogen electrodes are connected to form a concentration cell, the electromotive

force developed is equal to $\frac{RT}{nF} \log_e \frac{C}{C^1}$, where C and C^1 are the concen-

trations of hydrogen ion, since the ratio of the pressures may be taken as equal to the ratio of the concentrations.

In practice such a hydrogen electrode is connected by an inverted U-tube arrangement containing a solution of potassium chloride, with a calomel electrode, and the electromotive force of this cell is measured by means of a potentiometer, with all due precautions. The constants being evaluated, use is then made of the following equation to determine the hydrogen ion concentration :—

$$\left. \begin{array}{l} \text{E.M.F. (obs.)} - \text{E.M.F. (of normal} \\ \text{hydrogen and calomel electrode cell)} \\ \hline 0.0001983T \end{array} \right\} = \log \frac{1}{[\text{H}^+]} = \text{pH.}$$

Using an N/10 KCl—calomel electrode, this becomes at 25° C. :—

$$\text{E.M.F. (obs.)} - 0.336 = 0.0591 \log \frac{1}{[\text{H}^+]} = 0.0591 \text{pH.}$$

The fact that the term $\log \frac{1}{[\text{H}^+]}$ is thus directly determined is another reason for expressing hydrogen ion concentrations in pH values.

Full proofs of these equations and directions as to technique may be found in "The Determination of Hydrogen Ions," by Clark.

The method is used as the fundamental one for determining pH values. By its means buffer solutions of accurately reproducible pH values may be standardised for use in colorimetric determinations by means of indicators.

NEUTRALITY.

It has not been explained as yet what is meant by a neutral solution or neutrality. Pure water dissociates primarily into hydrogen and hydroxyl ions, and the product of the ionic concentrations is a constant at constant temperature, namely :—

$$[\text{H}^+] \times [\text{OH}^-] = k[\text{H}_2\text{O}] = K.$$

Since the ions are produced by pure water in equal numbers, the concentration is the same for both when reckoned in gram-equivalents. A

solution is accordingly termed neutral when the hydrogen and hydroxyl ions are present in equivalent amounts, as in pure water. With an acid solution the hydrogen ion is in excess, and the hydroxyl is correspondingly reduced, since the product is constant. In alkaline solutions hydroxyl ions preponderate, but it is possible and convenient to state the reaction of the solution in terms of hydrogen ion concentration rather than in terms of the hydroxyl. One scale, the pH or $-\log H$, is therefore obtained instead of two, based upon the concentrations in pure water as a starting point for both. Before the use of pH values became general it was however proposed by Walker and Kay (1912) to express the acidity or alkalinity of natural waters in terms of specific values, taking pure water at the same temperature as unity. More recently Wherry (1919) has re-introduced these specific values for work on soil reaction. Thus, taking neutrality at pH7, sea water, which is near pH8, would be of specific alkalinity 10, containing ten times the concentration of hydroxyl ions. The writer considers that such specific values are unnecessary, though in a general way they undoubtedly serve to give a readily grasped conception of the condition of a liquid. To adopt these specific terms would be to destroy the value of having one scale. The reasons have been given fully by Clark (1920) and have been again urged (1921) in reply to a further paper by Wherry and Adams (1921).

THE HYDROGEN ION CONCENTRATION OF PURE WATER.

It is of interest to determine the hydrogen ion concentration of pure water, but this is attended by many experimental difficulties. Those due to the solution of minute traces of glass may be avoided by the use of silica or platinum vessels, but the absorption of carbon dioxide is still a trouble. It is not possible to determine the pH value by the potentiometer on account of the great internal resistance of the hydrogen electrode half-cell when made up with pure water. The various methods adopted have recently been reviewed by Beans and Oakes (1920). They are as follows:—

1. By deduction from measurements of the electromotive force of concentration cells made up with dilute solutions.
2. By conductivity methods, giving the ionic mobilities of hydrogen and hydroxyl ions in very dilute solutions, these values are considered to be valid for pure water; the conductivity of the latter is then measured, and from it and the ionic mobilities the concentration of the ions is calculated. This is the method used by Kohbrausch and Heydweiller (1894), and is the only one of those already mentioned which is based upon an examination of pure water; but even then use is made of data derived

from solutions. For pure water these workers found the hydrogen ion concentration at 26° C. to be 1.10×10^{-7} or pH6.96. The value varies with the absolute temperature, as may be seen from the equation previously given. Michaelis (1914) gave for pure water at 10° C., pH7.10; at 22° C., pH7.00; and at 28° C., pH6.90.

3. By methods based on the hydrolytic dissociation of salts.
4. By measurements of the rates of certain reactions.
5. By the use of indicators, which give definite tints at known concentrations.

All these methods agree in giving values which are not very far from pH7.1. Method (5) is used by the writer to test the purity of freshly boiled distilled water and to test glass apparatus for solubility. As shown by its behaviour to bromthymol blue and phenol red, and compared with Clark's standard solutions, the purest, freshly boiled, thrice distilled water which has been prepared here gave pH7.10 to 7.05 at about 15° C. Boiling to remove carbon dioxide in certain types of "hard" glass tube may, however, give any value from about pH8 upwards, so every tube has to be tested and re-tested after use with alkaline precipitates. If used in the cold such "hard" glass tubes are safe for a time, whereas soft glass tubes are not. Pure water boiled in a soft glass test tube is at about pH9 or over. Once the indicator has been added the liquid is no longer pure water, hence method (5) is open to objection; but if due precautions are taken in making up the indicator, and if only a very minute amount, say, two drops of a 0.02 per cent solution, is added to 10 c.c. of liquid, the error from this source is slight. Precautions are necessary on account of the fact that pure water has a negligible buffer action.

An entirely new method has been introduced by Beans and Oakes (1920). In this the hydrogen electrode is set up with the purest water, and the cell $\text{Hg}|\text{HgCl}|\text{KCl}|\text{KCl}|\text{H}_2\text{O}|\text{H}_2$ is used to charge a condenser of one microfarad capacity, which it does in three to five minutes, whereas a cell of lower internal resistance in which dilute acid is substituted for pure water only requires an instant. Now, the quantity of electricity stored is equal to the product of the E.M.F. of the cell and the capacity of the condenser, viz. $Q=EC$. When discharged through a ballistic galvanometer a deflection d_1 is obtained when the pure water hydrogen electrode is used. Using a standard cell of known voltage a deflection d_2 is shown. Now, since d is proportional to Q , and $Q=EC$, therefore

$$d_1/d_2 = \frac{E_1 C}{E_2 C} \text{ or } \frac{E_1}{E_2} = d_1/d_2; \text{ and, since } E_2 \text{ is known, } E_1 \text{ may be found and}$$

the pH value calculated as in the potentiometer method. The value arrived at for pure water at 25° C. is pH7.91 or $[H^+] = 1.23 \times 10^{-8}$. This differs considerably from the results previously obtained, but the method seems very simple and direct. From the biological standpoint it is not of great importance to ascertain this constant precisely, as pure water is never found in nature, and its reaction is not necessarily the most favourable for living cells, which can, in different species, tolerate a large range of acidity and alkalinity, a reaction suitable for one being possibly fatal for another.

The uncertainty as to the precise pH value of pure water is another reason against taking this quantity as a unit and using specific acidity or alkalinity values. Furthermore, since pure water is never found in nature, and is most difficult both to prepare and to keep, its use as a standard has no practical utility. Rain water, at about 10° C., examined almost immediately after its fall has been found to be at pH5.9—6.0 at Plymouth and Malvern. It is presumably in equilibrium with the carbon dioxide of the air. On standing corked for about two months at room temperature in a "hard" glass tube the rain water changed to about pH6.4, owing to the solubility of constituents of the glass. These traces of alkali become evident at once and neutralise the carbonic acid, thus altering the reaction of this unbuffered liquid.

THE COLORIMETRIC METHOD OF DETERMINING HYDROGEN ION CONCENTRATIONS.

In addition to the electrical methods already mentioned the colorimetric method, introduced by Friedenthal (1904) and Salm (1904), is available. It is based upon the potentiometer method as a standard, the latter being used to determine the pH values of the buffer solutions, made up to be at convenient intervals on the pH scale. Measured amounts of various indicators are added to these solutions. The electrical method is also used to check sources of error such as those due to proteins and salts, which cause the indicators to give readings higher or lower than the true values.

The colorimetric method was improved and extensively tested by Sørensen (1909), who introduced new indicators, and eliminated those liable to mislead. More brilliant water-soluble indicators of the sulphone phthalein series were introduced by Clark and Lubs (1917), as well as standard buffer solutions, having certain advantages over those of Sørensen. The indicators and standard solutions used in this research are those introduced by Clark and Lubs, also some due to McClendon. A full account of the method has been given by Clark (1920) and by Cole (1920). Clark gives a coloured chart which can be purchased separ-

ately, and is a great aid in approximate work or in field work without standard tubes. In most cases the colours are faithful renderings of those in the standard tubes, with the indicator in the specified amount.

The intervals in the Clark and Lubs series are uniformly pH0.2 from pH1.2 to pH10.0. For sea water McClendon (1917) has given a very useful series at intervals of pH0.05. These are made up corrected for salt error at the normality of chloride usually found in sea water, corrections being given for slight differences in salinity. In work of this nature care should be taken to check and cross-check the solutions and indicators, both when freshly made up and after storing. It is always advisable to use two or more indicators in orienting experiments.

HYDROGEN ION CONCENTRATION OF SEA AND ESTUARINE WATERS.

The earliest determinations were those of Ringer (1908) by means of the electrical method. Samples were obtained and brought to the Laboratory after storage for some time, when it was found that the pH values lay between 8.24 and 7.86. The waters tested were from the Zuider Zee, North Sea, and Bømmelfjord. The values appear fairly normal, as viewed in the light of subsequent work, but are open to three sources of error, firstly owing to the sweeping out of carbon dioxide by hydrogen the values tend to be too high numerically, viz. more alkaline, though precautions were taken to minimise this error. Hasselbach (1910, 1911) and other workers have introduced modified apparatus and methods whereby the errors owing to loss of carbon dioxide from liquids are greatly reduced. Secondly, on account of the evolution of carbon dioxide by bacteria and plankton organisms the pH value tends to be lowered on keeping. Thirdly, owing to the possible giving off of alkali by the glass, especially in new bottles, the values may be high. It should be noted that ground glass stoppers and the ground portion of bottle necks are particularly liable to give off alkali, as may be seen in indicator bottles. It is advisable, therefore, to remove indicators with pipettes in preference to pouring them out.

The colorimetric method was then applied to sea water by Sørensen and Palitzsch (1910) as a development of the perfection of the method by Sørensen (1909). These workers (1910) also introduced *α*-naphtholphthalein as a useful indicator for the range covered by sea water. This along with phenolphthalein gave reliable results, when compared with the electrometric method so as to allow for errors due to the action of the neutral salts on the indicators. The values at first obtained, which vary from pH6.6 to 8.6 are, as pointed out by the authors, vitiated by storage.

Palitzsch continued the work in the *Thor* expedition (1911, 1912); and his numerous determinations on freshly taken samples are the first really reliable measurements over extended areas. In the western end of the Baltic, in the Sound, Skagerak, and south of the North Sea the surface water was between pH 8.00 and 8.05. Off Scotland and the Faroe Is. it varied from 8.08–8.22. Further south, off the coast of Portugal, it rose to 8.25. In the Mediterranean it was usually above 8.22, being as much as 8.27 in the eastern end. In the Sea of Marmora, Bosphorus, and Black Sea it was close to 8.35. These values are, of course, obtained by interpolation between the standard buffer solutions which, as given by Sørensen for the range, are at irregular intervals from pH 0.06 to over pH 0.3. It is thus a matter of opinion whether a shade differs by pH 0.03 or 0.04 from a standard, but if the sample is kept and tested with fresh indicator it is easy to see whether the next sample is nearer or further from the standard. Neither phenolphthalein nor *α*-naphtholphthalein remain constant in tint if kept for a day, even when protected from the carbon dioxide of the air.

Palitzsch further studied the relation of pH to depth, and found that there is always a noticeable, though not very great, diminution from the surface downwards. In the North Sea and Atlantic there is as a rule no colour with phenolphthalein below 400 metres, with this indicator a colour is given above pH 8.06 with salinity 35‰. It may be mentioned that the salt error is 0.21 and 0.16 at 35‰ and 20‰ respectively, and for *α*-naphtholphthalein 0.22 and 0.17; these amounts have to be subtracted from the pH value as found. The following figures given by Palitzsch are of interest. He does not mention the possibility of seasonal changes in pH values, so the dates are only recorded indirectly. The Faroe Is. results were, however, obtained in May and June, and the Mediterranean results between June and September inclusive.

Depth in metres.	Mediterranean, between Sardinia			
	N. Sea, E. of Faroe Is. pH	Atlantic, W. of Portugal. pH	and Italy. pH	Black Sea. pH
0	8.13	8.22	8.23	8.34
100	8.09	8.13	8.21	7.86
400	8.03	8.04	8.19	7.53†
1000	7.98*	8.01	8.14	7.26
2000	—	7.95	8.09	—
3200	—	—	8.07	—

The decrease in alkalinity with depth is clearly shown by the above figures. In the light of more recent work the extension of the region of high alkalinity into the deeper layers of the Mediterranean water may

* 700 metres.

† H₂S below 180 metres.

be interpreted as due to the measurements being made later in the season. Palitzsch also looked for a relation between increase in alkalinity and increase in oxygen content of the water. He notes, for example, that Vaag Fjord (Faroe Is.) water was very rich in oxygen and of high alkalinity pH8.22-8.24. In general a region of high pH value is also high in oxygen, and low pH values are found in regions where oxygen is in reduced amount, or even absent, as in the Black Sea; this results in sulphuretted hydrogen accumulating, as the sulphur is no longer oxidised to sulphate. The relation is not, however, one which holds always, for excess of carbon dioxide, over and above the amount in equilibrium with the air, is produced by the respiration of plants and animals. Photosynthesis, on the other hand, breaks up the oxide and sets free oxygen, which may also be obtained direct from the air, especially where vertical currents mix the water. Owing to the buffer action of the bi-carbonate, the carbon dioxide content of sea water cannot fluctuate as rapidly as can the oxygen, so water of low oxygen content may have its supply renewed from the air before its carbon dioxide content has come into true equilibrium with that of the air. The high alkalinity of the water in Vaag Fjord was probably due to the action of the coastal algal belt, or to a local abundance of algal plankton. Palitzsch further notes that at the level of the Murray Firth the sea water twenty miles out rose to pH8.15 to 8.18.

Palitzsch (1915, 1916) also introduced mixtures of borax and boric acid for preparing buffer solutions for work with sea water. These are at intervals of pH0.06-0.10 for the most part.

Following up this work Helland-Hansen (1914) investigated the Atlantic waters from the west of the Hebrides, viz. about 8-32° W. and between 54°-60° N. His interesting data, illustrated by graphs, bring out clearly the general correspondence between oxygen concentration and hydrogen ion concentration, or in hydroxyl ion, as this author prefers to state his results. He found that a surface alkalinity of pH8.22, converted from C_{OH} values by Gaarder's tables (1917), rose at 20 metres or so to 8.26, thereafter falling to pH8.00 at about 100 metres and to 7.95 at 500 metres; with slight rises, not exceeding pH8.01 at 1200 metres, the value pH7.95 was maintained to 2000 metres. These figures are from the most westerly station, but those from the most easterly follow much the same trend, the graphs intersecting five times. The measurements were all made in July, 1913.

During 1911 and 1912 Buch (1914) carried out a series of determinations of alkalinity, carbon dioxide, and hydrogen ion concentration in the Pojowiek (or Pojovik) as part of an elaborate hydrographic survey of this slightly brackish diverticulum of the Gulf of Finland. It is about thirty kilometres long and in breadth from about one-fifth to three

kilometres. The observations were made from August to August, in November, March, and June. The greatest acidity, pH6.53, was found in melted ice water in March, and the greatest surface acidity, pH6.90, was found at the same time in fresh water, salinity 0.07 parts per thousand. As a general rule the more saline bottom water is also more alkaline than the surface water; the relation is, however, frequently reversed in the summer. At this season, in addition to occasional very high values for acidity near the bottom, such as pH6.75 and 6.86, it is often found that, as in the ocean, the surface water is the more alkaline although less saline. For example, with salinity increasing from 5 (surface) to 6‰ (bottom) pH values decrease from 7.90 and 7.86 at 0 and 10 metres respectively to 7.65 and 7.57 at 20 and 27 metres. Furthermore, in the August measurements exceptionally high alkalinity values are found, pH being greater than 8.45 in one case, with salinity only 0.73‰ and above 8.37 in another with 3.64‰. These figures were obtained at different stations at the surface and 4.5 metres.

The much wider range of hydrogen ion concentration as compared with sea water is very striking. Apparently the low salinity of the water denotes also a great diminution in the magnesium carbonate and bi-carbonate, which act as a buffer mixture in the sea; owing to the lower solubility of the corresponding calcium salts the amounts brought down in the fresh water are so small as quickly to undergo change due to photosynthesis and respiration even in large masses of water. These interesting results are quite in keeping with the alkalinity determinations of Birge and Juday (1911) on the waters of the inland lakes of Wisconsin, but these workers did not determine hydrogen ion concentrations. Similar changes due to photosynthesis are recorded by Chambers (1912).

A further investigation was carried out from 1912-14 by Buch (1917) upon the same variables in the Baltic. The very comprehensive tables given are, as before, illustrated by charts. As a general rule the surface water is more alkaline than the bottom water, but the minimum alkalinity, though usually, is not always at the bottom. Particularly noticeable are the high values found in Gulf of Finland in summer, surface samples giving pH8.30-8.34 at the eastern end as against pH7.85 in the sea half-way to Sweden. The change with depth is often very noticeable, thus in May in the Gulf the warmer surface water at 5° C. and 4.5‰ salinity is at pH8.34, 8.27, and 7.93 at 0, 10, and 15 metres, while the colder water 1° to 2° at salinity 6‰ decreases from pH7.51 to 7.29 from 20 to 47 metres. In October in the same region the deep water is slightly over 2°, and the salinity slightly higher than before, 7‰, while the surface water is at 11° and 4.9‰, yet the reaction has altered to pH7.90 at the surface and at 50 metres to 7.57. These changes are illustrations of

the effect of photosynthesis upon large masses of water, as is made even clearer by the fact that the high pH values for surface water were accompanied by an oxygen content of 110% of saturation, whereas the lower October value corresponded to 92%.

From 1912 onwards special attention was given by Moore and his co-workers to the changes in alkalinity of sea water induced by photosynthetic activity of plankton and attached algæ. Thus Moore, Prideaux, and Herdman (1915) showed for sea water the existence of seasonal alterations in this medium such as had been noticed in fresh water by Birge and Juday (1911) and by Chambers (1912). They moreover showed that an epidemic of ulceration of the skin occurring in the Port Erin fish hatchery was due to the exceptionally high alkalinity of the water occasioned by the presence of numerous monocellular green flagellates and algæ. The values obtained varied from pH8.10 in December to 8.37 in May for the water of the Irish Sea. The original paper is readily accessible and should be consulted for details and computations of the magnitude of the crop of plankton algæ indicated as minimum values by the changes in alkalinity throughout the year. Calculating from the observed alteration in carbon dioxide content per litre and assuming that owing to efficient mixing this change affects the water to 100 metres, as seems justifiable in the open sea from Palitzsch's work, it is shown that a crop of about two tons of organic matter, dry weight, must result per acre, or at least ten tons of moist plant. These authors emphasize the value of the buffer effect of sea water and showed that about 1-3 c.c. of centi-normal hydrochloric are required to neutralise sea water, 100 c.c., to phenolphthalein and a further 21-24 c.c. to neutralise it to methyl orange. The figures give a measure of the buffer action of the sea water between the limits of the colour changes of these indicators, namely, approximately pH7.6 (allowing for the action of neutral salts) and pH4 (Prideaux 1919).

The alkalinity of the sea off the Norwegian coast and of the fjords has been the subject of a lengthy paper by Gaarder (1917). The results are recorded in "hydroxyl numbers," namely, the number of gram-equivalents of hydroxyl ion per litre multiplied by 10^7 , but conversion tables to pH values are given. The relationship between alkalinity and oxygen content is well brought out, as is also the seasonal variation in these two factors. Thus in the figures given for Mofjord the water is saturated with oxygen at 10 metres in October, but by June the saturation limit has sunk to 18 metres, after which it rises slowly again. Supersaturation (as measured at 760 mm. pressure) to the extent of 10 per cent occurs from March to September or October at a depth of 10 metres. It is also in May and June, and at a depth of 10 metres, that the maximum alkalinity occurs, a hydroxyl number of 14 being reached, corresponding to pH8.29,

whereas in the winter months at 10 metres the alkalinity is pH7.98. At the depth of 60 metres there is little variation from pH7.3 throughout the year.

Most noticeable of all are the figures for certain shut off basins and fjords, such as Inderöpollen, in which early in September, 1914, the water down to 2 metres was from 100 to 102 per cent saturated with oxygen while from 3 to 4 metres it was 188 per cent, 97 per cent at 7 metres and only 23 at 10 metres. Corresponding to these it was found that at 0—2 metres the alkalinity was pH8.43, at 3—4 metres 8.49 or over, at 7 metres 8.01, and at 10 metres 7.4 or less. The existence of sulphuretted hydrogen is recorded in some of the isolated basins with no free oxygen in the depths.

Some measurements are also given by Nansen (1915) of the pH values, determined with Palitzsch's mixtures, of the Spitzbergen waters. These were carried out during the cruise of the *Veslemøy* in July and August, 1912. They are of interest as being the only ones on very cold salt water, 4.8° to -0.55° . As might be expected the values are mostly low, pH7.94 to 8.08. Some remarkably high values are also given, pH8.25—8.19. The foregoing are all surface measurements. With the higher values the gradient of change with depth is steeper than in warmer seas, a decrease from pH8.24 at the surface to 8.07 at 50 metres being recorded.

McClendon (1916) and his co-workers Magoon, Gault, and Mulholland carried out a series of electrical measurements on sea water at various pressures of carbon dioxide (1916, 2, and 3; 1917, 1, and 2). In addition a new set of carefully standardised buffer solutions was prepared, at intervals of pH0.05 over the required range. These were made up with the stable sulphone phthalein indicators in sealed tubes. The data and graphs given are of permanent value to all workers in this field. McClendon drew attention to the small amount of residual buffer action found in natural sea water after removal of the carbonates and bicarbonates, the volatile buffers. These non-volatile buffers are of obscure identity, but minute amounts of boric acid added to artificial sea water give similar quantitative action, that with 0.0008 molecular boric acid being nearest to the Tortugas water, which must not be taken to mean that the water contains this amount.

McClendon (1917, 1918) also drew attention to the fact that all the sea water he examined was supersaturated with calcium carbonate and would lose some of it if shaken with calcite or aragonite crystals. He showed that, for example, in the Marquesas lagoon the removal of carbon dioxide by plants had raised the water to pH8.46 and a precipitate of the carbonate was coming down and incrusting the eel-grass.

The changes in the sea were also considered by McClendon (1918) in their biological aspect. The general relationship found between hydrogen

ion concentration and oxygen content found by Palitzsch and other workers was confirmed and illustrated by many examples. Thus during the day the surface water to the east of Loggerhead Key rose usually by pH0.03 to 0.08, pH8.20 being a very usual morning value with pH8.26 in the evening, the temperature being about 27–30° C. The depth at this station is not given, but it was well within the six fathom line. Closely similar results were obtained in a tank of sea water in the open, pH8.18 being obtained at 5.40 a.m. and 8.26 at 4 p.m. in a series of readings throughout twenty-four hours. During this time the oxygen varied from 3.1 to 5.3 c.c. per litre, reduced to N.T. and P. The rise in temperature from 28.0–35.2° C. lessened the solubility of oxygen and so resulted in more passing out of solution than would have been the case at the minimum temperature. Details are given of the action of the algæ symbiotic with corals, actinians and species of bottom medusæ in evolving oxygen in excess during daylight.

The surface water between Tortugas and New York was found by McClendon to vary from pH8.16–8.23, omitting certain values which are obviously not comparable, such as 8.46 in Marquesas lagoon. The measurements were made about the beginning of August. In the open sea far from land there does not appear to be any appreciable diurnal change in pH.

Mayer (1919) studied the water of the Pacific from Fiji to Honolulu, Samoa, and San Francisco. He found an average temperature of 27.5°, pH8.22 and pressure of carbon dioxide 3.15 ten thousandths of an atmosphere and concludes that the latter is slightly above that of the atmosphere in general. He, however, noticed that the water drifting in a westerly direction was at about pH8.23, back currents moving eastwards being at pH8.10 to 8.18, which he considers to indicate an upwelling of water from 200 to 400 metres roughly. Low values, such as pH7.85 at 10.5° C., about 50 miles off the coast of San Francisco and Vancouver point to a similar upwelling. In general McClendon and Mayer agree that surface water falls pH0.01 per degree fall in temperature, but this does not apply to water which has recently come up from a considerable depth.

Mayer also pointed out that the cold water of the shore current between Nova Scotia and Florida is relatively acid pH7.9 to 8.1 in winter as compared with Gulf Stream water, found by McClendon to be about pH8.2. But it must be added that the latter is a summer measurement, so this difference is quite probably only apparent.

Previously Mayer (1916) studied the solution of limestone in relation to the theory of coral atoll formation and the carbon dioxide content of sea water. This equilibrium was investigated by Henderson and Cohn (1916) as well as by McClendon.

More recently Michael (1921) has sought to correlate the abundance of

phytoplankton off the coast of Southern California with the upwelling of deep oceanic water rich in carbon dioxide and—it is suggested—in nutritive salts. These plankton estimations were made at sea, but the water was examined in July, 1919, at 8 a.m. daily at various points along the shore. There is a distinct connection between R , the reduction of temperature below that normal for the latitude, and the pH value found; thus at La Jolla, $R=0.3^{\circ}-1.1^{\circ}$, pH8.15-8.20; at Summerland, $R=1.8^{\circ}-4.3^{\circ}$, pH7.80-8.10; at Point Hueneme, $R=3.8^{\circ}-9.9^{\circ}$, pH7.60-7.95, and at Arguello, $R=8.1^{\circ}-10.6^{\circ}$ and pH7.55-7.80.

HYDROGEN ION CONCENTRATION PRODUCED BY CONSTITUENTS OF SEA WATER.

Haas (1916) examined the effect of the addition of alkali to sea water upon its hydrogen ion concentration. It had been shown by Moore, Prideaux, and Herdman (1915) that the earlier view that the alkalinity of sea water was in the main due to calcium salts was incorrect, because on boiling magnesium carbonate or hydroxide and very little calcium was deposited. Haas, however, found that the addition of 0.05 c.c. of approximately 2.5 N. sodium hydroxide at 21° C. to 24 c.c. of sea water raised it from pH7.9 to 10.1, thereafter little or no rise occurred while magnesium hydroxide was being precipitated, but the value subsequently rose, but not sharply, to pH12.0 to 12.7 with precipitation of calcium hydroxide. This explains why it is that magnesium hydroxide is precipitated first on boiling. It has been found by the writer that a solution of magnesium oxide, solid being in excess, gave in the presence of the carbon dioxide of the air pH9.9-10.0, and pH10.0 when boiled to remove carbon dioxide, using thymol phthalein and Clark and Lubs (1917) standards. Calcium hydroxide gave over pH10 and barium hydroxide well over this value. Thus it is seen that the hydroxyl ion concentration producible by calcium hydroxide is greater than that arising from magnesium hydroxide, yet owing to the lower solubility of calcium carbonate and its greater resistance to hydrolysis, the limiting pH value for the calcium salt is below that for the magnesium salt. The solubility of calcium carbonate in water free from carbon dioxide is given by Schloesing (1872) as 0.0131 grams per litre, or when in equilibrium with the carbon dioxide of the air, viz. about 3 parts per 10,000, it is 0.0646 grams at 16° C. (Cameron and Briggs, 1901). Rupp (1909) calculates the hydroxyl ion concentrations to be 1.05×10^{-5} and 17×10^{-7} respectively, which on conversion into pH values give 9.01 and 8.37. Wells (1915) gives the solubility of calcite in contact with the atmosphere as varying from 81 to 70, 61, 52, 44, 38 parts per million as the temperature rises from 0° - 50° in 10° steps, and it is probable that a similar relation obtains for mag-

nesium. These large changes in solubility are occasioned by the driving off of carbon dioxide as the temperature rises ; accordingly in a mixture of saturated calcium carbonate with the bicarbonate, in equilibrium with air, it appears that the ratio of carbonate to bicarbonate will rise with the temperature, for the former either remains constant or increases slightly while the latter decreases greatly. Thus neglecting the effect of other salts in the sea the pH value should be greater in the warmer regions, as appears to be the case, except in so far as results are affected by active photosynthesis.

Thus, as calculated, no solution containing only calcium carbonate can exceed pH9.01. A direct determination starting with calcite crystals and boiling to remove carbon dioxide gave a result very close to pH9.0 with Clark and Lubs buffer mixtures.

With magnesium carbonate and magnesite, however, a value as high as pH10.0 was obtained, so as this is identical with the maximum value for magnesium hydroxide it appears that the solution must be saturated with respect to this salt also, while the solution which is saturated with calcium carbonate does not become sufficiently rich in the corresponding hydroxide to give its maximum value, which lies well over pH10.

Thus neglecting the action of neutral salts in altering ionisation and solubility it is evident that pH9.0 would be the maximum attainable in sea water if no magnesium were present, whereas since magnesium is present as well as calcium a value up to pH10.0 might be reached. The action of neutral salts may, however, be shown to have an effect qualitatively ; to study the quantitative effects salt by salt in a mixture such as sea water would be very difficult.

Kahlbaum's magnesium chloride, tested and found neutral, was added to magnesium carbonate and boiled, when it was found that no colour was obtained with thymol phthalein and a tint corresponding to pH9.2 with thymol blue. Thus the solubility of the carbonate is lowered by the common ion sufficiently to depress the maximum from pH10.0. Similar results were obtained on adding magnesium sulphate. Again, on boiling solid calcium carbonate with solid calcium sulphate, cooling and testing, pH8.0 or near it was reached, instead of pH9.0.

Sodium carbonate could of course produce much higher pH values, but in presence of the carbonates of calcium and magnesium the immediate result would be the precipitation of these just as Haas found with sodium hydroxide. Moreover, carbonic acid in presence of the chlorides and sulphates of sodium cannot produce sodium carbonate. By insolating *Ulva* in sea water the value pH9.7 was attained and fresh water on Staddon Heights overlooking Plymouth Sound was raised to pH9.7 a so by insolation with the algæ found in it. Fresh inland water could not be got to surpass pH9.0 (Atkins, 1922).

VARIATIONS IN HYDROGEN ION CONCENTRATION IN REGARD TO HEALTH AND MOVEMENTS OF FISHES.

Within the last few years several researches have been carried out to test the sensitiveness of fishes to variations in the hydrogen ion concentration of the sea. The earliest work in this line appears to be that of Moore, Prideaux, and Herdman (1915) who correlated the development of a disease in plaice in the fish hatchery at Port Erin with the unusually great alkalinity of the water, which occasioned the appearance of ulcerated areas on the skin. They traced the increase in alkalinity to the action of very numerous unicellular algæ and a green flagellate infusorian.

Shelford and Powers (1915), continuing the work of the former on the reactions of fishes to dissolved gases, showed how sensitive are herring and other marine fish to increase in the carbon dioxide content of the sea, also to traces of hydrogen sulphide. They drew special attention to the influence of such factors upon the eggs and young fish. This work was continued for fresh water fish by Wells (1915), who pointed out the bearing that the work of Birge and Juday (1911), upon the alkalinity of the Illinois lakes in relation to algal photosynthesis, must have upon the movements of fishes. The subject has been further pursued by Shelford (1918), Hall (1918), Powers (1920, 1921) with the result that fishes have been proved capable of detecting very small changes in hydrogen ion concentration, the active migratory fishes being in this respect far more sensitive than those which normally rest on or near the bottom. Powers has also traced the limits within which various fish were found in Puget Sound and its neighbourhood. Thus herring were only once found in water with a pH above 7.90 and they were never found in water with a pH below 7.71. The greatest number of herring were observed in water at pH 7.76-7.73. On the other hand, salmon smolt were found only between pH 7.98 and 8.08. It must not, however, be left out of consideration that large numbers of fish themselves modify the hydrogen ion concentration by their respiration, and the water in a shoal must be less alkaline than the sea water in general. These shoal fish are presumably accustomed to this somewhat stuffy sea-atmosphere, and so it appears probable that if separated from the shoal a herring by making for a region of lower pH would be led back to the shoal. For the many interesting details the original papers should be consulted. Powers (1922) has further studied the respiration of fishes and correlated the hydrogen ion concentration of the sea water with their ability to utilize low concentrations of dissolved oxygen.

RELATION OF SOME PHYSICAL AND CHEMICAL FACTORS
TO ALGAL DISTRIBUTION.

The work of Gail (1918, 1919) has brought to light even more definitely the factors governing the distribution of *Fucus evaneszens* Ag. in the Puget Sound. It was shown that desiccation prevented growth on gravel, by killing the young plants, which also failed to grow when planted more than three decimetres below the surface of the water, ultimately dying from the deficiency in illumination. Furthermore, well-grown plants receiving less than one-fourth the normal daylight darkened in colour and died. This factor therefore limits the vertical distribution.

Gail also showed that the growth of both sporelings and larger plants of *F. evaneszens* is almost completely inhibited in sea water having a pH value above 8.6, it is also very much inhibited in water above pH 8.4. With a temperature above 24° C., pH 8.6 proved fatal. In the other direction there is very considerable inhibition below pH 7.2, and above 24° C. at pH 7.0 the plants die. It was observed that under conditions otherwise favourable, *F. evaneszens* was absent where much *Ulva* was present, as the latter causes the water to have too high pH values. The absence of the plant from tide pools is attributed to this and to the great variations in temperature.

LINES OF RESEARCH INDICATED.

Preliminary experiments and a study of the literature which has been summarised in the foregoing pages showed the desirability of obtaining information on the following :—

1. The hydrogen ion concentration produced by the constituents of sea water. This has already been discussed briefly.
2. The hydrogen ion concentration of the water of the aquarium tanks as compared with that of Plymouth Sound and the town fresh water supply.
3. The relation of the Sound water to that of the tide pools.
4. The relation of the Sound water to that over seaweeds in shallow parts.
5. The variation of the Sound water with tide and time of day.
6. The relation of the hydrogen ion concentration, salinity and temperature of the Sound water to the corresponding values in the open sea.

7. Factors affecting the hydrogen ion concentration of the open sea, such as sunlight and photosynthesis, respiration, aeration, temperature, and salinity.
8. Correlation of the hydrogen ion concentration and seasonal variations in the marine fauna and flora.

Before considering these questions an account must be given of the methods adopted in the colorimetric estimations.

COLORIMETRIC AND TITRIMETRIC DETERMINATIONS OF THE HYDROGEN ION CONCENTRATION AND THE LIMITS OF ACCURACY.

Standard solutions at intervals of pH0.2 were made up according to the directions given by Clark and Lubs. The indicator used for the work on sea water was cresol red, but for the more alkaline water produced by insolation with algæ thymol blue must be used. For the more acid water of the tanks phenol red is also of service. As previously mentioned, Sørensen and Palitzsch found α -naphtholphthalein and phenolphthalein suitable for work on sea water, and gave the corrections for salt error. According to Palitzsch the latter gives no perceptible pink tinge below pH8.06 at 35‰ salinity or pH8.27 with fresh water. Prideaux (1919) has pointed out that in titrating up to the bicarbonate limit, pH8.4-8.2, a trace of colour should be left in the solution when this is fresh water, but in sea water the bicarbonate equilibrium point, when in contact with the carbon dioxide of the air, is pH7.6 or about 7.8, allowing for the fact that it appears higher owing to the salt present. The last trace of colour should be removed when titrating sea water with acid.

It has been the writer's custom to titrate 100 c.c. of sea water in a conical flask of hard glass, in the cold, immediately upon the withdrawal of the sample from the sea. Alcoholic phenolphthalein was used, and enough added to give a light pink, usually forty drops of the solution. It was found that small differences in the quantity of indicator were unimportant. The titration was made by running in N/100 sulphuric acid till the last faint trace of lavender-pink vanished, the liquid being examined from the side, namely, through a thickness of about nine centimetres. The amount required was usually between two and three cubic centimetres. The limit of accuracy is apparently due to the fatigue of the colour sensitiveness of the eye to red. Titration with N/100 acid is always a difficult matter when accuracy to 0.1 c.c. is aimed at, and under the conditions met with at sea this accuracy could not be relied upon. From the winter of 1921 onwards the plan was adopted of testing the pH value

of the liquid, when colourless to phenolphthalein, by adding cresol red, and the figures for added acid were accepted as correct and truly comparable only when the liquid after titration was at pH7.85, as shown by cresol red without correction for salt error. On correction this figure becomes pH7.67, which is close to the equilibrium point given by Prideaux, pH7.6. This may be illustrated by examples from the L and E1 series (described further on) obtained on December 13th on water, in this case, taken on 12th. The pH values were estimated to pH0.05, the standards being at pH0.2 intervals. To save repetition the table also shows the sea temperatures, salinity and pH values corrected for salt error according to McClendon's standards as determined immediately the water was drawn up. The standards are at intervals of pH0.05, estimations to pH0.01.

December 12th :—

Samples.	Temperature. °C.	Salinity ‰	pH corrected.	c.c. of N/100 H ₂ SO ₄	
				per 100 c.c. after titration, sea water.	pH of liquid uncorrected.
L1 surface	10.6	33.12*	8.01	1.57	7.85
L2 „	11.4	34.34	8.07	2.04	7.85
L3 „	11.8	34.99	8.11	(2.63)	7.70
L4 „	12.3	35.35	8.13	2.43	7.85
L5 „	12.6	35.39*	8.14	(3.10)	7.60
L6 „	12.8	35.44	8.14	2.62	7.85
E1 „	12.95	35.40	8.14	2.83	7.85
E1, 25 metres	13.15	35.41	8.14	(3.01)	7.75
E1, 70 metres	13.11	35.42	8.12	2.71	7.85

High water at 3.20 a.m., L1 taken 9.30 a.m.; E1 at 12.30 noon. The salt error correction for the figures in the last column is pH0.18 to be subtracted.

It is evident that L3, L5, and E1, 25 metres were overshoot in titration. The water in this case became more alkaline as the harbour was left and the open sea entered. Inspection of the pH values for the sea water and of the titration results shows that the latter are less regular than the former, as it is easier to compare the intensity of colour of tubes that are a good red than to be sure that an absolutely colourless condition is attained and not overshoot.

By comparing the mean values obtained for L6 and E1 with those for L1, it is seen that over this range, pH0.14, the addition of 0.08 c.c., N/100, H₂SO₄ to 100 c.c. sea water produces a change of pH0.01. This is an approximate value and is open to the objection that the titrations were carried out on the day following the pH determinations.

* Duplicate determinations, mean value.

It may be objected, however, that since the titration values represent quantities of acid added and the pH values are $-\log H$ the two are not comparable. Over a small range it is, however, allowable to assume an inverse proportionality between differences in pH and C_H values, as may be seen from the following figures from Schmidt and Hoagland's tables:—

pH	C_H	
8.40(2)	0.396	
8.500	0.322	Half-way value in each case, but the
8.60(5)	0.248	C_H value is equivalent to pH8.49.

Thus the value judged to be half-way by tint, assuming no error, is in reality not pH8.50, but 8.49, since the colour change is proportional to C_H . The error, however, is only +pH0.01, and with intervals of pH0.05, as in McClendon's series, becomes altogether negligible. It is in any case within the error of judgment using Clark's standards.

Fresh determinations made by adding exactly 1.00 and 2.00 c.c. of N/100 acid to 100 c.c. sea water at pH8.07 showed that here 0.11 c.c. corresponds to a change of pH0.01. Over the limited range pH8.14 to 7.98 it may accordingly be taken that 0.1 c.c. corresponds to pH0.01 with the sea water at 35‰ salinity. With water of lesser salinity, the buffer action would be smaller, namely, the change due to the same quantity of acid would be greater.

By adding a very little methyl orange and titrating the liquid rendered colourless to phenolphthalein a measure of the bicarbonate is obtained. The sum of the two titrations affords a measure of the buffer action of the sea water. Since only slight differences in salinity were encountered titration with methyl orange was abandoned after a while, the results always being the same within the limits of error. The average of eleven determinations gave 24.65 c.c. as the amount of N/100 sulphuric acid. According to Prideaux (1919) 1 to 2 c.c. should be subtracted from this figure, as with salts present the result is somewhat high. Since, however, about 2 c.c. is required to neutralise to phenolphthalein, the total required is 26.6 c.c., or correcting, as suggested by Prideaux, the hydroxyl present amounts to about 2.46 milli-equivalents per litre at the time these determinations were made, July, in the English Channel, when the salinity was 35.2‰. The values given by Schloesing, 2.48, Dittmar, 2.41, Moore, Herdman, and Prideaux, 2.36–2.50, average 2.44 in the Irish Sea from November to July, do not appear to include such an allowance, so the writer's results are in reality higher, a different end point being reached in the titrations. Methyl orange ceases to be red beyond pH3.8, so this value is just reached in the titrations, or about pH4.0 correcting for salt error. By adding 30 c.c. of N/100 acid to 100 c.c.

of sea water initially at pH8.0 corrected for salt error, it was found that pH3.7 corrected was reached at a temperature of about 12° C. and with the minimum possible agitation of the liquid, so that carbon dioxide should not be lost. This 30 c.c. becomes 28 c.c. when corrected, a result noticeably higher than the value found in summer by titration, the addition of 25 c.c., however, left the liquid at pH4.4 corrected, to methyl red, methyl orange being, of course, yellow at this stage. The precise magnitude of the buffer effect depends, therefore, on the conditions of titration to a very marked degree. On plotting a graph pH values as ordinates and c.c. of N/100 acid as abscissæ a steep curve concave to the ordinates was obtained up to 5.0 c.c. and pH6.9 corrected for salt error, from that to 20 c.c. at pH5.4 the curve was almost a straight line with a much less steep slope, or the graph up to 25 c.c. at pH4.4 might be regarded as a second shallow concave curve with a straight line from 25 c.c. to 30 c.c. The end-point chosen, therefore, affects the result very largely.

The estimation of carbon dioxide by titration in respiration measurements, as carried out by Moore and his co-workers (1912, 1913), has been severely criticized by Morgulis and Fuller (1916). The method is admittedly subject to errors in titration as already noted. But for measurements of small differences it is certainly more accurate than these criticisms appear to indicate, as is shown by the uniformity of the results for sea water. Passing in considerable quantities of the gas and then estimating the amount recovered, as Morgulis and Fuller did, is not a permissible procedure as a criterion; under these conditions the liquid readily parts with the gas during titration; but with sea water more alkaline than bicarbonate the alkalinity is being measured and no carbon dioxide is free; beyond the bicarbonate point small amounts of the gas are free, but in the experiments dealt with here this was chosen as the end-point; as the bicarbonate point is left and pH7 is approached errors due to loss of gas become more serious, as was noticed in studying the titration—pH curve in the acid direction.

From these results it follows that titration is not as accurate in determining the condition of the sea as is the colorimetric determination of pH values by McClendon's standards. These were made up and marked, giving the corrected pH value for the salinity and amount of indicator added.

McClendon (1917) records values for sea water 0.4N, 0.5N, and 0.6N with respect to chlorine ions, the salt error increasing by pH0.05 for each decimal place. The sea water off Plymouth Sound and the adjacent parts of the English Channel usually lies between salinity 35.0 and 35.3‰, equivalent to 0.546 to 0.550 normality with respect to chloride. Using 0.5 c.c. indicator with 10 c.c. sea water these values become 0.520 and 0.524N. The salt error is accordingly for both pH0.01 more than

for 0.50N sea water. In marking the standard tubes this correction was introduced, pH8.20 being marked pH8.19. In making these comparisons, working to the second decimal place, it is essential to allow sufficient time to elapse for the freshly drawn water to attain the temperature of the standard tubes in the cabin, since the pH value varies inversely as the absolute temperature, the neutral point altering from pH7.10 to 7.00, with a rise from 16° to 22° C. Accordingly in winter the samples, when freshly drawn, always appear more alkaline than they are in reality, since they are colder than the standard tubes.

Furthermore, owing to the lessened solubility of carbon dioxide and the increased dissociation pressure of this gas in bicarbonates, rise of temperature leads to a new, but slowly attained, equilibrium. The alteration according to McClendon amounts, for sea water, to pH0.01 decrease per degree fall in temperature. Thus water at pH8.22 at 16° C. would at 10° C. be at pH8.16. This change is superposed upon that in the water itself, which alters by pH0.10 in the opposite sense, pH7.10 becoming at 10° C. pH7.20. Since, however, the water in the standard tubes also changes with temperature the latter alteration is automatically corrected in the observations, provided the two tubes are at the same temperature.

This temperature co-efficient, given by McClendon as pH0.01 decrease per degree fall in temperature, will be considered later in regard to the seasonal changes.

It may be added that a tube made up with indicator and buffer at pH8.14 on November 8th and kept in a test tube of hard glass, with a rubber cap, remained quite unaltered; this was shown by examination on February 28th against buffer from the standard bottle, waxed internally and never opened between the dates mentioned. The standard tube at pH8.16 was noticeably darker, so it may be considered that the estimations are correct to pH0.01. In comparing these tubes it is best to hold them slanting against ruled white paper, with blue lines. Differences in tint then become more easy to detect than with the plain white paper usually recommended.

For colorimetric work the sulphone phthalein indicators are much superior to the phthaleins, inasmuch as their solutions are far more stable. Standard tubes made up with phenol- and α -naphtholphthaleins were found to show marked diminutions in intensity of colour in less than a day, and thymol phthalein, though a most useful indicator for the region of pH10, fades in less than an hour. In contrast to this the stability of the sulphone phthaleins is remarkable; for one thing, being more soluble, they do not tend to precipitate. No trace of fading has as yet been observed in tubes made up with *o*-cresol sulphone phthalein four months ago. These were kept in the dark and the stock solutions before mixing

were saturated with toluene. If toluene is not added this indicator does fade slowly in intensity, even though its tint remains almost unaltered. The change appears to be due to bacterial action upon the indicator. In this respect phenol red and brom thymol blue seem to be somewhat more resistant. The fading of cresol red was, however, scarcely perceptible in ten days in warm summer weather. No change whatever could be detected in two days. In sea water the fading is more rapid, but quite apart from this there is a marked change in tint, also owing to the production of carbon dioxide by the bacteria acting upon the organic matter in the sea water. With sea water at pH8.1-8.2 it is, however, sometimes useful to use α -naphtholphthalein when comparing two closely similar samples, as in this region it shows a decided change in tint, whereas the change in cresol red is mainly one in intensity. The layers sometimes found in the sea in summer may thus be differentiated with greater certainty.

For some months much use was made of a Duboscq colorimeter for comparing water samples. It was found that exposure of the standard solution in one of the tubes for a working day had no measurable effect upon its pH value as tested against a freshly drawn portion. Such colorimeter comparisons are accurate only when the indicator change is one of intensity rather than of tint, namely, a one colour change. For this reason phenolphthalein was used, but abandoned as its low solubility leads to alterations in the standard inside a few hours. It is permissible to use cresol red over a narrow range, for samples slightly above or below the nearest standard; but when pH8.4 is matched in intensity against pH8.2 there is always a visible difference in tint. Working by intensity change rather than by alteration in tint is always open to the error due to small differences in the quantity of indicator added; it was found necessary to reject a number of measurements owing to this, since it was ascertained that if the pipette delivering the indicator drop by drop was not held vertically the size of the drops altered slightly, from 27 to 25 per c.c.; the greater the departure from the vertical the larger the drops, up to an increase of roughly 50% with an almost horizontal pipette. In rough weather it was impossible to avoid some inclination, so further work was done by adding 0.50 c.c. of indicator from a pipette delivering 1.00 c.c. from a length of 145 mm. With these precautions it was found possible to measure out fresh portions and obtain agreement to within 0.1 mm. on the scale of the colorimeter, taking the mean of four adjustments. This accuracy is not surpassed by successive sets of readings on the same solution. In making these readings the most accurate method seems to be to adjust the standard to a fixed depth, 12.5 mm. was used, and to screw the plunger in the sample till the tint is just perceptibly darker than the standard; then to reverse and screw till it is just a shade

lighter, after this to screw back half-way again, by judgment. This method minimises error due to fatigue of red-sensitiveness of the eye, lessens eye strain generally, and is more rapid than trying to adjust to exact equality. In the next measurement of the series the sample is adjusted from too light to too dark and half-way back. It was found that when one tube was at or near 12.5 mm. depth a difference of pH 0.01 with McClendon's standards corresponded to a scale reading of 0.1 mm. between the limits pH 8.07-8.23.

The determinations of pH values of sea water made with the Clark and Lubs standards prior to November, 1921, were corrected for salt error by comparison with the McClendon series with cresol red. Thus a sample of salinity 35‰, judged to be pH 8.40 by the former, lay between the tubes at pH 8.24 and 8.19, and was taken to be at pH 8.22.

Similarly the pH 8.20 Clark and Lubs standard was found to be pH 8.02 with McClendon's series. These results show that the salt error is pH 0.18, for cresol red with these borate solutions. It would be slightly larger with Palitzsch's mixtures, as the Clark and Lubs standards have M/5 KCl with the boric acid. There appears to be no appreciable inaccuracy in taking the salt error to be the same in the other sulphone phthaleins, namely, in the phenol and thymol homologues; McClendon (1917) considers this to be true for these three, and probably all of the series.

THE HYDROGEN ION CONCENTRATION OF THE WATER OF THE AQUARIUM TANKS.

The tanks are filled with salt water, with the exception of one which is fresh. There are two main salt water reservoirs of about 225 cubic metres capacity each. These are filled by pumping up from the Sound at high spring tide, when the salinity is not below 35‰ as a rule, but inspection of salinities for the Sound shows that this value is not often reached. Pumping is only carried out when the water is clear, and it is allowed to settle before introducing into the circulation. The reservoirs are used week about to supply the tanks, the water being delivered in numerous small jets which carry down much air. This bubbling of air also serves to mix the water and to remove carbon dioxide. The circulation is stopped twice a day for three hours, but a cessation for five hours is accompanied by distress to the fishes. Water is pumped in only at long intervals, about half a reservoir being changed every six months. Small quantities are added at irregular intervals to make good losses.

When the pH values of the various tanks are determined the uniformity and constancy of the values are somewhat surprising. The variations are,

however, considerably greater than in the sea and the tanks are always much more acid. The reservoirs were constantly at pH7.6 from April to July. In July, owing doubtless to the higher temperature and lessened solubility of carbon dioxide with increased dissociation pressure, the west reservoir water rose to pH7.65. Owing to the intake of sea water the east reservoir was then at pH8.0. The sea water at the slip near the intake was at pH8.27-8.32 during this period. There is thus a very considerable difference, pH0.6-0.7 between the water of the Sound and of the reservoirs. Taking McClelland's values for 20° C. this corresponds to a change in the carbon dioxide pressure from 0.16 mm. to 1.00 mm., the concentration of free carbon dioxide is accordingly more than six times as great in the reservoirs as in the Sound water inshore.

The water in the tanks on April 12th was found to vary between pH7.57 and 7.27. On 28th they were mostly between pH7.62 and 7.45. One was down to 7.32 and three tanks contaminated with prawns, which died after having been brought in from the sea, were at pH7.2-7.05. The figures for 28th correspond to a pressure of 1.0 to 1.7 mm. in the tanks generally, and of 3.7 to 5.7 mm. in the contaminated tanks. The water in the latter tank, although circulation was in progress. One of two *Sepia* died and the tanks were cleaned out, after which the pH value rose to 7.3 and then became normal.

In another instance two tanks occupied, A by conger eels, etc., and B by poor cod, turbot, etc., were both at pH7.45. Owing to a crack appearing in A most of the occupants were transferred to B. The pH value fell to 7.32 and remained constant at that for several days. This corresponds to a carbon dioxide pressure of 2.6 mm. or 30.4 parts per 10,000, about nine times the normal amount in sea water. The temporary cessation of the circulation did not appear to produce any alteration. It was noticed that the respiration of some of the fish seemed to be laboured, in spite of the numerous bubbles of air carried deep into the tank with the inflowing water. Two turbot in this condition respired at the rate of 30-32, whereas two breathing easily showed 23-24 per minute, the temperature being about 13° C. In January it was noticed that the turbot were all respiring easily at 13-15 per minute in water at pH7.62 at 9.5° C. The changes in the respiration rate of fish is probably worthy of attention, as the oxidation in their tissues must decrease with falling temperature. Furthermore, even when oxygen is abundant, since its quantity in sea water varies independently of the pH value—though in a general way an increase in one denotes a decrease in the other—it is probable that a low pH value may stimulate the fish to respire more rapidly. [See Kanitz (1915) for the temperature effect, and Powers (1922) for the variation of respiration with change in hydrogen ion concentration.] The constancy of the reservoirs was puzzling in view of the fact that water from the tanks

flowed back into them. Prideaux (1919) has pointed out that in sea water very dilute bicarbonate solutions in equilibrium with the air are at pH7·6, corrected for salt error, instead of at pH8·2 as in fresh water. It was at first thought that this explained the constancy of the reservoirs. Both McClendon (1917) and Prideaux state that the equilibrium value for sea water in contact with the air is close to pH8·1, so it is not to be expected that surface water will normally be much below this. On reducing water from the Sound to about pH7·5 by breathing into it, and then shaking with laboratory air in a test tube a value pH8·02 was reached, the initial value having been pH8·06. Similarly tank water at a little below pH7·6 was raised to about pH8·0 by agitation in a test tube. Both tubes were slightly warmed to hasten the expulsion of gas, but were cooled before determining the final pH values. Thus it is clear that the figure found for the reservoirs is due to the fact that conditions in this considerable mass of water are sufficiently constant to maintain a constant pH value.

The higher values found in the sea, pH8·2 and over at times, as against pH8·1, the equilibrium value, are due to the photosynthetic action of plants in removing carbon dioxide, but in addition the equilibrium value will shift somewhat with temperature, rising with increase of temperature. For this pH0·01 is taken as shown by McClendon.

The only algæ which flourish in the main aquarium tanks are certain minute species; these are not at all easy to identify, and may be abnormal forms; they include, what seems to be *Callithamnion Rothii*, Lyngb., *Polysiphonia* sp. (?) *urceolata*. Grev., or the smaller but very similar *P. pulvinata* Spreng., also *Sphacelaria* sp., and *Cladophora* (?) *fracta* Kg., with Naviculoid ensheathed diatoms. These appear only in the tanks next the southern windows. A tank in the yard close to the north side of the building was covered with "railway green" glass. In it larger red algæ were established and its pH value was identical with that of the reservoirs. An adjacent uncovered open air tank contained green algæ and was evolving oxygen bubbles. This was at pH8·4, namely, more alkaline than the water of the Sound, but like a tide pool.

It is clear, therefore, that if it is required more closely to approximate to the pH value of the sea in autumn it will be necessary to aerate with air partly deprived of carbon dioxide. With air altogether deprived of this gas the carbonate limit, almost reached in very active photosynthesis, might be attained in time—were it not for the respiration of the animals. This is injuriously alkaline for organisms. Less thorough aeration with CO₂ free air would doubtless attain the same result, or untreated air would bring the water to about pH8·0-8·1.

It was noticed that a newly made cemented shallow tank was at pH8·2, the same as the sea. The addition of lime in correct proportions might

also be made to the reservoirs to regulate the reaction. Inadequate illumination appears to be the most important factor in limiting the growth of brown and green algæ judging from Gail's work.

As a result of the examination of the aquarium tanks it may be concluded that water is suitable for many fish and invertebrates if the circulation and aeration are sufficient to maintain it close to pH7.6. For the more delicate organisms attempts must be made more nearly to maintain a reaction close to pH8.2.

It was found that small Ctenophores and medusæ, which die in the tanks, lived for several days in jars of sea water, provided very few organisms were present. The reason that the tow-net jars become malodorous and contain only dead animals inside a day or less, is that the oxygen supply becomes exhausted and the carbon dioxide so increased as to have poisonous effects. For example, a jar rich in *Phaeocystis globosa*, collected at 2 p.m. on April 26th and examined at 1 p.m. on 27th, was found to have changed from pH8.2, that of the sea where it was taken, to pH7.0, and this in spite of the fact that photosynthesis should have been possible in the jar on deck for some hours after the sample was obtained.

It was also observed that jars containing *Ulva sp.* brought up and placed in sunlight rapidly became more alkaline owing to photosynthesis. The limit reached was pH9.77 or 9.95 uncorrected for salt error with thymol phthalein. If too many algæ were present, however, such as in a closely packed mixture of green, brown, and red varieties, the pot developed a stench and the reaction became as acid as pH6.4, whereas a single *Ulva* plant might live for months in such a jar.

The only fresh water tank was found to be at pH7.25 in April, and pH7.4 a fortnight later, the tap water being then at pH7.0. Probably the presence of limestone pebbles tends slightly to increase the pH value. In January the value was pH7.05, that of the tap being pH6.8. The range, at least pH0.35, is greater than in the sea water tanks, as the buffer action of fresh water is very slight. The conditions in fresh water will be considered elsewhere.

THE WATER OF THE SOUND AT VARIOUS TIMES COMPARED WITH THAT OF TIDE POOLS AND LOW WATER *LAMINARIA* BELTS.

It was found that the Sound water at low tide in April was at pH8.27, whereas when taken from very shallow water over *Laminaria digitata* it was at pH8.42. A rock pool exposed for about two hours was also at pH8.42. This contained an abundance of green algæ, *Ulva sp.* A similar pool higher up exposed for about four hours was at pH8.47. This was on April 25th, but on May 10th water over *Laminaria* in the

same place with one hour flood tide was at pH8.07, while the Sound water both then and at full tide was at pH8.3, the temperature being 13° C. Water in among densely packed algæ may, therefore, fluctuate considerably, photosynthesis rendering it more alkaline and decomposition with its attendant abundance of bacteria and protozoa working in the opposite way.

Again, on July 11th, at 3 p.m., in full sunlight one of the exposed rock pools was found to be at pH8.57, 21.4° C., and took 3.7 c.c. N/100H₂SO₄ per 100 c.c. with phenolphthalein. High tide was at noon, the Sound water at the west slip was then at pH8.32, and took 2.0 c.c. for neutralisation, the temperature being 18.7°. When the pool was examined the Sound water was unchanged save for a rise in temperature to 19.2° in the shallow water by the west slip.

It may be stated that in the open sea there are no perceptible daily variations in pH value, but small changes may be noted close to the shore in the Sound.

pH, values taken.	High water.			
	July 26th. 8 a.m.	July 28th. 11.30 a.m. t=17.8° C. c.c.	Dec. 16th. 6.20 a.m. t=11.7° C.	Feb. 1st. 8 a.m. t=9.4° C.
10 a.m.	8.18	8.22 (0.73)	8.06	8.06
Noon	—	8.23 (0.67)	8.02	—
3 p.m.	8.28	8.24 (0.73)	8.02	8.04
5 p.m.	—	8.33 (1.12)	8.02	—

Such changes appear to be due to the effect of the photosynthesis of algæ on the shallow water, which at times may counterbalance the influence of a greater quantity of organic suspended matter as compared with open sea water. The July days were sunny, the December day completely overcast. The figures in brackets are c.c. of acid per 100 c.c. sea water as before. Some uncertainty exists as to the absolute values for pH found in July since the solutions had been made up some time and not—as later on—preserved with toluene. They appear considerably too high for the titration results, which, however, are unusually low.

THE RELATION OF THE WATER OF THE SOUND TO THAT OF THE OPEN SEA.

Since certain fish pass every year from fresh to salt water and return again to the rivers it becomes of interest to ascertain whether there are any differences in the water, as one approaches the shore, which may possibly serve as a guide to them. It may be stated at once that such differences have been found, but no proof has been adduced that they are adequate to direct the migration of the fish.

Moore, Prideaux, and Herdman, in discussing alkalinity determinations, state that "the degree of photosynthesis and the corresponding weight of ocean crop is probably much more abundant nearer to the littoral. It is frequently observable in the table, that water taken along shore is more alkaline than that taken from on board a vessel three to five miles from shore. Observations at great distances out at sea during the various seasons are most desirable, but difficult to obtain."

Since the calculations upon the annual crop of the sea made by these workers is based upon the magnitude of these photosynthetic changes it is important to determine the variations in alkalinity as precisely as possible.

Accordingly for such work carried out from this Laboratory stations were selected as follows:—

Station.	Situation.
L1	In the fairway of Plymouth Sound below the Laboratory near the Mallard buoy. Lat. $50^{\circ} 22' N.$, Long. $4^{\circ} 08' W.$
L2	In the fairway between the western extremity of the Breakwater and the Cornish coast north of Cawsand.
L3	Off Rame Hd., on the line between the Breakwater Lighthouse and the Eddystone.
L4	Half-way between Rame Hd. and the Eddystone. Lat. $50^{\circ} 15' N.$, $4^{\circ} 13' W.$
L5	Eddystone, 10 miles S. $42^{\circ} W.$ from Breakwater Lighthouse.
L6	Half-way between the Eddystone and the International Station, E1, viz. 5 miles on a S.W. course. Lat. $50^{\circ} 06' N.$, Long. $4^{\circ} 20' W.$
E1	Ten miles S.W. from the Eddystone. Lat. $50^{\circ} 02' N.$, Long. $4^{\circ} 22' W.$ Depth 40 fathoms. Bottom samples 70 metres.

This series gives a line of 22–23 miles, with estuary water, coastal water, and sea water at nearly as great depth as may be attained in the Channel. Fresh water effects and the action of coastal algæ should be shown if of sufficient magnitude.

The table already given on p. 737 for results obtained on samples taken on December 12th points to an increase in pH value as the Sound and coastal zone are left. Even when the values are corrected to the extent of pH0.01 per degree it is seen that there is a well-marked difference; the correction is added to the samples drawn in the colder regions to render them truly comparable as regards the photosynthetic change with those further from the land. This difference is not accounted for by any change in salt error, since the latter only amounts to pH0.05 for a difference of 0.1 in chloride normality, namely, an alteration of salinity of close on 20 per cent, and the necessary small corrections have been

introduced for this source. Similar results are given quite consistently by other autumn and winter determinations as shown in the following tables:—

Surface samples.	pH corrected.		c.c. of N/100 H ₂ SO ₄ per 100 c.c. sea water. July 4th.
	July 4th.	July 26th.	
L1	8.29	8.27	2.6
L2	8.27	8.24	2.5
L3	8.27	8.22	2.5
L4	8.23	8.22	2.6
L5	—	8.20	—
L6	—	—	—
E1 (July 2nd)	8.17	—	2.0

High water at 4.20 a.m. on 4th, L1 at 10 a.m. inward trip.

„ „ „ 9.10 a.m. „ 26th, L1 „ 9.20 a.m. „ L5 at 6.20 a.m.

E1, salinity 35.23‰, temp. 14.8°. Temp. about 16° on 26th.

Surface samples.	Temp. °C.			Salinity ‰/100.		pH corrected.	c.c. of N/100H ₂ SO ₄ per 100 c.c. sea water		
	Aug. 12.	Aug. 15	Aug. 22.	Aug. 12.	Aug. 15.		Aug. 12.	Aug. 15.	Aug. 22.
L1	16.2	15.9	15.6	34.6*	—	8.16	1.6	1.9	2.2
L2	15.5	15.7	15.2	35.0	35.0	8.25	2.5	2.2	2.5
L3	15.3	15.7	15.1	35.1	35.1	8.23	2.6	2.3	2.6
L4	15.5	15.8	15.0	35.1	35.2	—	2.1	2.4	2.7
L5	15.3	15.5	—	35.3*	35.2	8.22	2.1	2.4	—
L6	15.5	15.5	—	35.1*	35.2	8.24	2.4	2.2	—
E1	16.1	16.2	—	35.1	35.2*	8.27	2.3	2.4	—

High water.	L1 taken.	E1	Date.
Noon	8.30 a.m.	Noon	12th
3.30 p.m.	2.30 p.m.	5 p.m.	15th
7.40 a.m.	10.0 a.m.	—	22nd

Surface samples.	Temp. °C.		pH corrected.	c.c. of N/100H ₂ SO ₄ per 100 c.c. sea water.	
	Sept. 1st.	Sept. 6th.		Sept. 1st.	Sept. 6th.
L1	15.9	16.3	8.22	2.9	2.5
L2	15.8	15.7	8.23	2.9	2.5
L3	15.6	16.0	8.22	2.9	2.7
L4	15.6	15.9	8.24	3.3	2.6
L5	15.6	15.6	8.24	3.3	2.5
L6	—	16.3	—	—	2.8
E1	—	16.4	—	—	3.0

High water at 5 a.m., L1 taken at 8.30 a.m. Examined next day, September 2nd.

High water at 8.20 a.m., L1 taken at 11 a.m., E1 at 6 a.m. on inward trip. Titrations made next day.

* Denotes duplicate titrations. Salinity results given to the nearest decimal place.

September 15th :—

Surface samples.	Temperature °C.	Salinity ‰	pH corrected.	c.c. of N/100 H ₂ SO ₄ per 100 c.c. sea water.
L1	16.3	33.7*	8.20	—
L2	16.1	34.8	8.25	—
L3	15.9	34.9	8.23	—
L4	15.7	35.1	8.23	—
L5	15.5	35.2	8.25	—
L6	15.8	35.2*	8.25	—
E1	15.8	35.1	8.25	—

High water at 4.30 a.m., L1 taken at 9.30 a.m., E1 at 2 p.m.

October 18th :—

L1	16.0	35.0*	—	—
L2	16.0	35.2	—	—
L3	16.0	35.2	—	2.1†
L4	16.0	35.2	—	—
L5	15.9	35.4*	—	2.3†
L6	15.7	35.3	—	—
E1	15.6	35.3*	—	2.2†
E1 ₁	15.6	35.3	—	—

High water at 5.40 a.m., L1 taken at 8.30 a.m., E1 at 11 a.m., and 1 p.m.

November 9th :—

Surface Samples.	Temperature °C.	Salinity ‰	pH corrected.	c.c. of N/100 H ₂ SO ₄ per 100 c.c. sea water
L1	11.6	35.0	8.07	—
L2	13.0	35.2	8.16	2.4
L3	14.0	35.3	8.18	2.4
L4	14.3	35.3	8.22	—
L5	14.4	35.4*	8.23	—
L6	14.3	35.4*	8.23	2.9
E1	14.3	35.4	8.22	2.7
E1'	15.0	35.4*	8.23	—

High water at midnight, L1 at 8.30 a.m., E1 at 11.15 a.m.

The duplicate E1 was taken after the completion of a depth series in the water bottle. The other samples were from the bucket.

For December results see previous table p. 737.

* Denotes duplicate titrations. Salinity results given to the nearest decimal place.

† Not titrated till three days after drawing.

January 11th :—

Surface samples.	Temperature °C.	Salinity ‰.	pH corrected.	c.c. of N/100H ₂ SO ₄ per 100 c.c. sea water.
L1	10.0	30.69*	8.05	—
L2	10.1	32.25	8.09	—
L3	10.3	33.97	8.11	—
L4	10.3	34.67	8.11	—
L5	11.1	35.23	8.13	—
L6	11.2	35.26	8.13	—
E1	11.2	35.36	8.14	—

High water at 3.30 a.m., L1 at 9.45 a.m., E1 at 12.15, noon.

On January 10th water at the east slip was at pH8.07 at high water.

February 6th :—

Surface Samples.	Temperature °C.	Salinity ‰.	pH corrected.
L1	8.2	31.02*	8.12
L2	8.8	33.04	8.12
L3	8.9	34.93	8.11
L4	9.2	35.16	8.13
L5	9.5	35.17*	8.14
L6	9.9	35.33	8.14
E1	9.9	35.33	8.14

High water 8.10 a.m., L1 at 10 a.m.

March 29th :—

Surface Samples.	Temperature °C.	Salinity ‰.	pH corrected.
L1	8.0	33.46*	8.12
L2	8.4	34.37	8.14
L3	8.6	34.94	8.14
L4	8.7	34.97	8.14
L5	8.9	35.16	8.15
L6	9.1	33.23*	8.14
E1	9.7	35.35	8.16

High water at 6.20 a.m., L1 at 10.15 a.m.

The less saline estuary waters were corrected for salt error by adding the pH values as shown below to the values indicated on the standard tubes, the marking of which has been explained previously.

* Denotes duplicate titrations.

Salinity ‰	Chloride.	Chloride normality.	Chloride normality, with indicator.	pH correction added.
35.30	19.54	0.550	0.524	0.00
35.01	19.38	0.546	0.520	0.00
33.71	18.66	0.526	0.496	0.01
32.25	17.85	0.503	0.480	0.02
30.72	17.00	0.479	0.456	0.03

It was unfortunately necessary to reject a large number of careful determinations made with the colorimeter, owing to the variation in the size of the drops of indicator added. This has rather spoiled the series. With the exception of the July measurements, however, the titrations and pH values recorded and all the rejected series were in agreement in showing a decidedly lower alkalinity at L1 than at L2 and stations further out. The July values show a gradient in the reverse direction. It will be of interest to see what results obtained earlier in the summer are like. The McClendon series was used from November 9th inclusive onwards, so greater reliance is to be placed on the values obtained with standards at pH 0.05 rather than on those with the Clark and Lubs standards at pH 0.2 intervals. Since the tubes of a series were kept and compared with each other there is not, however, much risk of their order of magnitude being erroneous.

The salinity naturally varies more at L1 than at the other stations, and the dilution was greatest in the wet winter months. Calculating the range as a percentage of the maximum value the figures are L1, 12.3; L2, 8.3; L3, 3.2; L4, 1.9; L5, L6, and E1, 0.6-0.7 per cent. A variation in salinity, of course, affects the titration results for alkali, but not the pH values unless sufficiently marked to alter the salt error.

The titration results are more readily compared when tabulated together as follows:—

C.c. of N/100 H₂SO₄ to neutralise 100 c.c. sea water to phenolphthalein.

Date.	L1.	L2.	L3.	L4	L5.	L6.	E1.
July 4th	2.6	2.5	2.5	2.6	—	—	2.0
Aug. 12th	1.6	2.5	2.6	2.1	2.1	2.4	2.3
Aug. 15th	1.9	2.2	2.3	2.4	2.4	2.2	2.4
Aug. 22nd	2.2	2.5	2.6	2.7	—	—	—
Sept. 1st	2.9	2.9	2.9	3.3	3.3	—	—
Sept. 6th	2.5	2.5	2.7	2.6	2.5	2.8	3.0
Oct. 18th	—	—	2.1	—	2.3	—	2.2
Nov. 9th	—	2.4	2.4	—	—	2.9	2.7
Dec. 12th	1.6	2.0	—	2.4	—	2.6	2.8

The lowest values shown are those for the first part of August and in December, the highest in September.

The extremes are grouped together below :—

	Max. c.c.	Min. c.c.	Difference. c.c.	Max. °C.	Min. °C.	Difference. °C.
L1	2.9	1.6	1.3	16.3	10.0	6.3
L2	2.9	2.0	0.9	16.1	10.1	6.0
L3	2.9	2.1	0.8	16.0	10.3	5.7
L4	3.3	2.1	1.2	16.0	10.3	5.7
L5	3.3	2.1	1.2	15.9	11.1	4.8
L6	2.9	2.2	0.7	16.3	11.2	5.1
E1	3.0	2.0	1.0	16.4	11.2	5.2
	3.1	2.1	1.0	16.15	10.95	5.2

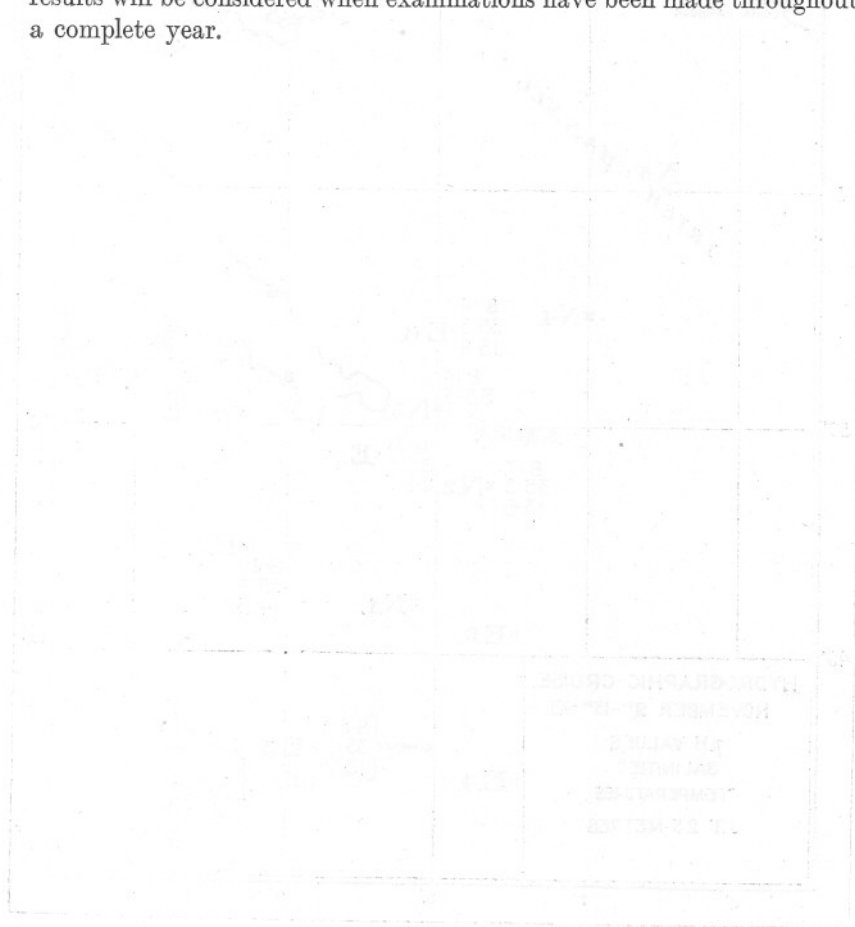
Mean of open sea values (in square).

The open sea values give a range of 1.0 c.c. from July to December, the temperature range corresponding being 5.2° C. Since over the range studied 0.1 c.c. corresponds to pH 0.01 and the latter change is brought about by alteration in bicarbonate equilibrium due to 1° C., it would be necessary to correct the total alteration in alkalinity, 1.0 c.c. for this, to arrive at a measure of the amount due to photosynthesis. Thus part of the fall in alkalinity and pH value which occurs in winter is a pure temperature phenomenon, more carbon dioxide being retained in the colder water. Almost equally great changes occur, however, between August and September, though the water was slightly warmer in the latter month. It appears, therefore, that 1.00 c.c. of N/100 acid may be taken as a reliable minimum value for the photosynthetic changes occurring in sea water between July and December inclusive. That it is only a minimum value is evident from the fact that two processes are at work in opposite directions, namely, photosynthesis and plant and animal respiration. In addition to this, since the sea has a higher pH value than that attained by its water when in equilibrium with the carbon dioxide of the air, it is steadily absorbing this gas, which tends to lower the pH value. The additional aeration taking place in stormy weather also lowers the pH value, as will be mentioned later on. This furnishes the surface of the sea with carbon dioxide more rapidly than does the respiration of the plankton.

The value 1.0 c.c. of N/100 acid per 100 c.c. sea water corresponds to 0.44 milligrams of carbon dioxide, namely, 4.4 mgrm. per litre, or 1.2 mgrm. expressed as carbon. This amount converted into carbohydrates throughout a large volume of water yields a considerable quantity. The discussion of this will be resumed after considering the results of other stations at sea.

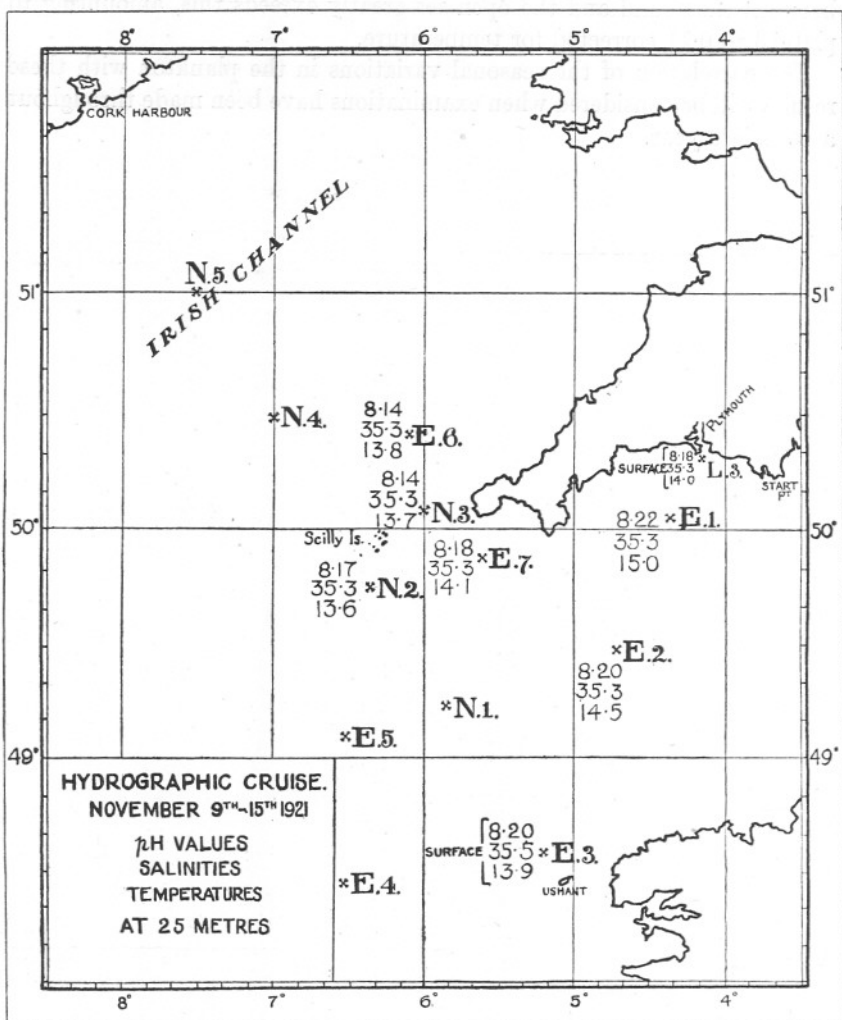
Taking into account only the pH values obtained with the short range, pH0.05 standards and tubes carefully selected for uniformity of bore, it may be seen that the change between November 9th and January 11th amounts to pH0.11 to 0.09 at L4 to E1; the fall in temperature amounted to 4° C., so correcting for this the alteration due to respiration and more complete aeration was at least pH0.07 to 0.05. The difference between the Sound and the open sea greatly exceeds this, amounting to pH0.13 to 0.11 corrected for temperature.

The correlation of the seasonal variations in the plankton with these results will be considered when examinations have been made throughout a complete year.



THE HYDROGEN ION CONCENTRATION OF OPEN SEA WATER AND ITS VARIATION WITH DEPTH AND SEASON.

The stations studied were all in comparatively shallow water, the greatest depth to which the water bottle could safely be lowered being 100 metres.



The alkalinity titrations and pH values were determined, some on the s.s. *Oithona*, but the majority on the s.s. *Salpa* in the course of the routine hydrographic cruises at the seasons arranged by international agreement.

The station E1 is studied monthly, the others five times a year as far

as weather permits, namely, early in February, about the time of maximum density as judged by E1, again six weeks later, in the middle of March, and twelve weeks later, at the end of April, also in June and November. The salinity determinations given in this paper were made in the usual way at the Government Laboratory, London. The June cruise had to be postponed till the second of July. As shown in the accompanying map the stations E1, E2, E3 lie on an approximately S.W. course from Plymouth to Ushant; N1 and N2 are on a line joining Ushant and Cork Harbour, N2 being south of the Bishop Light, Scillies. (The completion of the line, N4 and N5, has been undertaken by the Irish Fisheries Dept.) N3 lies near the Longships, 6° W. between Cornwall and the Scillies; E6 is about twenty miles further north, and E7 is S.E. from the Wolf Light off the Lizard. Of these it may be said that N1 and E2 are at any rate well removed from the effect of the shore algæ upon the hydrogen ion concentration, since the latter is about fifty miles from the coast of Brittany and Devon, though only thirty-five miles from the nearest Cornish headland. N1 is even further out, sixty miles from the nearest point of the French coast, and fifty-three from Cornwall.

The tables which follow give the monthly readings for E1 at the various depths and the readings for the others at longer intervals.

E1, April 26th :—

Depth in metres.	Temperature °C.	Salinity ‰	pH corrected.	c.c. of N/100H ₂ SO ₄ per 100 c.c. sea water.
0	10.18	35.12*	8.24	—
30	9.83	35.11	8.22	—
70	9.82	35.15	8.22	—

E1, July 2nd :—

0	14.79	35.23	8.17	2.0
30	13.20	35.17	8.12	1.8
70	12.51	35.18	8.12	1.7

E1, August 12th :—

0	16.13	—	—	2.3
5	16.17	35.10	—	2.3
10	16.13	35.11	—	2.6
15	16.12	35.10	—	2.6
20	15.46	35.14	—	2.2
25	13.34	35.16	—	2.2
30	13.32	35.19	—	—
40	13.30	35.19	—	2.1
50	13.28	35.19	—	2.1
60	13.28	35.17	—	—
70	13.28	35.13	—	2.0

* Denotes duplicate titrations.

E1, September 15th :—

Depth in metres.	Temperature °C.	Salinity ‰	pH corrected.	c.c. of N/100H ₂ SO ₄ per 100 c.c. sea water.
0	15.80	35.13	8.25	—
5	15.76	35.15	8.26	—
10	15.70	35.12	8.25	—
15	15.64	35.13	8.24	—
20	15.55	35.15	8.25	—
25	14.95	35.15	8.25	—
30	14.06	35.16	8.25	—
40	13.86	35.15*	8.24	—
50	13.80	35.14	8.23	—
60	13.80	35.14	8.23	—
70	13.80	35.10	8.22	—

pH determined on following day.

E1, October 18th :—

0	15.55	35.29*	—	2.2
5	15.51	35.33	—	2.9
10	15.50	35.25	—	—
15	15.46	35.31	—	2.6
20	15.46	35.25	—	—
25	15.44	35.30	—	2.6
30	15.43	35.22*	—	—
40	15.42	35.26	—	2.5
50	15.40	35.20	—	—
60	15.38	35.26	—	—
70	15.34	35.26	—	—

Titrations for alkalinity made three days after taking sample.

E1, November 9th :—

Depth in metres.	Temperature °C.	Salinity ‰	pH corrected.
0	14.96	35.37*	8.23
5	15.00	35.33	8.23
10	14.96	35.33	8.23
15	15.00	35.41	8.23
20	14.99	35.32	8.23
25	14.96	35.29*	8.22
30	14.98	35.33	8.21
40	14.95	35.32	8.21
50	14.96	35.35	8.21
60	14.96	35.38	8.21
70	14.98	35.28	8.20

* Denotes duplicate titrations.

E1, December 12th :—

Depth in metres.	Temperature °C.	Salinity ‰.	pH corrected.
0	12.95	35.40	8.14
5	13.13	35.41	8.14
10	13.13	35.42	8.14
15	13.15	35.41	8.14
20	13.15	35.42	8.14
25	13.15	35.41	8.14
30	13.12	35.40	8.14
40	13.12	35.41	8.14
50	13.13	35.41	8.14
60	13.12	35.40	8.14
70	13.11	35.42	8.12

E1, January 11th, 1922 :—

0	11.24	35.36	8.14
10	11.31	35.36	8.14
20	11.32	35.36	8.14
30	11.32	35.35	8.14
60	11.35	35.36	8.13
70	11.38	35.34*	8.13

E1, February 6th :—

0	9.9	35.33	8.14
5	10.51	35.31	8.14
25	10.52	35.33	8.14
70	10.50	35.33	8.14

E1, February 11th :—

0	9.9	35.36	8.11†
---	-----	-------	-------

E1, March 29 :—

0	9.7	35.35	8.16
5	9.64	35.28	8.16
10	9.64	35.32*	8.16
25	9.62	35.27	8.16
70	9.62	—	8.16

* Denotes duplicate titrations.

† Examined on 16th, drop of pH0.03 due to keeping, probably in view of identical values for January and February.

E2, July 2nd, 1921 :—

Depth in metres.	Temperature °C.	Salinity ‰	pH corrected.	c.c. of N/100H ₂ SO ₄ per 100 c.c. sea water.
0	14.98	35.14	8.17	1.9
40	12.31	35.13	8.12	1.7
95	12.30	35.20	8.12	1.7

E2, September 5th :—

0	14.68	—	8.2	2.7
5	14.55	—	—	2.8
10	14.54	—	—	2.9
15	14.50	—	—	2.9
20	14.46	—	—	2.8
25	14.46	—	—	2.7
30	14.40	—	—	2.9
40	14.40	—	—	2.7
50	14.40	—	—	2.8
60	14.40	—	—	2.8
70	14.41	—	—	2.8
80	14.45	—	—	2.7

E2, November 9th :—

0	14.45	35.26	8.20	—
5	14.45	35.28	8.20	2.2
10	14.48	35.32*	8.20	—
15	14.50	35.29	8.20	—
20	14.48	35.29	8.20	—
25	14.50	—	8.20	—
30	14.49	35.40	8.20	—
40	14.50	35.29	8.20	—
50	14.53	35.39*	8.20	—
60	14.53	35.29	8.20	—
70	14.52	35.36	8.16	—
85	14.50	35.29	8.16	—

Titration made two days after taking sample when it was at pH8.16.

E2, February 11th :—

Depth in metres.	Temperature °C.	Salinity ‰	pH corrected.
0	10.5	35.36	8.12
5	10.64	35.42	8.14
25	10.62	35.41	8.14
50	10.62	35.45	8.14
85	10.62	35.39	8.14

pH determinations made on 16th, results possibly low by pH0.03, probably less.

* Denotes duplicate titrations.

E2, March 29th :—

Depth in metres.	Temperature °C.	Salinity ‰.	pH corrected.
0	10.1	35.45*	8.17
25	9.90	35.46*	8.17
85	9.90	35.38*	8.17

E3, July 2nd, 1921 :—

Depth in metres.	Temperature °C.	Salinity ‰.	pH corrected.	c.c. of N/100H ₂ SO ₄ per 100 c.c. sea water.
0	14.39	35.22	8.18	2.0
40	12.82	35.27	8.17	2.0
100	12.81	35.35	8.17	2.0

E3, November 10th :—

0	13.9	35.48	8.20	2.5
---	------	-------	------	-----

E3, February 11th :—

0	10.7	35.42	8.11†	—
5	10.76	35.42	8.13	—
25	10.79	35.45	8.13	—
50	10.80	35.44	8.13	—
100	10.80	35.42	8.14	—

pH determinations made on 16th, results possibly low by pH0.03, probably less.

E3, March 30th :—

Depth in metres.	Temperature °C.	Salinity ‰.	pH corrected.
0	9.9	35.41	8.17
25	10.20	35.41	8.17
100	10.16	35.38	8.17

N1, July 3rd :—

Depth in metres.	Temperature °C.	Salinity ‰.	pH corrected.	c.c. of N/100H ₂ SO ₄ per 100 c.c. sea water.
0	15.50	35.29	8.22	2.2
40	11.10	35.22	8.17	2.0
100	11.10	35.25	8.17	2.2

N1, February 12th, 1922 :—

0	10.5	35.37	8.09†	—
---	------	-------	-------	---

* Denotes duplicate titrations.

† Examined on 16th.

N1, March 30th :—

Depth in metres.	Temperature °C.	Salinity ‰	pH corrected.	c.c. of N/100H ₂ SO ₄ per 100 c.c. sea water.
0	9.6	35.25	8.16	—
25	9.80	35.21	8.16	—
100	9.83	35.25	8.16	—

N2, Ju'y 3rd :—

0	16.88	35.26	8.22	2.3
27	14.12	.22	8.22	2.2
32	12.07	.16	8.17	2.1
40	11.65	.17	8.17	2.0
95	10.90	.11	8.16	2.0

The break between 27 and 32 metres was examined for pH with α -naphtholphthalein and phenolphthalein as well as the usual cresol red. The difference was estimated at pH0.05 with the first and last named, and pH0.03 with the second. The difference between top and bottom was judged to be pH0.06 with α -naphtholphthalein, and pH0.05 with the other two indicators.

N2, November 12th :—

Depth in metres.	Temperature °C.	Salinity ‰	pH corrected.	c.c. of N/100H ₂ SO ₄ per 100 c.c. sea water.
0	13.43	35.28	8.14	—
5	.52	.32	8.14	—
10	.55	.33*	8.16	—
15	.55	.30*	8.16	—
20	.56	.26	8.17	—
25	.57	.28	8.17	—
30	.56	.26	8.17	—
40	.52	.24	8.17	—
50	.52	.24	8.17	—
60	.45	.25	8.16	—
75	.30	.31*	8.16	—
90	.32	.26	8.16	—

N2, February 12th, 1922 :—

0.	10.2	35.21	8.12†	—
5	10.23	35.23	8.14	—
25	10.25	35.20	8.15	—
85.	10.26	35.20	8.14	—

* Denotes duplicate titrations.

† Examined on 16th, results possibly low by pH0.03, probably less.

N2, March 30th :—

Depth in metres.	Temperature °C.	Salinity ‰.	pH corrected.
0	9.5	35.20	8.15
85	9.37	35.19	8.15

N3, November 12th :—

0	13.70	35.32	8.14
25	13.67	35.26	8.14
65	13.68	35.29	8.14

The usual intermediate depths were done, but gave identical readings for temperature and pH.

N3, February 12th, 1922 :—

0	9.4	35.23	8.10
---	-----	-------	------

pH determined on 16th.

N3, March 30th :—

0	9.7	35.22*	8.15
65	9.35	35.17	8.15

E6, November 13th :—

Depth in metres.	Temperature °C.	Salinity ‰.	pH corrected.	c.c. of N/100H ₂ SO ₄ per 100 c.c. sea water.
0	13.80	35.28	8.14	—
30	13.83	35.28	8.14	—
83	13.83	35.27	8.14	—

E6, March 30th :—

0	9.1	35.17	8.14	—
70	9.30	35.16	8.14	—

E7, July 4th :—

0	15.90	35.24	8.25	2.30
40	14.28	35.28	8.17	2.28
45	13.27	35.26	8.21	2.22
70	11.98	35.28	8.17	—

Taken in order 70, 40, 45, 0 metres. Note undulating upper surface of warmer more alkaline layer. Values for pH at 40 and 70 metres identical with two indicators, for 45 metres pH 0.02 to 0.04 lower than surface.

* Denotes duplicate titrations.

E7, November 12th :—

Depth in metres.	Temperature °C.	Salinity ‰	pH corrected.	c.c. of N/100H ₂ SO ₄ per 100 c.c. sea water.
0	14·10	35·25	8·13	2·1
5	·12	·27	8·15	—
10	·10	·23*	8·16	—
15	·10	·26	8·16	—
20	·12	·27	8·18	—
25	·12	·25	8·18	—
30	·12	·26	8·18	—
40	·10	·24*	8·18	—
50	·10	·25	8·16	—
60	·12	·26	8·15	—
70	·15	·28	8·15	2·6 ?

E7, February 12th, 1922 :—

0	9·9	35·29	8·10†	—
5	10·10	35·26	8·12	—
25	10·18	35·31	8·14	—
65	10·18	35·28	8·14	—

The results obtained for pH values and alkalinity titrations show that there is normally a decrease of pH 0·05 to 0·01 from top to bottom, and about 0·3 c.c. diminution in the amount of acid required to neutralise to phenolphthalein. This is quite in agreement with the results obtained by Palitzsch. Sometimes, however, the water at 5–10 metres appears to be considerably more alkaline than at the surface, cp. E1, August 12th, October 18th, and possibly E2, September 5th. Other instances in which this was thought to occur have not been recorded, owing to the previously mentioned uncertainty in the colorimeter work. However, Helland-Hansen and Gaarder have obtained similar results with masses of water in a comparatively undisturbed condition, subjected to the action of plankton algæ in sunlight.

Sometimes, however, the surface water is undoubtedly less alkaline than the deeper layers at 20–40 metres, beyond which the gradient is in the normal direction. This is illustrated by the results of the cruise of November 9th. Here E1 and E2 were almost uniform in temperature from top to bottom, but showed normal gradients in pH value, from pH 8·23 to 8·20 and pH 8·20 to 8·16 respectively. E3, surface, was also at pH 8·20, but it was impossible to obtain the usual series of deep water samples as the weather became too rough. It was necessary to run to Falmouth for shelter, and on emerging early on November 12th a great change was observed.

* Denotes duplicate titrations.

† Determined on 16th.

The stations were taken in the order E7, N2, N3, and E6. Station E7 had a reversed gradient, pH 8.13 to 8.18, followed by a normal gradient, pH 8.18 to 8.15. N2 gave similar results, the gradients in both cases being less steep. Neither N3 nor E6 showed any gradient at all. These changes appear to be due to the aeration of the surface layers of the sea, resulting in absorption of carbon dioxide, and a marked lowering in the pH value. Owing to the mixing the less alkaline water is carried down and decreases the alkalinity of the deeper layers by an amount depending on the extent of the mixing. The February 11th cruise showed similar reversed gradients in pH values.

With regard to the seasonal photosynthetic changes in alkalinity, the results given by the mid-channel station, E2 for July and September, show as mean values 1.8 c.c. and 2.8 c.c. acid per 100 c.c. sea water for neutralisation. These give as difference 1.0 c.c., which is just what the mean maximum and minimum values for L4-E1 inclusive gave, though the actual values were higher, 2.1 c.c. to 3.1 c.c. The probability is that the variation is even greater when the whole year is considered. The figures obtained from the July and November cruises are not helpful in judging this change as the autumn alkalinity maximum has been passed apparently, though the pH values for E1 were still high. Attempts will be made to obtain data bearing on the vernal maximum which Moore, Herdman, and Prideaux showed to be so important.

The value 1.0 c.c., however, corresponds as previously explained to 4.4 milligrams per litre of carbon dioxide, or 1.2 mgrm. expressed as carbon. This is a well-established minimum value for the open sea in the English Channel between July and December. For the harbour water a larger change, up to 1.3 c.c., was noted. Taking the open sea figure, 1.2 mgrm. of carbon, since a sugar such as dextrose contains 40 per cent of this element, the amount suffices to provide 3 mgrms. per litre of dextrose, or slightly more than that amount of starch. This is equivalent to 3 grams of dextrose per cubic metre of water, or taking the depth of the Channel off Plymouth as 80 metres the total amount of carbohydrate expressed as dextrose synthesised in the column of water with a base of one square metre is 240 grams. Taking the depth as 83.3 metres, which is probably as accurate as 80 metres,* the amount synthesised is 250 grams, or one kilogram per four square metres. Over an area of one square kilometre this amounts to 250,000 kilograms.

Were photosynthesis to remain uniform and respiration in abeyance it is obvious that there would be a vast accumulation of carbohydrate in the sea. As it is the amount present is an equilibrium between the production due to photosynthesis and the destruction by plant and animal respiration. Under conditions which limit respiration, viz. by ensuring

* The depths at E1, E2 and E7 are respectively 74, 94 and 78 metres, mean 82.

the absence of animal life and in the presence of abundant supplies of necessary salts, as for example in a pure culture of diatoms, the amount of carbohydrate photosynthesised, as judged by the alkalinity, is greatly in excess of that actually found in the sea; in good illumination the water of the culture is maintained in a strongly alkaline condition, at about pH 9.4. This, however, is abnormal. The conditions in nature are regulated by the illumination, for with increasing sunlight in these latitudes the effects of photosynthesis becomes noticeable in the altered reaction of the water in spring. It might be expected, therefore, that on the score of more intense illumination, life ought to be maintained in greater abundance in the warmer than in the colder regions of the oceans. The reverse is by some alleged to be the case. The action of Brandt's denitrifying bacteria has been invoked to explain this, the small amount of nitrate present being considered to act as a limiting factor. It has, however, been shown by Moore, Whitley, and Webster (1920) that algæ may themselves fix gaseous nitrogen, or that bacteria normally occurring on their surfaces can do so in sunlight. The more intense illumination of the equatorial oceans ought therefore to be more favourable to plant development, and accordingly to the animal life which depends upon the former. Against this, however, is the fact that in summer the polar regions have a longer period of daylight, but this is counterbalanced by a shortened illumination in winter.

On considering Blackman's work on limiting factors and the quantitative results obtained by Miss Matthaei (1905), it is seen that an increase of temperature may effect a very decided increase in the rate of photosynthesis. If, however, the light intensity is low, a point is reached beyond which a further temperature rise, even when not injurious, is unaccompanied by any rise in assimilation. The amount of light energy available is insufficient to decompose carbon dioxide at a rate in excess of that already attained at the lower temperature. From the results obtained, when light was not the limiting factor, Kanitz (1915) has shown that the van't Hoff rule holds approximately, the ratio being 2.40 per 10° C. rise from 0°-10° and 2.12 from 10°-20°. For respiration similar coefficients are given, so it is only when light is a limiting factor that increase of temperature is unattended by increase in assimilation as well as in respiration. It appears that in the sea light must often be a limiting factor at anything more than a relatively small depth. Under such conditions the full effect of increase in temperature would be exerted in increasing respiration, whilst assimilation would not increase. Accordingly the amount of carbohydrate actually in the sea would diminish. It seems to be quite possible that the ultimate limit to the weight of living organisms found in unit—a large unit—volume of water at any mean temperature depends upon the quantity of carbohydrate available in that

volume; the level at which the latter stands must be regulated by the relative rates of photosynthesis and respiration. Since the temperature only fell 3° C. between August and December it is scarcely necessary to correct this factor, but the full correction, assuming the temperature extremes to correspond with the alkalinity extremes, is 0.3 c.c., reducing the result by 30 per cent.

In order the more easily to compare the pH values of the various stations at different seasons the results for the surface, or in some cases for 5 metres, have been tabulated together. In reviewing these it must again be pointed out that, as previously explained, there may be a small error in the results prior to November, 1921, and the determinations are less accurate, being interpolated over a larger range, pH0.2 instead of pH0.05. The values at any time, the July cruise for example, are believed to be strictly comparable *inter se*.

pH values of the surface sea water at the stations, 1921-22.

	E1	E2	E3	N1	N2	N3	E6	E7
April	8.24	—	—	—	—	—	—	—
July	8.17	8.17	8.18	8.22	8.22	—	—	8.25
August	8.27	—	—	—	—	—	—	—
Sept.	8.25	—	—	—	—	—	—	—
Nov.	8.23	8.20	8.20	—	8.14	8.14	8.14	8.13
Dec.	8.14	—	—	—	—	—	—	—
Jan.	8.14	—	—	—	—	—	—	—
Feb.	8.14	8.12*	8.13*	8.09*	8.12*	8.10*	—	8.10*
Range	0.13	0.08	0.07	0.13	0.10	0.04	—	0.15

As far as these incomplete data permit of the drawing of any conclusions it appears that the more westerly stations have a higher pH value than the more easterly in July. The reverse is the case in November, though the effects of the storm seem to have modified the latter results very considerably as already noted. In February, even allowing for the necessary correction, there appears to be a slight decrease in a westerly direction.

With regard to the seasonal range in pH values, owing to the limited number of observations only those for E1 should be considered as truly representative, the value pH0.13 which results is equivalent to 1.3 c.c. of acid per 100 c.c. of sea water. This is somewhat reduced if corrected for the change in the equilibrium brought about by alteration in temperature, a difference between August and December of 3° C. brings the figure to pH0.10 as due to the photosynthetic changes alone, this is equivalent to 1.0 c.c. of acid.

* These determinations were made on 16th, samples taken on 11th and 12th. The corresponding E1 sample gave pH8.11, but one on 6th and examined at once gave pH8.14, so it appears that there was a small decrease, not exceeding, and in some cases not as much as, pH0.03, owing to the samples having been stored for three or four days.

SUMMARY.

The experimental results obtained seem to warrant the following conclusions :—

(1) The salt error of cresol red for sea water of salinity 35 ‰ is pH0.18 when determined with Clark and Lubs standard borate buffer mixtures, and compared with McClelland's set as corrected by his potentiometer measurements. When tightly closed with rubber caps tubes of McClelland's series mixed with cresol red were found to have undergone no measurable change in four months, using toluene as a preservative. The measurements can detect a change of pH0.01, and are believed to be accurate to plus or minus pH0.01. To attain this accuracy the indicator added must be measured with exactness, not by drops.

(2) Sea water may become as alkaline as pH9.7 as a result of very active photosynthesis. This it does in virtue of the presence of magnesium salts, since the limiting pH value of magnesium carbonate is pH10.0, the same as for magnesium hydroxide; calcium carbonate in the form of pure calcite gives as a limiting value pH9.0.

(3) The salt-water tanks of the aquarium are always less alkaline than the water of Plymouth Sound, the values being respectively pH7.6 and 8.1 on an average. Any lowering of the value for the tanks below pH7.6 denotes abnormal excess of carbon dioxide, and when the decrease amounts to pH0.3, viz. a fall to pH7.3, symptoms of distress may appear among the fishes; water at pH7.1 is definitely foul and evil smelling. The water round rotting sea weed in a jar may be as acid as pH6.4. Agitation of water from the tanks with air results in the removal of carbon dioxide, and a value close to pH8.0 is attained.

(4) The water of the Sound varies slightly with the state of the tide, a drop of pH0.05 may be observed between high and low water. Over *Laminaria* in shallow water, through which the tops of the algæ appear, the water may be pH0.15 more alkaline than the general mass of water. Rock pools in summer may be at least as much as pH0.25 more alkaline than the Sound water, and up to 3.7 c.c. of N/100 acid may be required per 100 c.c. for neutralisation to phenolphthalein; they may be over 2.5° C. warmer.

(5) During July the water of the Sound is definitely more alkaline than that of the open sea, a difference estimated at pH0.12 having been observed. From August to January the Sound water is less alkaline than that of the sea, the latter being from pH0.02 to 0.16 greater. These

results are confirmed by the figures given by titration. The pH values are considered more reliable than the latter, since with a carefully measured volume of indicator it is unlikely that the error will be as great as pH0.02, more probably pH0.01, with the McClelland standards at pH0.05 intervals; the order in a series will always be correct if tubes of uniform bore are compared at the same temperature. On the other hand, it is quite possible to have fluctuating errors of 0.2 c.c. in each titration, which corresponds approximately to pH0.02 over the range studied, using N/100 H_2SO_4 and 100 c.c. of sea water with phenolphthalein.

The lowest value observed for the Sound water was pH8.01 at low water in December. The highest was pH8.29 in July. From 1.6 to 2.9 c.c. of N/100 acid are required to neutralise to phenolphthalein. These figures relate only to the period, July to March.

(6) In the open sea between July and December the pH value varies from pH8.27 to 8.14, the April figure being pH8.24. In the second six months of the year titration as before varied between 2.0 and 3.3 c.c., the mean minimum and maximum being 2.1 and 3.1 c.c. around Station E1. The decrease with depth amounts to about pH0.03, or 0.3 c.c. from surface to seventy metres. Occasionally the change is quite abrupt, within five metres, more usually it is gradual. A storm may reverse the normal gradient by mixing atmospheric carbon dioxide with the surface water. The range at E2 is also 1.0 c.c.

(7) Calculating on the basis of an alteration in titration of 1.0 c.c. of N/100 acid and taking the mean depth of the Channel off Cornwall as 83.3 metres an approximate value, the minimum amount of carbohydrate, as dextrose, photosynthesised is one kilogram per four square metres of surface, or 250,000 kilograms per square kilometre between July and December. It is suggested that the limiting factor for the amount of living matter present in any considerable area may be the amount of light available as energy for photosynthesis. The thorough mixing of the water, as shown by the pH measurements, makes it permissible to calculate the seasonal changes as from bottom to surface, rather than in the surface layers where they originate. These results are subject to a correction for alteration in alkalinity due to rise of temperature; this as a maximum cannot exceed 0.3 c.c., viz. reducing the values found by 30 per cent. The pH range for E1 was observed to be 0.13, or corrected for the part possibly due to the establishment of a temperature change equilibrium, and it is doubtful that equilibrium is reached, the range is pH0.10. This corresponds to 1.0 c.c. of acid, so the figure 250,000 kilograms given above may stand as an approximate value.

(8) In order that the conditions under which marine animals and plants exist at the various sites examined may be the more readily compared

the following data have been tabulated. The values are, of course, not necessarily the actual maximum and minimum values that occur at the places named.

	pH	Temperature °C.	Salinity ‰
Aquarium tanks, normal	7.6-7.45	18.9-9.1	36.14-36.85
" " abnormal	8.0-7.05	—	—
Rock pool	8.57-8.01	21.4-8.2	—
Shallow water	8.42-8.01	19.2-8.2	—
L1, Plymouth Sound	8.29-8.01	16.3-8.2	35.00-30.69
L2 " Breakwater	8.27-8.07	16.1-8.8	35.17-32.25
E1, about 20 miles out to sea from Breakwater	8.27-8.14	16.2-9.9	35.40-35.13

The ranges of the above data are shown below.

	pH	Temperature °C.	Salinity ‰
Aquarium, normal	0.15	9.8	—
" abnormal	0.95	—	—
Rock pool	0.56	13.2	—
Shallow water	0.41	11.0	—
L1	0.28	8.1	4.31
L2	0.20	7.3	2.92
E1	0.13	6.3	0.27

The writer is indebted to Messrs. E. W. Nelson, R. S. Clark, and H. W. Harvey for many of the temperature readings at sea, and for help in the taking of samples and in other ways. The cost of the special reagents for hydrogen ion determinations was defrayed by a grant from the Department of Scientific and Industrial Research. The laborious salinity titrations were carried out by the Government Chemist London, to whom thanks are also due.

BIBLIOGRAPHY.*

- ATKINS, W. R. G. 1922. Some factors affecting the hydrogen ion concentration of the soil and its relation to plant distribution. *Sci. Proc. Roy. Dublin Soc.*, **16**, No. 30, 369-412. Reprinted in Notes from the Botanical School of Trinity College, Dublin, 1922, **3**, No. 3.
- BAYLISS, W. M. 1915. Principles of general physiology. London.
- BEANS, H. T., and OAKES, E. T. 1920. The determination of the hydrogen ion concentration of pure water by a method for measuring the electro-motive force of concentration cells of high internal resistance. *J. Amer. Chem. Soc.*, **42**, 2116.
- BIRGE, E. A., and JUDAY, C. 1911. The inland lakes of Wisconsin. The dissolved gases of the water and their biological significance. *Wisconsin Geol. and Nat. Hist. Survey*. Madison, Wis.
- BUCH, K. 1914. Über die Alkalinität, Kohlensäure und Wasserstoffionenkonzentration in der Pojowiek. *Fennia, Bull. de la Soc. de géographie de Finlande*, **35**, No. 3.
- 1917. Über die Alkalinität, Wasserstoffionenkonzentration, Kohlensäure und Kohlensäuretension in Wasser der Finland umgebenden Meere. *Soc. Scient. Fennica, Finländische hydrographisch-biologische Untersuchungen*, No. 14, p. 135.
- CAMERON, F. K., and BRIGGS, L. J. 1901. Equilibrium between carbonates and bicarbonates in aqueous solution. *J. Phys. Chem.*, **5**, 537.
- CHAMBERS, C. O. 1912. The relation of algæ to dissolved oxygen and carbon dioxide, with special reference to carbonates. 23rd Ann. Report, *Missouri Bot. Gardens*, 171-207.
- CLARK, W. M. 1920. The determination of hydrogen ions. Baltimore.
- 1921. Reply to Wherry and Adams' article on methods of stating acidity. *J. Wash. Acad. Sci.*, **11**, 199.
- COLE, S. W. 1920. Practical physiological chemistry. Cambridge.
- GAIL, F. W. 1918. Some experiments with *Fucus* to determine the factors controlling its vertical distribution. *Publ. Puget Sound Biol. Sta.*, **2**, 139.
- 1919. Hydrogen ion concentration and other factors affecting the distribution of *Fucus*. *Loc. cit.*, **2**, 287.
- HALL, A. R. 1918. Some experiments on the resistance of sea-urchin eggs to sulphurous acid. *Publ. Puget Sound Biol. Sta.*, **2**, 113.

* With but few exceptions papers given in Clark's (1920) list have been omitted here.

- HELLAND-HANSEN, B. 1914. Eine Untersuchungsfahrt im Atlantischen Ozean mit dem Motorschiff "Armauer Hansen" im Sommer 1913. Internat. Rev. d. ges. Hydrobiol. u. Hydrogr. **7**, 61.
- KANITZ, A. 1915. Temperatur und Lebensvorgänge. Berlin.
- MATTHAEI, G. L. C. 1905. Experimental researches on vegetable assimilation and respiration. III. On the effect of temperature on carbon dioxide assimilation. Phil. Trans. Roy. Soc. B. **197**, 47-105.
- MAYER, A. G. 1916. Sub-marine solution of limestone in relation to the Murray-Agassiz theory of coral atolls. Proc. Nat. Acad. Sci., U.S.A., **2**, 28.
- MAYER, A. G. 1919. Detecting ocean currents by observing their hydrogen ion concentration. Proc. Amer. Phil. Soc., **58**, 150.
- MCCLENDON, J. F. 1916. On changes in the sea and their relation to organisms. Dept. of Marine Biol., Carnegie Inst., Washington, **12**, 213-58. Carnegie Publ. No. 252.
- 1917. The standardisation of a new colorimetric method for the determination of the hydrogen ion concentration, CO₂ tension, and CO₂ and O₂ content of sea water, of animal heat, and of CO₂ of the air, with a summary of similar data on bicarbonate solutions in general. J. Biol. Chem., **30**, 265-88.
- MICHAEL, E. L. 1921. Effect of upwelling water upon the organic fertility of the sea in the region of Southern California. Special Publications of B.P. Bishop Museum, No. 7, 555-95.
- MOORE, B., EDIE, E. S., WHITLEY, E., and DAKIN, W. J. 1912. The nutrition and metabolism of marine animals in relationship to (a) Dissolved organic matter and (b) Particulate organic matter of sea water. Biochem. J., **6**, 255.
- MOORE, EDIE, and WHITLEY. 1913. The nutrition and metabolism of marine animals; the rate of oxidation and output of carbon dioxide in marine animals in relation to the available supply of food in sea water. Rep. Lancashire Sea Fisheries, Liverpool, **22**, 297.
- MOORE, B., PRIDEAUX, E. B. R., and HERDMAN, G. A. 1915. Studies of certain photosynthetic phenomena in sea water. Proc. & Trans. Liverpool Biol. Soc., **29**, 233-64.
- MOORE, B., and WEBSTER, T. A. 1920. Studies of photosynthesis in fresh-water algæ. Proc. Roy. Soc., B. **91**, 201.
- MOORE, B., WHITLEY, E., and WEBSTER, T. A. 1921. Studies of photosynthesis in marine algæ. Proc. Roy. Soc., B. **92**, 51.
- MORGULIS, S., and FULLER, E. W. 1916. Can CO₂ in sea water be directly determined by titration? J. Biol. Chem., **24**, 31.

- NANSEN, F. 1915. Spitzbergen Waters. Videnskaps-Selskapets Skrifter. I. Math. naturv. Klasse, No. 2, 1-132.
- POWERS, E. B. 1914. The reactions of cray fishes to gradients of dissolved carbon dioxide and acetic and hydrochloric acids. Biol. Bull., **27**, 177.
- 1920. The variation of the condition of sea water, especially the hydrogen ion concentration, and its relation to marine organisms. Publ. Puget Sound Biol. Sta., **2**, 369.
- 1921. Experiments and observations on the behaviour of marine fishes toward hydrogen ion concentration of the sea water in relation to their migratory movements and habits. *Loc. cit.*, **3**, 1.
- 1922. The physiology of the respiration of fishes in relation to the hydrogen ion concentration of the medium. J. Gen. Physiol., **4**, 305.
- PRÉDEAUX, E. B. R. 1919. The effect of sea salt on the pressure of carbon dioxide and alkalinity of natural waters. J. Chem. Soc., **115**, 1223.
- ROAF, H. E. 1920. Graphic conversion of Sørensen's pH ($-\log H$) into concentrations of hydrogen ions. J. Physiol., **54**, p. xvii.
- SCHLOESING, TH. 1872. Sur la dissolution du carbonate de chaux par l'acide carbonique. Compt. Rend., **74**, 1552, **75**, 70.
- SCHMIDT, C. L. A., and HOAGLAND, D. R. 1919. Table of P_H , H^+ , and OH^- values corresponding to electromotive forces determined in hydrogen electrode measurements, with a bibliography. Univ. of California, Publ. in Physiology, **5**, No. 4, 23-69.
- SHELFORD, V. E. 1918. The relation of marine fishes to acids with particular reference to the Miles Acid Process of sewage treatment. Publ. Puget Sound Biol. Sta., **2**, 97.
- WALKER, J., and KAY, S. A. 1912. The acidity and alkalinity of natural waters. J. Soc. Chem. Ind., **31**, 1013.
- WELLS, R. C. 1915. The solubility of calcite in water in contact with the atmosphere and its variation with temperature. J. Wash. Acad. Sci., **5**, 617.
- 1918. The solubility of calcite in sea water in contact with the atmosphere, and its variation with temperature. Dept. of Marine Biol., Carnegie Inst., Washington, **9**, 316. Carnegie Publ., No. 213.
- 1920. The salt error of cresol red. J. Amer. Chem. Soc., **42**, 1260.
- WHERRY, E. T., 1919. The statement of acidity and alkalinity with special reference to soils. J. Wash. Acad. Sci., **9**, 305.
- WHERRY, E. T., and ADAMS, E. Q. 1921. Methods of stating acidity. J. Wash. Acad. Sci., **11**, 197.