

DEPARTMENT OF THE INTERIOR

FRANKLIN K. LANE, Secretary

UNITED STATES GEOLOGICAL SURVEY

GEORGE OTIS SMITH, Director

PROFESSIONAL PAPER 120—A

NEW DETERMINATIONS OF CARBON DIOXIDE IN
WATER OF THE GULF OF MEXICO

BY

ROGER C. WELLS

Published June 20, 1918

Shorter contributions to general geology, 1918

(Pages 1-16)



WASHINGTON

GOVERNMENT PRINTING OFFICE

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NOTE.—The papers included in the annual volume "Shorter contributions to general geology" are issued separately, with the final pagination, as soon as they are ready. The last paper will include a volume title-page, table of contents, and index for the use of those who may wish to bind the separate parts. A small edition of the bound volume will also be issued, but copies can not be supplied to those who have received all the parts.

SHORTER CONTRIBUTIONS TO GENERAL GEOLOGY, 1918.

NEW DETERMINATIONS OF CARBON DIOXIDE IN WATER OF THE GULF OF MEXICO.

By ROGER C. WELLS.

INTRODUCTION.

Although the carbon dioxide in sea water is the subject of a very extensive literature and many determinations of it have been made, recent advances in geochemistry have brought out new relations that require further determinations in order to show the connection, if any exists, between the history of the water, its temperature, its geographic location, the life it contains, and its saturation with calcium and magnesium compounds. In 1914 Clarke and Wheeler,¹ in a paper on crinoid skeletons, pointed out for the first time that the proportion of magnesium carbonate in crinoids is in some way dependent on temperature. This observation led to the publication of a number of papers presenting facts and theories bearing on the subject.²

Even earlier the investigations of Vaughan³ on coral reefs and those of Branner⁴ on the stone reefs of Brazil had led to the consideration of physical factors in the deposition of calcium carbonate in certain localities. Johnston has pointed out that the deposition of calcium carbonate by organic agencies may be closely related to the inorganic factors that determine

how nearly saturated the water is with respect to that substance.

I have been enabled to make the determinations described in this paper through the interest and cooperation of T. W. Vaughan, of the United States Geological Survey, and H. F. Moore, of the Bureau of Fisheries. Mr. Vaughan pointed out the need of such determinations, particularly for American waters, and Mr. Moore authorized the collection of the samples, which were actually collected by W. W. Welsh and shipped in "citrate of magnesium" bottles to the chemical laboratory of the Geological Survey for analysis. It is a great pleasure to express appreciation for the assistance offered by all those who helped to make the study possible.

There is no question that the water of the Gulf of Mexico is essentially similar to that of the open ocean. An analysis of the salts in water off Loggerhead Key, near Florida, made by George Steiger in the chemical laboratory of the United States Geological Survey, is shown in Table 1, together with Dittmar's mean of 77 analyses of ocean water.

TABLE 1.—*Analyses of oceanic salts.*^a

	1	2
Cl.	55.24	55.29
Br.17	.19
SO ₄	7.54	7.69
CO ₃34	.21
Na.....	30.80	30.59
K.....	1.10	1.11
Ca.....	1.22	1.20
Mg.....	3.59	3.72
	100.00	100.00

¹ Clarke, F. W., and Wheeler, W. C., The composition of crinoid skeletons: U. S. Geol. Survey Prof. Paper 90, pp. 33-37, 1915.

² Wells, R. C., The solubility of magnesium carbonate in natural waters: Am. Chem. Soc. Jour., vol. 37, pp. 1704-1707, 1915. Johnston, John, The solubility-product constant of calcium and magnesium carbonates: Idem, pp. 2001-2020. Wells, R. C., The solubility of calcite in water in contact with the atmosphere, and its variation with temperature: Washington Acad. Sci. Jour., vol. 5, pp. 617-622, 1915. Johnston, John, and Williamson, E. D., The complete solubility curve of calcium carbonate: Am. Chem. Soc. Jour., vol. 38, pp. 975-983, 1916. Johnston, John, Merwin, H. E., and Williamson, E. D., The several forms of calcium carbonate: Am. Jour. Sci., 4th ser., vol. 41, pp. 473-512, 1916. Johnston, John, and Williamson, E. D., The rôle of inorganic agencies in the deposition of calcium carbonate: Jour. Geology, vol. 24, pp. 729-749, 1916.

³ Vaughan, T. W., The present status of the investigations of the origin of barrier coral reefs: Am. Jour. Sci., 4th ser., vol. 41, pp. 131-135, 1916. See also Carnegie Inst. Washington Pub. 133, pp. 173-177, 1910; Pub. 182, pp. 69-78, 1914; Year Book 14, p. 222, 1916, and Pub. 213, p. 227, 1918.

⁴ Branner, J. C., Stone reefs on the northeast coast of Brazil: Geol. Soc. America Bull., vol. 16, pp. 1-12, 1905.

^a Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 123, 1916.

1. Salts in water of Gulf of Mexico; George Steiger, analyst.
2. Salts in ocean water, mean of 77 analyses; W. Dittmar, analyst.

Although the analysis of Gulf water cited in this table shows the essential similarity of the water to sea water, it seems likely that the total carbon dioxide has been stated as CO_3 . The value stated amounts to 0.091 gram CO_2 per liter, which is about that of ordinary sea water. Dittmar's figure, on the other hand, does not account for all the CO_2 normally present in sea water. It is generally believed that carbon dioxide, in so far as it constitutes part of the salts in sea water, is present both as carbonate and as acid carbonate, commonly termed "bicarbonate." It was to ascertain the relative proportions of carbonate and bicarbonate in the water that the determinations recorded in this paper were made.

Such determinations have also been made by Dole,¹ by titration methods, on water from Southwest Channel, Tortugas, Fla. Dole's results are as follows:

	Gram per liter.
CO_2 as HCO_3 :	
Highest.....	0.088
Lowest.....	.059
Mean.....	.069
CO_2 as CO_3 :	
Highest.....	.022
Lowest.....	.011
Mean.....	.017
Total CO_2 :	
Highest.....	.099
Lowest.....	.080
Mean.....	.086

Titration methods, however, have been called in question by Johnston,² and for that reason it seemed especially desirable to apply new methods where possible. The present contribution by no means exhausts the subject. Further determinations are needed in connection with the alkalinity of the water determined at the source.

DEFINITION OF TERMS.

Much of the haze that has long befogged the subject of the carbonates in sea water is due to the different meanings given to the same terms by different investigators. It is surprising how tenaciously old terms persist in spite of well-proved facts warranting their abandonment. Some of these terms are so indefinite

that they convey no exact meaning unless they are repeatedly defined by the author who uses them. The word "salinity," for example, is used by some writers to include only part of the salts that exist in sea water and by others to include them all. The word "alkalinity" is used by some as a measure of the combined carbonate and bicarbonate concentration expressed in the same unit, and by others to indicate the hydroxide or hydrogen ion concentration. There are many modes of attack in this problem, but nearly every one involves some theory, so that it becomes most necessary to keep clearly in view how much is fact and how much is theory and not to confuse the two so that neither is of any assistance.

In the present paper sea water is held to be a "phase" in the sense of the phase rule—that is, a liquid capable of dissolving certain solids and gases up to the point of "saturation." Carbon dioxide is one of the gases that can thus be dissolved in sea water, and the determinations made (see Table 2) give the total carbon dioxide that can be extracted from the water after the addition of acid—that is, all the carbon dioxide that exists in the water in any form.

As already stated most of the carbon dioxide in sea water is commonly considered to be present as bicarbonate and carbonate, thus constituting the acid radicles of corresponding salts. Thus practically all the dissolved matter in sea water can be thought of as a group of salts the sum of whose basic radicles is chemically equivalent to the sum of their acid radicles. This equivalence holds very closely for the analyses cited in Table 1 when the various forms in which carbon dioxide is combined are correctly stated. Nothing leads to greater confusion, however, than to attempt to make an arbitrary combination of the various acid and basic constituents determined by analysis, and for this reason it is well to realize that such an expression as "the solubility of calcite in sea water" does not imply that calcium carbonate exists as such in sea water any more than that carbon dioxide exists as such, although both substances are doubtless present in these forms to some extent. When such compounds are added to sea water they react with other substances and enter into the complex kinetic equilibrium that exists in the

¹ Dole, R. B., Some chemical characteristics of sea water at Tortugas and around Biscayne Bay, Fla.: Carnegie Inst. Washington Pub. 182, p. 73, 1914.

² Johnston, John, Determination of carbonic acid, combined and free in solution, particularly in natural waters: Am. Chem. Soc. Jour., vol. 38, p. 947, 1916.

water between all the salts and their ions, hydrates, and hydrolytic products. The single word "carbonate" will therefore express the group constituting the carbonate radicle (CO_3), which would have to be taken in the form of a salt with the various other salts to make up an artificial sea water. The term "bicarbonate" will have a similar meaning. The chemical symbols for these radicles will be CO_3 and HCO_3 . When ions are meant the symbols will bear additional signs for the electric charges, thus: CO_3^- and HCO_3^- . The same symbols inclosed in brackets are generally used to represent concentrations in gram molecules, or mols, per liter, thus: $[\text{CO}_3]$ or $[\text{CO}_3^-]$.

poured into a graduated 250 cubic centimeter flask and then into the distilling flask, and the boiling was begun immediately. The results obtained are stated in Table 2.

The locations given in Table 2 correspond to the following station numbers of the Bureau of Fisheries:

Lat. $29^\circ 38' \text{ N.}$, long. $87^\circ 0' \text{ W.}$, station 10447.

Lat. $29^\circ 53' \text{ N.}$, long. $87^\circ 7' \text{ W.}$, station 10448.

Lat. $30^\circ 5' \text{ N.}$, long. $87^\circ 12' \text{ W.}$, station 10449.

4 miles northwest of Pensacola Light, station 10450.

Sample 1, obtained near Fowey Rocks Light, outside Biscayne Bay, Fla., was a portion of water collected at regular intervals between July 26 and August 3, 1915,² and had stood for part of the time to April, 1917, in a green glass

TABLE 2.—Total carbon dioxide in samples of water from the Gulf of Mexico.

Sample No.	Location.	Depth.	Temperature.	Chlorine.	Total CO_2
		Meters.	$^\circ \text{C.}$	Grams per liter.	Gram per liter.
1	Lat. $25^\circ 35' \text{ N.}$, long. $80^\circ 6' \text{ W.}$	0		20.37	0.106
2	Lat. $29^\circ 38' \text{ N.}$, long. $87^\circ 0' \text{ W.}$	0	18.9	20.21	.093
3do.....	50	19.4	20.23	.092
4do.....	100	18.5		
5do.....	150	13.3	20.20	.099
6do.....	210	10.2	19.94	.100
7	Lat. $29^\circ 53' \text{ N.}$, long. $87^\circ 7' \text{ W.}$	0	20.0	20.52	.092
8do.....	25	20.1	20.39	.092
9do.....	50	19.6	20.40	.094
10do.....	100	18.2	20.52	.100
11do.....	130	15.8	20.40	.098
12	Lat. $30^\circ 5' \text{ N.}$, long. $87^\circ 12' \text{ W.}$	0	18.3	20.48	.095
13do.....	20	18.4	20.38	.092
14	4 miles northwest of Pensacola Light.....	0	16.7	18.34	.088
15do.....	10	16.4	19.66	.092

DETERMINATION OF TOTAL CARBON DIOXIDE.

The total carbon dioxide was determined by boiling 250 cubic centimeters of the water, after the addition of hydrochloric acid, for 10 to 15 minutes, driving out the gas with a stream of pure air and collecting it in weighed tubes containing soda lime, the apparatus used being that generally employed in the analysis of carbonate rocks.¹ The water had been preserved and shipped, after collection, in "citrate of magnesium" bottles, with only a very small bubble of air space. After the bottle was opened a portion of the sample was

bottle with considerable air space. The result for the total CO_2 in this sample may have been affected by exposure of the sample before analysis. The other samples were collected in January, 1917, preserved in "magnesium citrate" bottles with practically no air space, and analyzed in April, 1917.

The results seem to show that the total content of carbon dioxide increases slightly with increase of depth. The average content for the samples of surface waters is 0.092 gram per liter. The average for all samples is 0.094 gram per liter. Naturally it is interesting to

¹ Hillebrand, W. F., The analysis of carbonate and silicate rocks: U. S. Geol. Survey Bull. 422, p. 180, 1910.

² Dole, R. B., and Chambers, A. A., Salinity of ocean water at Fowey Rocks, Fla.: Carnegie Inst. Washington Pub. 213, p. 284, 1918.

compare these figures with those obtained by other investigators.

Dittmar gives only four determinations on surface waters that are comparable with these, and all of them involve determinations of the "loosely combined" carbon dioxide, which were made by J. Y. Buchanan by a method that is not generally considered to yield exact results. However, they are as follows:¹

the total carbon dioxide is a little higher than in intermediate waters, for reasons that are discussed on page 11. The average for the bottom waters is 0.101; that for the intermediate waters is 0.095.

Tornøe found the average in 78 analyses of sea water to be 0.096 gram of carbon dioxide per liter, and results of the same order were obtained by Natterer.² Ruppin³ found in the

TABLE 3.—Dittmar and Buchanan's determinations of total carbon dioxide in surface waters.

Sample No.	Locality.	Temperature.	CO ₂ .
		° C.	Gram per liter.
265	South Atlantic Ocean, lat. 22° 15' S., long. 35° 37' W.	22.8	0.106
1573	South Atlantic Ocean, lat. 23° 27' S., long. 13° 51' W.	25.1	.099
1581	South Atlantic Ocean, lat. 19° 55' S., long. 13° 56' W.	24.7	.093
1687	North Atlantic Ocean, lat. 21° 23' N., long. 31° 15' W.	22.8	.092

The results of the analyses of the 14 samples of Gulf water are in fair agreement with the four results of Buchanan's analyses of four samples of water from the surface of the open ocean.

North Sea, at a depth of 5 meters, 0.091 gram of carbon dioxide per liter, and at 460 meters 0.095 gram.

Estimates by Dole of the total carbon dioxide in the Gulf water at Tortugas are given on

TABLE 4.—Dittmar and Buchanan's determinations of total carbon dioxide in deep waters.

Sample No.	Locality.	Depth.	Temperature.	CO ₂ .
		Fathoms.	° C.	Gram per liter.
21	North Atlantic Ocean, lat. 23° 10' N., long. 38° 42' W.	B 2,720	2.5	0.096
66	North Atlantic Ocean, lat. 19° 41' N., long. 65° 7' W.	B 3,878		.112
120	North Atlantic Ocean, lat. 32° 54' N., long. 63° 22' W.	B 2,360	2.4	.102
283	South Atlantic Ocean, lat. 29° 35' S., long. 28° 9' W.	1,000	2.8	.109
353	Indian Ocean, lat. 46° 46' S., long. 45° 31' W.	B 1,375	2.0	.118
378	Indian Ocean, lat. 60° 52' S., long. 80° 20' W.	B 1,260		.128
383	Indian Ocean, lat. 65° 42' S., long. 79° 49' W.	B 1,675		.149
(556)	South Pacific Ocean, lat. 14° 7' S., long. 153° 43' E.	B 2,450	2.2	.101
594	West Pacific Ocean, lat. 5° 24' S., long. 130° 37' E.	400	6.4	.094
791	North Pacific Ocean, lat. 11° 24' N., long. 143° 16' E.	B 4,475	1.8	.086
912	North Pacific Ocean, lat. 36° 23' N., long. 174° 31' E.	B 2,775	1.6	.090
1221	South Pacific Ocean, lat. 32° 36' S., long. 137° 43' W.	B 2,375	1.7	.103
1300	South Pacific Ocean, lat. 38° 7' S., long. 94° 4' W.	B 1,500	1.8	.102
678	West Pacific Ocean, lat. 5° 47' N., long. 124° 1' E.	50	25.4	.081
1270	South Pacific Ocean, lat. 39° 13' S., long. 118° 49' E.	B 2,250	1.4	.100
1313	South Pacific Ocean, lat. 38° 6' S., long. 88° 2' E.	B 1,825	1.8	.108
1356	South Pacific Ocean, lat. 32° 50' S., long. 77° 6' W.	50	12.0	.102
1388	South Pacific Ocean, lat. 42° 43' S., long. 82° 11' W.	B 1,450	2.0	.112
1405	South Pacific Ocean, lat. 48° 27' S., long. 74° 30' W.	B 345	7.8	.097
1438	South Pacific Ocean, lat. 52° 45' S., long. 73° 46' W.	B 245	7.8	.102
1494	South Atlantic Ocean, lat. 35° 39' S., long. 50° 47' W.	B 1,900	0.6	.098
1697	North Atlantic Ocean, lat. 26° 21' N., long. 33° 37' W.	B 2,965	3.1	.092
1707	North Atlantic Ocean, lat. 32° 41' N., long. 36° 6' W.	400	9.8	.091

The results obtained by combining the data of Dittmar and Buchanan for deeper waters are given in Table 4. Most of these were "bottom" waters (marked "B"), in which

page 2, but it should be noted that Dole did not directly determine the total carbon dioxide.

¹ Challenger Rept., Physics and chemistry, vol. 1, p. 215, 1884.

² Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 144, 1916.

³ Ruppin, E., Die Alkalinität des Meerwassers: Zeitschr. anorg. Chemie, vol. 66, p. 122, 1910.

Dole also obtained figures ranging from 0.055 to 0.109 in Biscayne Bay, the lowest being for water in Featherbed Bank, at 26.4° C., and he concluded from the salinities that evaporation was going on in the shallow water of the bay at the time his samples were taken. This action should also be accompanied by a loss of carbon dioxide, as actually observed. His average for the total carbon dioxide is 0.084 gram per liter.

THEORETICAL AMOUNT OF CARBON DIOXIDE IN SEA WATER.

If there are sources of carbon dioxide in the deep sea and the circulation of the water is slight, one might expect, theoretically, to find very considerable concentrations of carbon dioxide in such water. The pressure of the water would hold far larger proportions of any gas in solution than could remain dissolved at atmospheric pressure or smaller partial pressures. As very little is known about the extent to which moving creatures transfer carbon dioxide from place to place, the regulation of the concentration at depth would appear to be governed chiefly by the supply of carbon dioxide and by the rate of circulation of the water. At the surface, on the other hand, there is a tendency toward an equilibrium between the water and the atmosphere in respect to carbon dioxide, which Schlösing believed to be the governing factor in determining the carbon dioxide content of the atmosphere. This equilibrium can be studied in the laboratory and the results compared with those obtained by observations made in different parts of the ocean.

The equilibrium referred to may also involve the solution or deposition of calcium carbonate. A water in contact with calcium carbonate should theoretically dissolve more carbon dioxide from the atmosphere than one without access to calcium carbonate, but my own experiments on this point indicate that sea water exposed to a normal atmosphere gives off carbon dioxide at all temperatures above the very lowest, so that under surface conditions sea water in and between the temperate zones must be regarded as saturated with calcium carbonate. Therefore, laboratory experiments dealing with the equilibrium at ordinary temperatures yield the same results in the presence and in the absence of calcium carbonate.

In 1916 I performed two experiments with sea water to determine its total content of carbon dioxide at two definite temperatures, 1° C. and 28° C., after prolonged agitation of the water with outdoor air, an excess of calcite also being present in the water. The mean partial pressure of CO₂ was 0.000318 atmosphere, according to my determinations, and the two normalities found for CO₃ + HCO₃ were 0.00236 and 0.00196, respectively. The result for total CO₂ at 1° C. was 0.101 gram per liter, and that at 28° C. was 0.078 gram. These results agree essentially with those calculated by the formula of Fox,¹ which gives 0.100 and 0.075, respectively.

Fox's formula, expressed in the terms used in the present discussion, is

$$\text{Total CO}_2 \text{ (grams per liter)} = na + pb$$

where n = the normality of CO₃ + HCO₃, a = value given in Table 5, p = partial pressure of CO₂ in atmospheres, and b = value given in Table 6.

TABLE 5.—Values of "a" for a solution of normality 1 at different temperatures and partial pressures of CO₂.

p .	0°.	2°.	10°.	16°.	20°.	28°.
0.0002	40.42	40.08	38.70	37.69	37.00	35.64
.0003	42.09	41.79	40.58	39.67	39.07	37.86
.0004	43.11	42.83	41.71	40.87	40.31	39.19
.0005	43.77	43.51	42.47	41.69	41.17	40.13
.0006	44.37	44.15	43.24	42.56	42.11	41.21

TABLE 6.—Values of "b" for different salinities and temperatures.

[Chlorine in grams per thousand.]

Temperature (° C.).	Cl=0.	Cl=2.	Cl=10.	Cl=18.	Cl=20.
0	3.39	3.34	3.16	2.98	2.93
4	2.91	2.87	2.69	2.53	2.50
8	2.53	2.50	2.34	2.18	2.14
12	2.21	2.18	2.07	1.96	1.93
16	1.95	1.92	1.81	1.70	1.67
20	1.73	1.71	1.63	1.56	1.54
24	1.54	1.53	1.47	1.42	1.40
28	1.38	1.36	1.28	1.21	1.19

¹ Fox, C. J. J., On the coefficients of absorption of nitrogen and oxygen in distilled water and sea water and of atmospheric carbonic acid in sea water: Faraday Soc. Trans., vol. 5, p. 82, 1909.

COMPARISON OF RESULTS WITH EQUILIBRIUM CONDITIONS.

We are now in a position to compare the determinations of the total carbon dioxide in the samples of Gulf water with those representing equilibrium with the atmosphere. For this purpose I shall use 0.000318 atmosphere for the average carbon dioxide content of the atmosphere.¹ The normalities required in the calculation were determined as described in succeeding pages and are stated in Table 10. The comparison is shown in Table 7.

Other data than this comparison (see p. 5) incline me to the view that surface sea water is generally fully saturated with respect to atmospheric conditions; if so, there is some small constant error in the determinations or in one of the factors on which the comparison is based. The most interesting feature of the comparison is the fact that the deeper waters seem to be as near to an equilibrium with the atmosphere, for their temperature, as the surface waters. That being true, what is the source of their carbon dioxide? It seems diffi-

TABLE 7.—Comparison of total carbon dioxide found in the Gulf waters with that representing equilibrium with the atmosphere.

Sample No.	Locality.	Depth.	Temperature.	Total CO ₂ found.	CO ₂ for equilibrium.
		Meters.	°C.	Gram per liter.	Gram per liter.
2	Lat. 29° 38' N., long. 87° 0' W.....	0	18.9	0.093	0.094
3	do.....	50	19.4	.092	.098
5	do.....	150	13.3	.099	.099
6	do.....	210	10.2	.100	.100
7	Lat. 29° 53' N., long. 87° 7' W.....	0	20.0	.092	.095
8	do.....	25	20.1	.092	.094
9	do.....	50	19.6	.094	.098
10	do.....	100	18.2	.100	.098
11	do.....	130	15.8	.098	.099
12	Lat. 30° 5' N., long. 87° 12' W.....	0	18.3	.095	.097
13	do.....	20	18.4	.092	.097
14	4 miles northwest of Pensacola Light.....	0	16.7	.088	.091
15	do.....	10	16.4	.092	.097

The agreement between the last two columns of Table 7 is striking. In content of CO₂ the Gulf waters appear to be very nearly in equilibrium with the atmosphere—so nearly that the probable experimental error in the determinations of the normality of CO₂ + HCO₃ would account for a positive or negative difference between many of the figures in the two columns. The same might be said of an error in the carbon dioxide content of the atmosphere used in the calculations or in the other factors entering into the comparison. From the data of Table 7 I do not feel warranted in concluding that any of the waters is either saturated or unsaturated with carbon dioxide under atmospheric conditions, but all the samples are evidently very near the condition of equilibrium.

¹ The higher value, 0.000353, recently published by Kendall, is for laboratory air. See Kendall, James, The specific conductivity of pure water in equilibrium with atmospheric carbon dioxide: Am. Chem. Soc. Jour., vol. 38, p. 1490, 1916.

cult to account for this adjustment by assuming that portions of the water have come from cold regions where they were in contact with the atmosphere and have transported carbon dioxide all that distance. A portion of water in passing from the polar regions might lose and gain carbon dioxide a number of times before arriving in the Gulf of Mexico. Has the water of the Gulf of Mexico access to more immediate sources of carbon dioxide than the atmosphere? Where the facts are so suggestive it is natural to seek for some hypothesis to explain them, and the most plausible one appears to be that living forms either carry or supply the carbon dioxide necessary to maintain equilibrium.

Even Dittmar's results for carbon dioxide in the cold bottom waters of the ocean (Table 4) are approximately equal to the requirements for equilibrium with the atmosphere, although

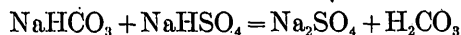
a few of the individual determinations show variations in one direction or the other. Inasmuch as the figures given by Dittmar include Buchanan's determinations and as the other factors on which the above comparisons rest are the work of many investigators, it must be admitted that the close approach of these waters to equilibrium with the atmosphere is really remarkable, as is also the fact that this relation is found in waters as deep as 3,000 fathoms. It seems as if organic agencies must contribute carbon dioxide to these deep waters, for it is difficult to see how currents in the ocean could possibly carry carbon dioxide from the surface in the colder regions to all the localities in the ocean that have been investigated and could produce by mere mixture samples approaching so closely the requirements for equilibrium. Buchanan¹ writes on this point:

Down to nearly 2,000 fathoms life is still abundant; below this depth, however, the amount rapidly decreases till, at about 2,800 fathoms, it is, for carbonic acid producing purposes, practically extinct.

The preceding discussion suggests that the conditions maintained by organic and biochemical activity in the ocean correspond almost exactly with the physico-chemical conditions of equilibrium between sea water and a normal atmosphere at the temperatures involved.

DETERMINATION OF TOTAL CARBONATE AND BICARBONATE.

The determination of total carbonate and bicarbonate is sometimes referred to as that of the "alkalinity" and sometimes as that of the total base balancing carbonate and bicarbonate. Following Dittmar, investigators generally assume that there is no free base in sea water and that acid is consumed solely in setting free carbonic acid from carbonate and bicarbonate. The determination mentioned was made by titration with 0.02 normal sodium hydrogen sulphate. Methyl orange may be used as indicator, but the determinations were in fact carried out with paranitrophenol. The results obtained in titrating depend somewhat on the end point selected. The final reaction in the neutralization is



From this reaction it is evident that the indicator used should not give an indication for H_2CO_3 but for the first excess of NaHSO_4 .

Although carbonic acid is commonly considered to exert no action upon methyl orange, it really, as has long been known, develops a marked shade of red, and on this fact depends Küster's method of titrating to the same shade as that produced in water saturated with carbonic acid.² His method gives correct results with relatively concentrated solutions of bicarbonates. In the present case, however, the concentration of bicarbonate is very small and the solution is far from being saturated with carbon dioxide at the true end point. After neutralizing with acid sulphate there will be present about 0.0047 gram of CO_2 for 50 cubic centimeters of sea water. Evidently, the proper end point is indicated by the color produced by this amount of CO_2 in the same volume of water as that finally present in an actual determination. Experiment showed that this amount of CO_2 effects a scarcely perceptible change in methyl orange. If titration is carried to the first perceptible change in tint, or better, to a standard color produced by the amount of CO_2 known to be present, the acid used will correspond, as nearly as can be determined, to the total base balancing carbonate and bicarbonate.

In the hope of obtaining better results with some other indicator than methyl orange the behavior of paranitrophenol was studied. The indicator solution contained 1 gram in 250 cubic centimeters of water. The tests made are shown in Table 8.

TABLE 8.—Comparisons of color in 50 cubic centimeter solutions in casseroles.

Solution.	Color.
1a. Distilled water.....	No color.
2a. Distilled water, 0.0047 gram CO_2 , 4 drops indicator.	Scarcely perceptible color at first; a faint color appears slowly on standing.
3a. Distilled water, 1 drop indicator.	Clearly perceptible color.
1b. Distilled water.....	No color.
2b. A solution of neutral sea salts (prepared by neutralizing the carbonates in actual sea water with the calculated quantity of acid and boiling out the carbon dioxide), 0.0047 gram CO_2 , 4 drops indicator.	Scarcely perceptible color at first; a faint color appears slowly on standing.
3b. Distilled water, 1 drop indicator.	Clearly perceptible color.

² Küster, F. W., Kritische Studien zur volumetrischen Bestimmung von karbonathaltigen Alkalilösungen und von Alkalikarbonaten; Zeitschr. anorg. Chemie, vol. 13, p. 127, 1897.

¹ Buchanan, J. Y., Roy. Soc. London Proc., vol. 22, p. 483, 1874.

The shades of color produced by the indicator were found to depend considerably on the quality of the distilled water used. Freshly boiled water, after cooling, is perceptibly more alkaline than water as it comes regularly from the still or water that has stood in the laboratory some time, on account of the difference in carbon dioxide content. Solutions made up as described under 2a and 2b were used as furnishing the standard color for the proper end point. For the greatest possible accuracy it would appear that the preparation of the standard should be deferred until after the determination of total CO_2 . It is possible that better results could be obtained in Nessler tubes than in casseroles, but the glass of certain Nessler tubes was found to be rather too soluble for the purpose. No error seemed to be introduced in the very weak solutions of CO_2 under investigation by working in casseroles, and the color showed up well in diffused daylight. However, it is doubtful if the results obtained with paratitrophenol were more accurate than those obtained with methyl orange.

As nearly as could be determined the titrations were significant to about 1 per cent of the quantities being titrated, so that the combined normality of carbonate and bicarbonate in sea water ought to be determinable within 1 per cent by this method. Practically, however, the attainment of such accuracy would probably require a number of titrations on each sample.

As the small samples of water available for the determinations recorded in this paper did not permit more than two titrations, and some samples only one, any single result is probably not nearer the true value than 2 per cent.

The solution of NaHSO_4 used for titrating the samples of sea water, to determine the total base balancing carbonate and bicarbonate, was standardized with a solution containing sodium carbonate and bicarbonate in essentially the same proportion and concentration as in sea water. In this way the conditions at the end point were similar in both the standardization and the determinations. The results obtained in the standardization are shown in Table 9.

TABLE 9.—Standardization of NaHSO_4 solution with solutions of NaHCO_3 and Na_2CO_3 .

NaHCO_3 .	Na_2CO_3 .	NaHSO_4 .	Normality of NaHSO_4 .
Gram.	Gram.	c.c.	
0.00794.....	0.00143.....	5.89	0.0206
.00794.....	.00143.....	5.87	.0207
.00794.....	.00143.....	5.82	.0209
.00794.....	.00143.....	5.81	.0209
.00794.....	.00143.....	5.92	.0206
.00794.....	.00143.....	5.86	.0207
Mean.....			.0207

The results of the titrations are shown in the fourth column of Table 10. They are expressed in terms of normality, a normal solu-

TABLE 10.—Determinations of carbonate and bicarbonate in water from the Gulf of Mexico.

Sample No.	Locality.	Temperature (°C.).	$\text{CO}_3 + \text{HCO}_3$ normality.	HCO_3 normality.	CO_3 normality.
1	Lat. 25° 35' N., long. 80° 6' W.....		0.00268	0.0021	0.0006
2	Lat. 29° 38' N., long. 87° 0' W.....	18.9	.00239	.0018	.0006
3do.....	19.4	.00250	.0017	.0008
4do.....	18.5	.00242		
5do.....	13.3	.00245	.0020	.0004
6do.....	10.2	.00245	.0021	.0004
7	Lat. 29° 53' N., long. 87° 7' W.....	20.0	.00242	.0018	.0007
8do.....	20.1	.00239	.0018	.0005
9do.....	19.6	.00250	.0018	.0007
10do.....	18.2	.00249	.0020	.0005
11do.....	15.8	.00249	.0020	.0005
12	Lat. 30° 5' N., long. 87° 12' W.....	18.3	.00245	.0019	.0006
13do.....	18.4	.00245	.0017	.0007
14	4 miles northwest of Pensacola Light.....	16.7	.00230	.0017	.0006
15do.....	16.4	.00241	.0018	.0006
	Mean, exclusive of No. 1.....		.00244	.00185	.00058

tion being one containing 1 gram equivalent of reacting substance per liter—that is, as many grams as the molecular weight reduced to a univalent basis. As is mentioned on page 3, sample 1 had stood for most of the time from July, 1915, to April, 1917, in a green glass "acid" bottle with some air space. The other samples were collected in January, 1917, preserved in bottles with practically no air space, and analyzed in April, 1917. Without doubt it would have been better if the titrations could have been made on shipboard immediately after the samples were taken. The high value of the carbonates in sample 1 may be due to attack of the glass bottle. The figures for the other 14 samples may also be slightly high for the same reason, but if the difference between sample 1 and the others represents the effect of standing in glass for 17 months, the correction for any one of the 14 results is only about 2 per cent of its value, a correction just about equal to the possible experimental error.

DISCUSSION OF RESULTS FOR THE TOTAL CARBONATE AND BICARBONATE.

Dittmar made determinations of the "alkalinity"—that is, the combined carbonate and bicarbonate—in 130 samples of water collected on the *Challenger*.¹ It was his opinion that the results were unaffected by long preservation of the water in glass bottles. The mean of all his determinations gives a normality of 0.00249. The mean for the Gulf waters, as shown above, is 0.00244. Ruppel obtained on shipboard in the North Sea 0.00238. Dole's figures for the water at Tortugas (p. 2) give a normality of 0.00234.

Now, as pointed out in the introduction, there is a need for study of the relation between the solubility of calcium and magnesium compounds and temperature. In 1915 I investigated the solubility of magnesium and calcium carbonates in pure water and determined the relation between the solubility of calcite in water in contact with the atmosphere and the temperature. (For reference see p. 1.) Further determinations seemed desirable for sea water, and such determinations have now been made on a portion of the water collected at Fowey Rocks Light, outside Biscayne Bay, Fla. The water, in contact

with an excess of calcite, was agitated by a current of outdoor air for long periods at different temperatures, and the dissolved carbonates were determined by titration with 0.02 normal NaHSO_4 , methyl orange being used as indicator. The results obtained are shown in Tables 11 and 12.

TABLE 11.—Determinations of total $\text{CO}_3 + \text{HCO}_3$ when calcite is added to sea water at 1°C . and air passed daily.

Time.	Carbonates per liter normality.
Start.....	0.00247
10 days.....	.00246
12 days.....	.00241
14 days.....	.00238
33 days.....	.00239
40 days.....	.00236

TABLE 12.—Determinations of total $\text{CO}_3 + \text{HCO}_3$ when calcite is added to sea water at room temperature and air passed daily.

Time.	Temperature ($^\circ \text{C}$.)	Carbonates per liter normality.
Start.....		0.00247
10 days.....	25	.00225
12 days.....	25	.00221
14 days.....	26	.00215
33 days.....	28	.00199
35 days.....	29	.00208
40 days.....	28	.00196

The results obtained show that under conditions otherwise similar there is a tendency for the colder sea water to retain more carbonate in solution than the warmer sea water. What was not expected, however, is the fact that the colder water did not dissolve fresh calcite but appears rather to have remained almost unchanged during the 40 days' run. In other words, sea water appears to be so far saturated with respect to calcium carbonate that in contact with the atmosphere at 1°C . it neither has nor acquires an appreciable solvent action on calcite. At higher temperatures it undergoes a slow diminution in its content of carbonates on being agitated in contact with outdoor air.

To compare with the above determinations, I had, fortunately, been able to make a few titrations at sea. At two points in the

¹ Dittmar, W., *Challenger Rept.*, Physics and chemistry, vol. 1, p. 124, 1884.

Caribbean Sea, about latitude 13° N., longitude 81° W., the normality of the carbonates was found to be 0.00236 and 0.00238 at 25° C. Water from the Pacific off Payta, Peru, at 24° C., gave 0.00226. These figures are a little higher than those found in the laboratory after a few days' agitation and suggest a condition of saturation, under atmospheric conditions, although they throw no light on the variations with temperature.

Let us now consider all the data available on surface sea water to see if the results show a definite relation between the normality of carbonate and bicarbonate and the temperature.

Of Dittmar's 130 results the 14 for surface waters are reproduced in Table 13, after recalculation to the terms used here.

It is difficult to see much if any regularity with regard to temperature in the results given in Table 13. There is a slight indication that the normality of $\text{CO}_3 + \text{HCO}_3$ decreases with rising temperature, but the results are too few and too unreliable to show the relation with certainty.

TABLE 14.—Ruppin's determinations of $\text{CO}_3 + \text{HCO}_3$ for water of the North Sea, depth 5 meters.

Date.	Temperature ($^{\circ}$ C.).	$\text{CO}_3 + \text{HCO}_3$ normality.
Feb. 18, 1907.....	4.5	0.00236
May 6, 1907.....	6.0	.00236
May 10, 1907.....	6.2	.00232
May 8, 1907.....	6.4	.00240
May 5, 1907.....	6.7	.00237
May 12, 1906.....	7.5	.00242
May 19, 1906.....	9.1	.00241
Nov. 14, 1906.....	9.3	.00238
Do.....	9.4	.00238
May 11, 1906.....	9.4	.00242
Nov. 14, 1906.....	9.5	.00238
Do.....	11.4	.00239
Nov. 13, 1906.....	12.4	.00240
Aug. 17, 1906.....	15.1	.00232
Do.....	15.3	.00236
Aug. 15, 1906.....	15.9	.00239
Do.....	16.2	.00234
Mean.....		.00238

Apparently, then, although the variation in the normality of $\text{CO}_3 + \text{HCO}_3$ with temperature can be shown in the laboratory, it is not very evident in published determinations for surface water of the open ocean.

TABLE 13.—Dittmar's determinations of $\text{CO}_3 + \text{HCO}_3$ for surface waters.

Sample No.	Locality.	Temperature ($^{\circ}$ C.).	$\text{CO}_3 + \text{HCO}_3$ normality.
384	Indian Ocean, lat. $65^{\circ} 42'$ S., long. $79^{\circ} 49'$ E.....	-1.1	0.00255
1271	South Pacific Ocean, lat. $38^{\circ} 56'$ S., long. $116^{\circ} 8'$ W.....	11.9	.00234
1471	South Atlantic Ocean, lat. $41^{\circ} 39'$ S., long. $54^{\circ} 48'$ W.....	15.3	.00235
2	North Atlantic Ocean, lat. $27^{\circ} 24'$ N., long. $16^{\circ} 55'$ W.....	18.0	.00286
9	North Atlantic Ocean, lat. $24^{\circ} 22'$ N., long. $24^{\circ} 11'$ W.....	19.4	.00260
1700	North Atlantic Ocean, lat. $30^{\circ} 20'$ N., long. $36^{\circ} 6'$ W.....	21.9	.00248
1687	North Atlantic Ocean, lat. $21^{\circ} 33'$ N., long. $31^{\circ} 15'$ W.....	22.8	.00248
265	South Atlantic Ocean, lat. $22^{\circ} 15'$ S., long. $35^{\circ} 37'$ W.....	22.8	.00260
327	Indian Ocean, lat. $36^{\circ} 48'$ S., $19^{\circ} 24'$ E.....	22.8	.00253
1581	South Atlantic Ocean, lat. $19^{\circ} 55'$ S., long. $13^{\circ} 56'$ W.....	24.7	.00250
1573	South Atlantic Ocean, lat. $23^{\circ} 27'$ S., long. $13^{\circ} 51'$ W.....	25.1	.00246
201	North Atlantic Ocean, lat. $10^{\circ} 25'$ N., long. $20^{\circ} 30'$ W.....	25.5	.00241
1127	South Pacific Ocean, lat. $3^{\circ} 48'$ S., long. $152^{\circ} 56'$ W.....	26.1	.00240
668	Near Philippine Islands, lat. $9^{\circ} 10'$ N., long. $124^{\circ} 25'$ E.....	27.2	.00234
	Mean.....		.00249

Further determinations were made in the North Sea by Ruppin on the *Poseidon*.¹ Some of his results are shown in Table 14.

In Ruppin's results, also, no relation between the carbonate content and the temperature can be discovered.

¹ Ruppin, E., Die Alkalinität des Meerwassers: Zeitschr. anorg. Chemie, vol. 66, p. 122, 1910.

Analyses of some of the warmer and nearly inclosed seas, on the other hand, show a decrease in the carbonate content. Natterer² found that in the Red Sea, for instance, the carbonates are low and the deposition of solid carbonates takes place. It is evident that chiefly in such portions of the ocean or in the

² Natterer, K., Monatsh. Chemie, vol. 20, p. 1, 1899.

polar regions will there be found marked manifestations of the temperature effect on the normality of $\text{CO}_3 + \text{HCO}_3$.

In Dittmar's determinations for cold bottom waters, however, high values of the normality are found. But as the mean of his figures for the surface waters of Table 13, 0.00249, agrees with the mean of all his determinations, it follows that the intermediate samples actually show a lower normality of carbonates than either surface or bottom samples. I obtain from his data 0.00243 for 49 samples from intermediate depths. Moreover, the mean for 25 samples at temperatures below 11° is exactly the

Table 15 contains a summary of the conclusions so far suggested concerning the total CO_2 and the normality of the bases balancing CO_3 and HCO_3 with reference to a condition of equilibrium with the atmosphere.

The conclusions concerning ocean water do not involve the greatest depths or the cold polar regions. It will be seen that by postulating a slight deficit of CO_2 and bases in the intermediate ocean waters these waters will be ready to increase their CO_2 if they come into contact with the bottom. As a matter of fact, however, they must be surrounded by extensive layers of water in which equilibrium pre-

TABLE 15.—Conclusions suggested from the investigation with reference to a condition of equilibrium with the atmosphere.

	Depth.	CO_2 .	Bases.
Ocean water of temperate regions down to 3,000 fathoms.	Surface.....	Slight excess.....	Slight excess.
	Intermediate.....	Slight deficit.....	Slight deficit.
	Bottom.....	Equilibrium or excess.....	Equilibrium or excess.
Gulf of Mexico water.....	Surface.....	Slight excess.....	Slight excess.
	Intermediate.....	Equilibrium.....	Equilibrium.

same as the mean for 24 samples at temperatures above 11° . The value 0.00243 would therefore appear to be the most representative value of the normality for the whole ocean. But the variation with temperature, except for the bottom samples, does not appear in Dittmar's results. Such a variation, however, is found in the Gulf waters. It may be that in the intermediate waters of the open ocean there is lacking a source of the bases or possibly of CO_2 . On the bottom there may be a source of carbon dioxide in the decay of organic matter and of the bases in the inorganic material, which would explain high results for bottom samples. The slight excess in the $\text{CO}_3 + \text{HCO}_3$ normality for the surface waters, however, is more difficult to account for. If it is due to additional bases, where do they come from? Possibly river water or organic life at the surface—such as algae—act as competent sources of the bases. The atmosphere or organic life could furnish the carbon dioxide, but in view of the experiments whose results are given in Tables 11 and 12 sea water does not appear to be in a condition to receive carbon dioxide from the atmosphere except at the very coldest temperatures. This leaves river water and organic life as the chief probable agencies contributing carbon dioxide to the surface waters of the ocean.

vails, as the surface and bottom concentrations are excessive. It is interesting to recall in this connection that the waters of the southern and western Pacific seem to be deficient in both carbon dioxide and bases balancing CO_3 and HCO_3 . These very general conclusions are the best that can be drawn from all the evidence. In any actual series of samples, however, variations seem to occur which suggest that there may well be local variations due to organic activity that operates faster than the mixing of the water. Chemical tests are commonly made on comparatively small samples of the water, and it may be that greater constancy would be obtained if larger samples could be employed.

CALCULATION OF CARBONATE AND BICARBONATE.

The amounts of carbonate and bicarbonate present may first be calculated on the assumption that all the CO_2 found is combined as CO_3 and HCO_3 balancing bases. Thus, for water 7 in Tables 2 and 10 let x =normality of CO_3 and y =normality of HCO_3 . Then

$$22x + 44y = 0.092$$

$$\text{and } x + y = 0.00242$$

whence $y = 0.0018$ and $x = 0.0007$.

The results thus obtained for the 15 samples are shown in the last two columns of Table 10.

These results average, as they stand, 0.0018 for the bicarbonate normality and 0.0006 for the carbonate normality. Dole's average results for Tortugas water, obtained exclusively by titration methods, are 0.0016 and 0.0008, respectively (from 0.069 and 0.017 gram CO_2 in the two forms; see p. 2). From Dittmar's figure of 0.092 gram per liter for the total CO_2 in water of the North Atlantic at 22.8°C . (Table 3) and a normality of 0.00243 for $\text{HCO}_3 + \text{CO}_3$, I obtain 0.0018 and 0.0006 for the normalities of HCO_3 and CO_3 , respectively, which are identical with the figures for the Gulf surface water, given in Table 10.

Let us next consider the magnitude of the error introduced by neglecting free carbon dioxide in the above calculations. The combination of Dole's mean values for CO_3 and HCO_3 with my mean value for the total CO_2 in surface Gulf water gives 0.006 gram per liter free CO_2 . If this figure correctly represents the free CO_2 it would leave for sample 7, for example, $0.092 - 0.006 = 0.086$ gram CO_2 for the HCO_3 and CO_3 . The calculation will then be as on page 11:

$$22x + 44y = 0.086$$

$$\text{and } x + y = 0.00242$$

whence $y = 0.0015$, the normality of HCO_3 , and $x = 0.0009$, the normality of CO_3 balancing an equivalent amount of base. These results differ markedly from those first obtained, namely, 0.0018 and 0.0007 for the normalities of HCO_3 and CO_3 respectively, and show clearly the order of the uncertainty involved in the concentrations under discussion. It should be noted, however, that the uncertainty is no longer in the amount of total CO_2 but only in the separate concentrations of the three forms in which the CO_2 is conventionally stated.

Johnston¹ states that the free carbon dioxide can be calculated if the total ion concentration of base, $[\text{B}^+]$, and the hydrogen-ion concentration, $[\text{H}^+]$, are known. The hydrogen-ion concentration can be determined by indicators or by the hydrogen electrode, but for several reasons it was not determined in the waters under scrutiny. The determination of $[\text{B}^+]$ involves some theory and uncertainty, and

therefore a few illustrative calculations must suffice. Johnston gives the following figures for the free carbon dioxide when $[\text{B}^+]$ equals 0.001, which is comparable with the normality of HCO_3 found in sea water:

$[\text{H}^+]$	Free carbon dioxide.
	<i>Gram per liter.</i>
10^{-6}	0.130
10^{-7}	.013
10^{-8}	.0013
10^{-9}	.00016

For $[\text{B}^+] = 0.01$ the corresponding values are ten times those given above.

Suppose that in sample 7 $[\text{H}^+] = 10^{-7}$ and $[\text{B}^+] = 0.002$, then free $\text{CO}_2 = 0.026$ gram per liter, leaving $0.092 - 0.026 = 0.066$ gram for $\text{HCO}_3 + \text{CO}_3$. The calculation will then be, as before,

$$22x + 44y = 0.066$$

$$\text{and } x + y = 0.00242$$

whence $y = 0.0006$, the normality of HCO_3 , and $x = 0.0018$, the normality of CO_3 . These results may probably be regarded as extreme, as $[\text{H}^+]$ for sea water may be as low as or lower than 10^{-8} . If $[\text{H}^+] = 10^{-8}$ the free CO_2 will be 0.0028 gram, making $\text{HCO}_3 = 0.0016$ and $\text{CO}_3 = 0.0008$. If $[\text{B}^+]$ is less than 0.002 the quantity of free CO_2 will be less.

In a paper on the alkalinity of sea water Sørensen and Palitzsch² record determinations on a series of 24 samples of surface water from the Atlantic in which $[\text{H}^+]$ ranges from $10^{-8.84}$ to $10^{-7.81}$.

Recent determinations by Gaarder³ yield values for $[\text{OH}^-]$ running from 0.5×10^{-7} to 25×10^{-7} ; or, for 20° , $[\text{H}^+] = 1.3 \times 10^{-7}$ to 2.6×10^{-9} , which is somewhat less acid than that obtained by Sørensen and Palitzsch.

According to the determinations of McClen-don⁴ the water at Tortugas gives $[\text{H}^+] = 10^{-8.1}$ to $10^{-8.2}$.

¹ Sørensen, S. P. L., and Palitzsch, S., Sur le mesurage de la concentration en ions hydrogène de l'eau de mer: Lab. Carlsberg. Compt. rend. trav., vol. 9, p. 8, 1910.

² Gaarder, Torblorn, Hydroxyl number of pure water and sea water: Tidskrift Kemi Farm. Terapi, vol. 13, pp. 93-105, 135-137, 152-156, 169-172, 181-187, 198-201, 1916.

³ McClen-don, J. F., Experiments with Tortugas sea water: Carnegie Inst. Washington Year Book 15, p. 207, 1916. See also Mayer, A. G., Observations upon the alkalinity of the surface water of the tropical Pacific: Nat. Acad. Sci. Proc., vol. 3, p. 518, 1917.

⁴ Johnston, John, The determination of carbonic acid, combined and free, in solution, particularly in natural waters: Am. Chem. Soc. Jour., vol. 38, p. 955, 1916.

Some further light is thrown on this problem by the comparison brought out in Table 7. It was shown that the Gulf waters appear to be very near equilibrium with the atmosphere. That being true, we may evaluate the free CO_2 by the second term of Fox's equation (p. 5), as that term is intended to represent the CO_2 present in physical solution, the average partial pressure of CO_2 for all the waters being taken as, say, 0.00032 atmosphere. The free CO_2 thus calculated ranges from 0.0005 to 0.0006 gram per liter. Although Henry's law is now known to be inapplicable with exactness to very dilute solutions of CO_2 , the figures just given are far smaller than those calculated above for $[\text{H}^+] = 10^{-7}$ and 10^{-8} . Further investigation is needed to clear up this discrepancy.

In view of the uncertain factors here noted the figures in Table 10 may be allowed to stand as preliminary estimates of the proportions of carbonate and bicarbonate. In future determinations it will be desirable to evaluate $[\text{H}^+]$ along with the other determinations and correct for the free CO_2 as far as possible. It would obviously be incorrect to calculate the CO_3 and HCO_3 separately from the total CO_2 without correcting for the free CO_2 when the total CO_2 is exceptionally high and the total $\text{HCO}_3 + \text{CO}_3$ low, but such high total CO_2 seems to be the exception in warm ocean water. If we assume a mean value of 0.003 gram per liter of free CO_2 in all the samples of Gulf water analyzed, the mean values for the HCO_3 and CO_3 normalities for the Gulf water would be 0.0017 and 0.0007 respectively. As a matter of fact, however, the free CO_2 varies from one sample to another, like the other concentrations, and a complete statement for each sample would require the determination of at least three unknown quantities—better four, in order to check the results.

An examination of the results for the carbonate and bicarbonate given in Table 10 shows that there is a slight increase of the bicarbonate concentration and a slight decrease of the carbonate concentration indicated with increase in depth, or, one may say, with decrease in temperature. The variation is not great but appears to be real; if it is real, an increase in temperature corresponds to a decrease in total CO_2 , in the total $\text{CO}_3 + \text{HCO}_3$, and in HCO_3 , and an increase in CO_3 .

These relations correspond to the known effect of temperature on the solubility of carbon dioxide in water, on the solubility of calcium carbonate in water, and on the hydrolysis of carbonates. An increase in total CO_2 therefore corresponds to an increase in HCO_3 but not in CO_3 .

For the sake of completeness, Buchanan's determinations, made during the cruise of the *Challenger*, of the amount of carbon dioxide eliminated from sea water by boiling are presented for comparison. There has long been some uncertainty as to the exact significance of the results,¹ but they must be of

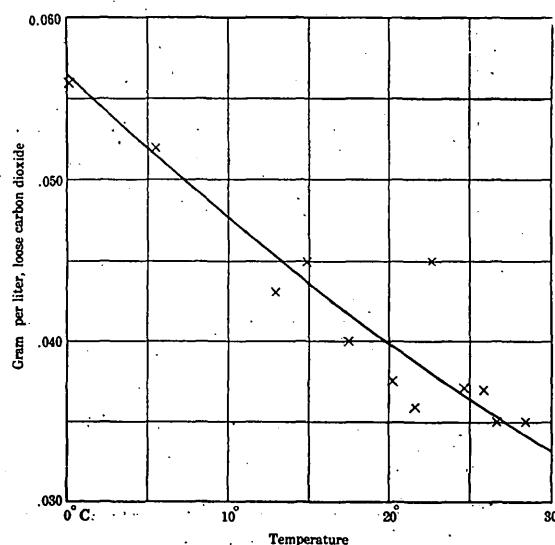


FIGURE 1.—Curve showing variation of loosely combined carbon dioxide in surface sea water with temperature. The crosses represent the 12 means given in Table 16.

value as comparative determinations, having all been made by the same method. I have studied Buchanan's results for surface waters with reference to the equilibrium that should exist between the waters and the atmosphere in respect to carbon dioxide, and I find the clearest indication of a relation between the temperature of the water and its content of loosely combined carbon dioxide. Apparently, also, there is a difference between the Atlantic and the Pacific waters, but if the results for the surface waters are arranged solely according to temperature the general relation is that the amount of loosely combined carbon dioxide is greater in the colder waters. (See Table 16 and fig. 1.)

¹ *Challenger Rept.*, Physics and chemistry, vol. 1, p. 103, 1884. Presumably Buchanan's results give the CO_2 of bicarbonate together with free CO_2 if present.

TABLE 16.—*Buchanan's determinations of loosely combined carbon dioxide in surface ocean water, arranged according to the temperature of the water.*

Sample No.	Locality	Temperature.	Loose carbon dioxide.
		°C.	Gram per liter.
389	South Indian Ocean, lat. 64° 52' S., long. 83° 12' E.	-1.7	0.049
386	South Indian Ocean, lat. 66° 29' S., long. 78° 18' E.	-.7	.056
396	South Indian Ocean, lat. 64° 1' S., long. 87° 41' E.	.4	.049
382	South Indian Ocean, lat. 64° 2' S., long. 79° 55' E.	.7	.066
387	South Indian Ocean, lat. 65° 10' S., long. 78° 42' E.	.7	.052
380	South Indian Ocean, lat. 62° 22' S., long. 80° 4' E.	1.1	.064
	Mean.....	1.	.056
415	South Indian Ocean, lat. 53° 13' S., long. 109° 23' E.	4.3	.052
354	South Indian Ocean, lat. 46° 16' S., long. 48° 27' E.	5.0	.054
364	South Indian Ocean, lat. 46° 53' S., long. 51° 52' E.	5.0	.047
360	South Indian Ocean, lat. 46° 8' S., long. 49° 40' E.	5.8	.051
417	South Indian Ocean, lat. 50° 54' S., long. 118° 3' E.	7.2	.054
	Mean.....	5.5	.052
1272	South Pacific Ocean, lat. 38° 43' S., long. 112° 31' W.	11.8	.037
1287	South Pacific Ocean, lat. 39° 19' S., long. 101° 19' W.	12.5	.042
1378	South Pacific Ocean, lat. 42° 19' S., long. 84° 47' W.	12.7	.047
1390	South Pacific Ocean, lat. 45° 31' S., long. 78° 9' W.	12.7	.049
1314	South Pacific Ocean, lat. 38° 19' S., long. 84° 25' W.	13.6	.037
1375	South Pacific Ocean, lat. 39° 41' S., long. 86° 33' W.	13.9	.046
	Mean.....	12.9	.043
1462	South Atlantic Ocean, lat. 42° 32' S., long. 56° 29' W.	14.2	.039
1374	South Pacific Ocean, lat. 38° 59' S., long. 83° 53' W.	14.2	.051
1301	South Pacific Ocean, lat. 37° 55' S., long. 93° 56' W.	14.7	.035
1366	South Pacific Ocean, lat. 36° 17' S., long. 83° 50' W.	15.5	.048
1367	South Pacific Ocean, lat. 36° 58' S., long. 83° 40' W.	15.5	.047
471	South Pacific Ocean, lat. 37° 2' S., long. 160° 48' E.	15.6	.050
	Mean.....	15.0	.045
1342	South Pacific Ocean, lat. 33° 20' S., long. 74° 24' W.	16.9	.036
1352	South Pacific Ocean, lat. 32° 50' S., long. 77° 6' W.	17.5	.038
497	South Pacific Ocean, lat. 31° 23' S., long. 177° 48' W.	17.8	.059
949	North Pacific Ocean, lat. 37° 35' N., long. 163° 46' W.	17.9	.029
	Mean.....	17.5	.040
504	South Pacific Ocean, lat. 28° 25' S., long. 177° 93' W.	19.4	.041
276	South Atlantic Ocean, lat. 27° 54' S., long. 31° 22' W.	19.4	.043
1508	South Atlantic Ocean, lat. 36° 55' S., long. 44° 50' W.	20.0	.034
1699	North Atlantic Ocean, lat. 29° 50' N., long. 35° 55' W.	20.5	.034
836	North Pacific Ocean, lat. 28° 23' N., long. 137° 45' E.	20.8	.032
267	South Atlantic Ocean, lat. 24° 43' S., long. 34° 17' W.	21.0	.042
	Mean.....	20.2	.038
136	North Atlantic Ocean, lat. 37° 52' N., long. 42° 1' W.	21.1	.053
117	North Atlantic Ocean, lat. 34° 51' N., long. 63° 59' W.	21.4	.045
910	North Pacific Ocean, lat. 35° 55' N., long. 171° 54' E.	21.7	.035
826	West Pacific Ocean, lat. 24° 47' N., long. 138° 34' E.	21.8	.021
926	North Pacific Ocean, lat. 36° 59' N., long. 178° 56' W.	21.9	.027
512	South Pacific Ocean, lat. 23° 18' S., long. 173° 26' W.	21.9	.036
	Mean.....	21.6	.036
75	North Atlantic Ocean, lat. 27° 49' N., long. 64° 59' W.	22.2	.048
1687	North Atlantic Ocean, lat. 21° 33' N., long. 31° 15' W.	22.8	.037
1684	North Atlantic Ocean, lat. 17° 49' N., long. 28° 28' W.	22.7	.038
265	South Atlantic Ocean, lat. 22° 15' S., long. 35° 37' W.	22.8	.059
119	North Atlantic Ocean, lat. 32° 54' N., long. 63° 22' W.	23.3	.042
	Mean.....	22.8	.045

TABLE 16.—*Buchanan's determinations of loosely combined carbon dioxide in surface ocean water, arranged according to the temperature of the water—Continued.*

Sample No.	Locality.	Temperature.	Loose carbon dioxide.
		°C.	Gram per liter.
990	North Pacific Ocean, lat. 30° 51' N., long. 154° 23' W.	23.9	.019
68	North Atlantic Ocean, lat. 21° 26' N., long. 65° 16' W.	24.4	.046
515	South Pacific Ocean, lat. 20° 9' S., long. 176° 47' W.	24.5	.061
1581	South Atlantic Ocean, lat. 19° 55' S., long. 13° 56' W.	24.7	.038
572	West Pacific Ocean, lat. 11° 37' S., long. 142° 59' E.	25.0	.027
1573	South Atlantic Ocean, lat. 23° 27' S., long. 13° 51' W.	25.1	.035
1590	South Atlantic Ocean, lat. 14° 59' S., long. 13° 42' W.	25.1	.035
256	South Atlantic Ocean, lat. 14° 51' S., long. 37° 1' W.	25.3	.033
	Mean.....	24.7	.037
209	North Atlantic Ocean, lat. 7° 7' N., long. 16° 11' W.	25.7	.043
817	West Pacific Ocean, lat. 21° 17' N., long. 140° 40' E.	25.8	.025
214	North Atlantic Ocean, lat. 6° 15' N., long. 16° 5' W.	25.9	.038
539	South Pacific Ocean, lat. 16° 32' S., long. 163° 12' E.	25.9	.032
228	North Atlantic Ocean, lat. 1° 47' N., long. 24° 26' W.	26.0	.043
216	North Atlantic Ocean, lat. 4° 34' N., long. 13° 52' W.	26.1	.043
	Mean.....	25.9	.037
215	North Atlantic Ocean, lat. 5° 48' N., long. 14° 20' W.	26.2	.046
581	West Pacific Ocean, lat. 7° 13' S., long. 134° 18' E.	26.4	.039
557	South Pacific Ocean, lat. 13° 50' S., long. 151° 49' E.	26.7	.036
661	West Pacific Ocean, lat. 12° 21' N., long. 122° 15' E.	26.7	.037
1097	North Pacific Ocean, lat. 7° 26' N., long. 149° 22' W.	26.8	.029
682	North Pacific Ocean, lat. 4° 33' N., long. 127° 6' E.	26.9	.025
	Mean.....	26.6	.035
602	West Pacific Ocean, lat. 1° 42' S., long. 127° 7' E.	27.9	.042
760	North Pacific Ocean, lat. 4° 21' N., long. 145° 18' E.	28.4	.030
1662	North Atlantic Ocean, lat. 7° 10' N., long. 15° 10' W.	28.6	.034
	Mean.....	28.3	.035

We are now in a position to make a statement of the constituents of the salts in Gulf water, say for the surface at a temperature of 18° to 20°C., which shall include the total CO₂ as carbonate and bicarbonate. Based on Steiger's analysis (Table 1), it is given in Table 17, which includes also a similar statement, based on Dittmar's analysis, for ocean water, say the open Atlantic at moderate depth at 18° to 20°.

TABLE 17.—*Revised analyses of salts in the Gulf of Mexico and ocean water.*

	Gulf of Mexico.	Ocean.
Cl.....	55.23	55.21
Br.....	.17	.19
SO ₄	7.54	7.68
HCO ₃31	.31
CO ₃05	.05
Na.....	30.79	30.54
K.....	1.10	1.11
Ca.....	1.22	1.20
Mg.....	3.59	3.71
	100.00	100.00

Table 18 gives the results of a calculation of the chemical equivalence of the basic and acid radicles that constitute the salts in the water based on the percentages of the constituents shown in Table 17.

TABLE 18.—*Equivalence of basic and acid salt constituents whose percentages are given in Table 17.*

Basic radicles.	Reacting values.		Acid radicles.	Reacting values.	
	Gulf.	Ocean.		Gulf.	Ocean.
Na.....	1.339	1.328	Cl.....	1.558	1.557
K.....	.028	.028	Br.....	.002	.002
Ca.....	.061	.060	SO ₄157	.160
Mg.....	.295	.305	HCO ₃005	.005
			CO ₃002	.002
Sum of basic equiv- alents....	1.723	1.721	Sum of acid equiv- alents....	1.724	1.726

SUMMARY.

The determinations of carbon dioxide in water of the Gulf of Mexico recorded in this paper show that the total carbon dioxide increases with depth, that is with decreasing temperature, and the amounts found are very near though slightly below those required for equilibrium with atmospheric carbon dioxide, as calculated by Fox's equation. Determinations of the total concentration of base held in balance with the carbonate and bicarbonate radicles were also made; this quantity apparently increases slightly with decreasing temperature. The data presented

do not permit an exact evaluation of the "free" carbon dioxide in the water, but a consideration of the uncertain factors upon which computation of the free carbon dioxide rests indicates that the amount is probably so small in the Gulf water that no appreciable error is made by expressing the total carbon dioxide found as a mixture of carbonate and bicarbonate. At any rate, the constituents thus determined, taken in the form of salts and dissolved in the appropriate amount of pure water, would reproduce the Gulf water under the conditions existing when the samples were collected.