

On the Total Carbonaceous Matter and Hydrogen Ion Concentration in Sea Water

— A study on the Metabolism in Natural Water (I) —

by

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(Received November 6, 1953)

Abstract

As to the quantitative analysis of the total carbon dioxide in water, there are many methods such as those contrived by VAN SLYKE, SUGAWARA-KOYAMA etc. In each method, it is necessary to make an apparatus to drive off and absorb quantitatively the carbon dioxide expelled from water. Since they are complicated, the determination of carbon dioxide is generally replaced by that of excess base or alkalinity. The present author made an attempt to apply Conway's micro-diffusion method to the analysis of the total carbon dioxide in sea water. It is convenient and suitable for rapid determination of carbon dioxide with sufficient accuracy. She also considered the relation between pH and the total carbon dioxide in sea water and deduced a theoretical formula. The agreement between the theoretical and the observed values was fairly good.

1. Introduction

The amount of the carbon dioxide gas contained in the air is 0.03% in volume and its total amount on the earth has been estimated at about 0.0233×10^{20} g. In the ocean the carbonaceous matter is present in the forms of CO_2 or H_2CO_3 , HCO_3^- and CO_3^{2-} among which a complicated equilibrium exists. Its total mass is about 1.30×10^{20} g, which is sixty times as much as that in the air. The mean concentration of the carbonaceous matter in the ocean is about 2.4 mg atoms C/L in the surface layer. The partial pressure of CO_2 in the ocean has always an inclination to attain equilibrium with that in the air. Since the ocean is a great reservoir of carbonaceous matter, it may be said that it plays an important role in the constancy of the carbon dioxide in the air. Though the amount of CO_2 gas in the air is considerably small, it is the only source of the carbon which goes to compose the body of all living matter on land. On the other hand, living matter in water forms itself with the carbon dioxide dissolved in it. Therefore, we can hardly discuss

the metabolism in the ocean without a study of the behaviour of carbonaceous matter in sea water taking the state of equilibrium into account. A part of the carbonaceous matter in sea water is consumed by the photosynthesis and it is reproduced by the decomposition of organic matter. It is also removed from water by the formation of shells and their deposition. In this case, the redissolution of such calcareous matter must be considered.

There are a lot of studies on carbonaceous matter in sea water. However, many difficult problems still remain to be solved. To clarify these problems, development in the analytical method of the total carbon dioxide is desired. Up to the present day, methods such as by L.W. WINKLER[1], VAN SLYKE[2] or SUGAWARA-KOYAMA[3] etc. have been generally used for the quantitative determination of the carbon dioxide in water. But in each method it is necessary to make an apparatus to drive off the carbon dioxide completely from water and absorb it quantitatively. Moreover, the procedure of these methods is somewhat complicated. Therefore, the determination of the carbon dioxide is replaced in general by that of the excess base or the alkalinity. But, needless to say, it is difficult to make an exact estimation of the total carbon dioxide in water by such easy methods.

The present author made an attempt to apply the micro-diffusion method contrived by E. J. CONWAY[4] to the analysis of the total carbon dioxide in sea water. She succeeded in this trial and obtained good results.

The merit of this method is that it renders it unnecessary to construct an apparatus to drive off the carbon dioxide gas and that we are enabled to treat a number of samples in parallel within a short time. Therefore, it is especially convenient for oceanographical purposes.

In the next place, the author derived the theoretical expression between pH and the total carbon dioxide in sea water.

2. The apparatus and the procedure

A micro-diffusion apparatus consisting of a small dish with a ground lid and a horizontal micro-burette is used. The inner diameter of the dish is 6.0 cm and the depth is 1.1 cm. It is separated into two parts by a concentric circle of 3.5 cm dia. The horizontal micro-burette is graduated into 0.002 cc.

The principle of the analysis is as follows. A small quantity of an absorbent of carbon dioxide gas such as the barium hydroxide solution is poured into the inner part of a dish and some sample water is put in the outer part and some acid is added to the sample to make free the dissolved carbonaceous matter. After keeping the dish air-tight for a while, carbon dioxide is absorbed into the absorbent by diffusion of gas molecules. Then the solution of barium hydroxide is titrated back by the standard acid solution.

The author used each 0.5 cc of barium hydroxide solution of 0.045 N as an

absorbent of the carbon dioxide. Each 2.0 cc of sample water and 0.2 cc of 1 N sulphuric acid solution were taken in the outer circular part. After standing the dish for about fifty minutes in air-tight condition, the author made a back-titration with 0.0895 N hydrochloric acid solution using a horizontal micro-burette. A mixed indicator of thymol-blue and cresol-red was used. To make sure the accuracy of the method, the analysis of the sodium carbonate solution of a known concentration from 1 mg to 10 mg atoms C/L was made. Within the range of the concentration, the mean error of the analysis was only a few percent, which is comparable to that of the method of Sugawara-Koyama etc.

3. Water samples

The author made the analysis of sea water regarding the total carbon dioxide which had been collected near the Hachijo Island (33°05'N 139°50'E) in August, 1951, and stored in the laboratory for about seven months.

pH *in situ* of these waters were from 8.3 to 8.4. Since pH of ordinary sea water is 8.2~8.3, it seems that a part of the total carbon dioxide had been consumed by photosynthesis thus showing higher pH. But, pH of the waters was decreased to 7.6~8.1 in course of time. This means that pH became lower by increasing the total carbon dioxide by the oxidation of organic matter in the water during the storage. However, when the air was passed into the water, pH of all samples became 8.2 and also it became 8.6 when boiling.

The author attempted a quantitative analysis of the carbon dioxide by the method explained above. The results of the determination will be mentioned below.

4. Analytical results

About forty samples of water were used for the determination. Results of the analysis were shown in Fig. 1. We can see here a remarkable decrease in the total carbon dioxide with increasing pH. The amount of the total carbon dioxide was about 2 mg atoms C/L which is the same as previous determinations. It is shown that the depletion of about 0.4 mg atoms C/L of the total carbon dioxide is brought about with the increase of pH from 7.5 to 8.5. On the other hand, since the absolute amount of free carbon dioxide is less than 0.05 mg atoms C/L in the pH range higher than 7.5, a part of the bicarbonate ion must change into the free carbon dioxide which escapes into the air. Thus, it is important to consider the relation between the amount of the total carbon dioxide and the pH of water. The author will give some discussions on this problem in the next chapter.

5. A consideration on the relationship between pH and the total carbon dioxide

The author intends to obtain the theoretical relation between the total carbon

dioxide and pH.

There are, in the next place, three fundamental formulae expressing the equilibrium among different carbonaceous matters dissolved in water :

$$[H_2CO_3] = CP_{CO_2},$$

$$[H^+]\gamma_1[HCO_3^-]/\gamma_0[H_2CO_3] = K_1,$$

$$[H^+]\gamma_2[CO_3^{2-}]/\gamma_1[HCO_3^-] = K_2.$$

P_{CO_2} is the partial pressure of free carbon dioxide or H_2CO_3 which changes with pH. C is the absorption coefficient of the carbon dioxide gas in sea water and it is a function of temperature and chlorinity. The value of C is estimated by BUCH *et al*[5] as 34.2 mg atoms C/L at 20°C and 19‰Cl. K_1 and K_2 are respectively the dissociation constants of free carbon dioxide and bicarbonate ion in pure water. γ_0 , γ_1 and γ_2 are respectively the activity coefficients of H_2CO_3 , HCO_3^- , CO_3^{2-} in sea water and they depend on the chlorinity. K_1' and K_2' are regarded as the apparent dissociation constants in sea water and there are the following relation between K_1 , K_2 and K_1' , K_2' .

$$K_1' = K_1\gamma_0/\gamma_1$$

$$K_2' = K_2\gamma_0/\gamma_2$$

K_1' and K_2' vary with temperature and chlorinity. By BUCH[6], pK_1' and pK_2' are respectively 5.97 and 9.07. From the above three formulae, the author obtained the following relations between pH and the concentration of the free carbon

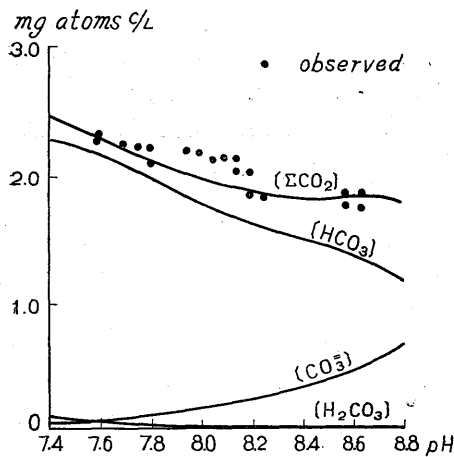


Fig. 1. Amount of ΣCO_2 , HCO_3^- and CO_3^{2-} in sea water

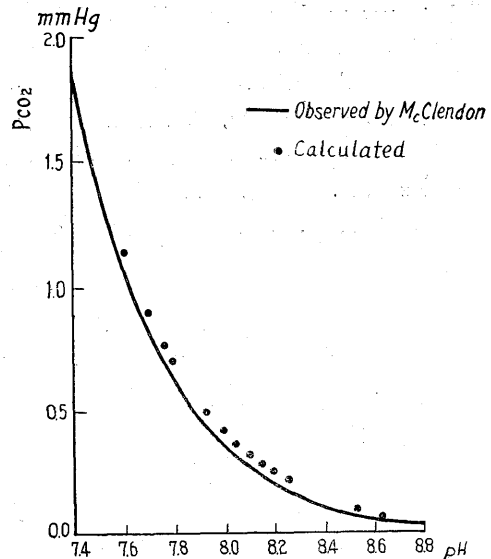


Fig. 2. Partial pressure of carbon dioxide in sea water

dioxide, the bicarbonate ion and the carbonate ion. In regard to P_{CO_2} which depends on pH, she used the values observed by McCLENDON [7].

$$\log[\text{H}_2\text{CO}_3] = 7.74 - 1.19 \text{ pH},$$

$$\log[\text{HCO}_3^-] = 1.77 - 0.19 \text{ pH},$$

$$\log[\text{CO}_3^{2-}] = -7.30 + 0.81 \text{ pH}.$$

Then, the total carbon dioxide for different pH can be calculated by using these formulae. Calculated values of $[\text{H}_2\text{CO}_3]$, $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$ and the concentration of the total carbon dioxide are shown in Fig. 1.

From these values the author calculated the partial pressure of the free carbon dioxide in sea water, the result is shown in Fig. 2 by dots. The calculated values of P_{CO_2} are in good agreement with McClendon's measurements.

Acknowledgement——In conclusion, the author expresses her hearty thanks to Dr. Y. MIYAKE for his valuable advices throughout the study.

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