THE CARBONIC ACID-CARBONATE EQUILIBRIUM AND OTHER WEAK ACIDS IN SEA WATER.

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Sea water is a salt solution of about 3.5 per cent concentration whose various constituents are maintained in almost constant proportions. A notable exception to these constant relations occurs in the case of carbon dioxide, which is found to vary greatly in concentration. These facts of variation are undoubtedly related to the conditions of organic activity, and the concentration of carbonic acid is one determining factor for photosynthesis and an indication of energy releasing metabolic processes (Henderson, 1913; McClendon, 1918).

A pure carbonate solution is determined in its characteristics by three factors of base and hydrogen ion concentration and carbon dioxide tension. According to the work of Johnston (1916), starting with the condition

\[ cP_{CO_2} = [H_2CO_3] \]

the expressions for dissociation of carbonic acid

\[ [H_2CO_3] = k_1 [H^+] [HCO_3^-] \]

and

\[ [HCO_3^-] = k_2 [H^+] [CO_3^{2-}] \]

and substituting in the equation expressing electroneutrality

\[ [B^+] + [H^+] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] \]

then

\[ P_{CO_2} = \frac{[H_2CO_3]}{[c]} = \frac{(B^+ + [H^+]) [H^+]^2 - K_a [H^+]}{k_1 [H^+] + 2 k_1 k_2} \] (1)
where $P_{\text{CO}_2}$ is the pressure of carbon dioxide in atmospheres and $c$ is the absorption coefficient in grams per liter divided by 22.4.

The terms $[B^+]$ and $[H^+]$ would appear easily determinable in pure carbonate solutions. Titration of sea water with acid to pH about 4.0 has been used for determining the excess base (McClendon, Gault, and Mulholland, 1917). This end-point has been selected by a number of investigators because it marks the limit for carbonic acid to exist in any form at ordinary tensions. The quantity of acid required appears to rest regularly around 25 ml. of 0.01 N acid per 100 ml. of sea water. At Tortugas, McClendon found the number about 24, off the south coast of England, Atkins (1922) found 25, and for Pacific Coast sea water in these experiments, I have found it about 24.

This titration shows the quantity of all of the weak acids combined with strong bases in sea water. Carbonates constitute about half of these weak acids, but direct evidence of the normal condition of the others is difficult to attain. By comparison of sea water titration figures with those for pure carbonate solutions evidence is presented here on: (1) the nature of sea water as a carbonate solution, and (2) the part occupied by other weak acids in the equilibrium.

**EXPERIMENTAL METHODS.**

It was found that the addition of hydrochloric acid in quantities less than 0.0025 M in added acid produced changes in pH which only slowly became permanent when exposed to air. Therefore, in order to prepare samples of sea water whose pH was determined and constant at the start, the acid was added and the sample aerated in a Pyrex flask for a number of hours. The fact that 12 hours of constant bubbling with air were often required before constant pH readings were reached shows how slowly equilibrium is attained in such a mixture.

For the electrometric titrations the sea water samples were treated as follows: Standard HCl was prepared by the convenient distillation method of Hulett and Bonner (1909) and checked through NaOH standardized against benzoic acid obtained from the Bureau of Standards. Appropriate quantities of this standard HCl were added to sea water, and the pH determined in a Clark electrode vessel, using a Leeds and Northrup hydrogen ion potentiometer and Eppley standard cell, with 0.1 N calomel electrode,
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and saturated KCl agar liquid junctions as suggested by Schmidt and Hoagland (1919). Temperature was controlled in an air bath with a maximum deviation from 25°C. of 0.5°. Many determinations were carried out in duplicate, using two vessels and electrodes simultaneously.

Hydrogen-carbon dioxide mixtures were made in a tonometer of about 35 liters capacity, using acidified water covered with neutral paraffin oil. After partly filling the tonometer with hydrogen, the required amount of carbon dioxide was introduced and washed in with more hydrogen. Analyses were made of the mixture, using a Hempel absorption pipette and a calibrated gas pipette with mercury. Consistent agreement of duplicate determinations was obtainable to within 5 per cent for gas mixtures of 5 parts of carbon dioxide per 10,000.

Hydrogen was generated electrolytically by the electrolysis of 10 per cent sodium hydroxide solution with nickel electrodes. It was then passed over a tube of concentrated potassium hydroxide similar to that described by Clark (1920). To remove possible residual oxygen, the hydrogen was then passed through a tube of asbestos wool containing a palladium deposit and heated to about 150° by a nichrome wire coil. The hydrogen was then passed through moist glass wool in order to resaturate it with water vapor. On account of the possibility of contamination of the gas mixture by oxygen during the time of hydrogen production, a second tube of palladized asbestos was placed between the tonometer and electrode vessel.

Carbon dioxide might interfere with the electrode measurements by reducing the hydrogen pressure. Each gas mixture used was consequently standardized against 0.05 M potassium hydrogen phthalate, and no departures were found from the potential with pure hydrogen.

DISCUSSION.

Titrations with $P_{CO_2} = 0$.

Fig. 1 shows the curves representing two sea water titrations and the typical titration or dilution curve for a strong base. The sea water curve was obtained from titration of sea water, aerated and shaken with hydrogen until a constant pH was reached, and then titrated with standard HCl. The second sea water sample was first acidified with HCl, aerated with hydrogen, and then titrated back with standard CO$_2$-free NaOH, giving the points represented by +.

In considering the results of the experiments represented in Fig. 1, it is seen that the curves generally coincide in the acid range. This would be expected, for the sea water buffers in these ranges are not effective and would have a similar influence with each method. The important fact bearing on titration to deter-
mine the "excess base" is seen in the sharp upward turn of all curves at pH 4. This is about the usually accepted end-point for the determination of base combined with carbonates, but the method is obviously open to errors unless the definite proper end-point can be accurately determined.¹

The direction taken by the curves on the alkaline side has a particular biological interest. A solution of strong base alone would have a pH of about 11.8 in 0.0024 N concentration, but sea water cannot be titrated to such an alkaline end-point with-

out precipitation of calcium and magnesium (Hildebrand, 1913) and consequent disturbance of the equilibrium. When the acidified sea water was titrated back with CO₂-free alkali, it reached a pH of 9.0 at base concentration $5 \times 10^{-4}$, while the concentration of strong base alone at such a pH would be only about $10^{-5}$ N. The area between the two curves, then, represents the buffering of sea water by buffers which are not expelled by acidification and aeration. These are said to be principally borates, phosphates, and silicates.²

¹ Johnston, 1916, p. 958.
² McClendon, Gault, and Mulholland, 1917, p. 27.
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The curve for direct titration with HCl coincides very closely with the two others in the range below the neutral point. Above, however, still another buffer effect is manifest, which must be attributed principally to residual carbonates. From a consideration of Johnston's basic formula expressing the conditions in a carbonate solution, it appears that the existence of carbonate and bicarbonate ions in a solution theoretically requires a real pressure of carbon dioxide. If this is so, the aeration with pure hydrogen would be expected to remove all of the carbon dioxide and consequently carbonate ions, and the solution should be equivalent to the sea water first acidified and titrated back with CO₂-free base. But the slope of the curve is quite different. Sørensen³ says that the pH of solutions containing CO₂ cannot be measured with the hydrogen electrode unless they are more acid than carbonic acid or so alkaline that all of the CO₂ is bound as carbonate. He determined and found a constant pH for 0.05 M Na₂C₂O₃, but stated that 0.1 M NaHCO₃ when bubbled with hydrogen went from pH 8.22 to 9.19 in about 5 hours. McClendon, Gault, and Mulholland⁴ attained a pH of 9.18 on bubbling sea water with hydrogen. They consider that the CO₂ remaining is still sufficient to convert most of the excess base to carbonate. From the curves presented here, however, it appears that the difference between the titration curve for NaOH and the titration curve for sea water, first acidified and then titrated back with NaOH, represents the non-volatile buffers; the difference between this latter curve and the curve for direct titration of aerated sea water represents the effect of unremoved CO₂.

This alkaline end-point is related to the conditions limiting photosynthesis, for Atkins (1922), has found that marine alge can render sea water more alkaline by the removal of CO₂ during active photosynthesis to a limiting pH of about 9.2 to 9.3 at 25°. Persistent aeration with hydrogen and active photosynthesis, then, can reduce the hydrogen ion concentration of sea water to about the same limits. Ulva, however, was found capable of rendering sea water as alkaline as pH 9.9. Even in 1904, when the means for following such changes were only roughly developed, Loeb had observed that Ulva considerably

³ Sørensen, 1909, p. 190.
⁴ McClendon, Gault, and Mulholland, 1917, p. 50.
SEA WATER TITRATIONS
at various $P_{CO_2} = 0.8$ and $3.74 \times 10^{-3}$ bar
experiment; the others from McConnochie
Guill, and Malmqvist (1957) for Excess Base
0.0024 curve completed.

Fig. 2.
increased the alkalinity of sea water during photosynthesis. When *Ulva* was kept in the dark and in artificial sea water containing no carbonates it still increased the alkalinity. In explanation he suggested that the alga gave out alkali, a process analogous to the secretion of carbonates by land plants. Bubbling with hydrogen and photosynthesis result in approximately the same final hydrogen ion concentration, one where, according to the conditions, some carbonate, but no bicarbonate, still remains. Hydrogen ion concentration may be the limiting factor in photosynthesis, but it is a point which might suggest profitable evidence on the nature of the carbonate substance actually absorbed by the plant.
Titrations at Other Carbon Dioxide Tensions.

Fig. 2 shows the considerable difference between the acid titration curves of sea water at various carbon dioxide tensions. This suggests the reason for the apparent paradoxical condition shown in titrations of natural waters, where occasionally a sample will have a higher excess base concentration than another which is initially more alkaline.

Figs. 3 and 4 compare the titration values calculated from Johnston's formula for typical carbonate solutions with those found for sea water of corresponding excess base and carbon dioxide tension. There is to be seen a conspicuous difference,

<table>
<thead>
<tr>
<th>$P_{CO_2}$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8 \times 10^{-3}$</td>
<td>6.90</td>
</tr>
<tr>
<td>$3.74 \times 10^{-3}$</td>
<td>7.14</td>
</tr>
</tbody>
</table>

so that it is apparent that the conditions may not be predicted from the carbonate formula. McClendon, Gault, and Mulholland\(^6\) show values for the pH of normal sea water from Tortugas at different carbon dioxide tensions. Comparing their figures and those of Henderson and Cohn\(^6\) at 20° with mine (as in Table I) shows a close agreement.

The calculated curves given are from substitutions in equation (1), with values taken as follows, all at 25°.

\[
\begin{align*}
 k_1 & = 3.5 \times 10^{-7} \quad (\text{Lewis and Randall, 1923}^7). \\
 k_2 & = 5.4 \times 10^{-11} \quad (\text{" " " 1923}^8). \\
 2k_1k_2 & = 3.78 \times 10^{-17} \quad (\text{" " " 1923}). \\
 K_w & = 1 \times 10^{-14} \quad (\text{" " " 1923}^9). 
\end{align*}
\]

\(^{6}\) McClendon, Gault, and Mulholland, 1917, p. 36.
\(^{6}\) Henderson and Cohn, 1916, p. 619.
\(^{7}\) Lewis and Randall, 1923, p. 311.
\(^{8}\) Lewis and Randall, 1923, p. 312.
\(^{9}\) Lewis and Randall, 1923, p. 486.
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\[ c = 0.03 \text{ for a } 0.5 \text{ n NaCl solution (Bohr}^{10}). \]

[B⁺] is taken as 0.9 times the excess base, less the HCl added.

Other Acids than Carbonic in Sea Water and Their Dissociation Constants.

The difference between the calculated and determined excess base represents the part combined with non-volatile acid. Henderson and Cohn’s artificial sea water was equivalent to the natural in buffer effect. It was 0.0022 M in (excess) base and 0.0015 M in boric acid, with various CO₂ pressures. According to the analyses quoted by Vernadsky\(^{11}\) sea water is 0.0011 M in silicon, 0.00018 M in boron, and 0.000032 M in phosphorus. These give a combined concentration of the three weak acid-forming elements of 0.0013 M. The condition of silicic acid and its salts can hardly be suggested with our present analytical figures and constants, and so it is impossible to determine its precise influence. But a series of comparisons may indicate more exactly the effect of these acids.

If the non-volatile acid in sea water is HA and the excess base B, then

\[
[HA] = \frac{[H^+] [A^-]}{k}
\]

As practically all of the anions of a weak acid are furnished by its salts,

\[
\frac{[A^-]}{0.9} = [BA]
\]

and

\[
[BA] = [B] - [BC]
\]

where [BC] is the calculated base in a carbonate salt solution of the same pH, and [B] is the total excess base (0.0024 M in OH⁻), less acid added.

Therefore

\[
[HA] k = [H^+] \times 0.9 [BA]
\]

and [HA] k may be calculated from the data. For certain points on Figs. 3 and 4 these values are given in Table II.

\(^{10}\) Bohr, cited from Johnston, 1916, p. 951.

\(^{11}\) Vernadsky, 1924, p. 8.
Carbonic Acid-Carbonate Equilibrium

If the other acids than carbonic in sea water are quite non-volatile, like silicic and boric, and if they are not altered by these changes, the free acid and that combined with base will have a constant sum under all conditions. Therefore, at two different acidities, 1 and 2

\[
\frac{[HA]}{k} \cdot [BA] = \frac{[HA]}{k} \cdot [BA]
\]

and

\[
k = \frac{[HA] - [HA]}{[BA] - [BA]}
\]

Taking pairs from each figure, it is seen that \( k \) does have a value constant at \( n \times 10^{-8} \), as far as the limits of experimental accuracy.

**TABLE II.**
Calculations for the Dissociation Constants of Acids Other than Carbonic in Sea Water.

<table>
<thead>
<tr>
<th>No.</th>
<th>pH</th>
<th>[BA]</th>
<th>[HA]</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.0</td>
<td>( 1.4 \times 10^{-3} )</td>
<td>( 1.26 \times 10^{-10} )</td>
<td>( 11.7 \times 10^{-8} )</td>
</tr>
<tr>
<td>2</td>
<td>6.0</td>
<td>( 0.35 \times 10^{-3} )</td>
<td>( 3.2 \times 10^{-10} )</td>
<td>( 30 \times 10^{-8} )</td>
</tr>
<tr>
<td>3</td>
<td>6.7</td>
<td>( 0.85 \times 10^{-3} )</td>
<td>( 1.53 \times 10^{-10} )</td>
<td>( 2 \times 10^{-8} )</td>
</tr>
<tr>
<td>1</td>
<td>6.7</td>
<td>( 1.14 \times 10^{-3} )</td>
<td>( 2.0 \times 10^{-10} )</td>
<td>( 8 \times 10^{-8} )</td>
</tr>
<tr>
<td>2</td>
<td>6.4</td>
<td>( 0.68 \times 10^{-3} )</td>
<td>( 2.4 \times 10^{-10} )</td>
<td>( 6 \times 10^{-8} )</td>
</tr>
<tr>
<td>1</td>
<td>7.0</td>
<td>( 0.18 \times 10^{-3} )</td>
<td>( 1.62 \times 10^{-11} )</td>
<td>( 9 \times 10^{-7} )</td>
</tr>
<tr>
<td>2</td>
<td>6.0</td>
<td>( 0.11 \times 10^{-3} )</td>
<td>( 0.99 \times 10^{-10} )</td>
<td></td>
</tr>
</tbody>
</table>

and these methods of calculation suggest. Calculations from pairs 1 to 3 are unsatisfactory because the points compared are too close and on unfavorable slopes for comparison.

Even calculating for \( P_{CO_2} \) equals 0, \( k \) has a value in general agreement with the others at pH 6 and 7. In the more alkaline range of this curve, the values of \( k \), however, would be calculated as far too small. If the real value of \( k \) is constant, as is to be expected, the low value calculated suggests a much higher concentration of the free acid HA than can really exist in the solution. The behavior of silicates, especially in the presence of calcium and magnesium, is an uncertain factor, but it is probable that there is still some residual carbonic acid, as was suggested by the titration back with alkali of sea water first acidified (Fig. 1).
This accounts for the apparent high concentration of these other still weaker acids.

**Acid Limits of CO₂ Solubility.**

The acid end-point of carbonate titrations is usually taken as at pH about 4.0. At this pH, in a pure carbonic acid solution, the CO₂ tension would approach 1 atmosphere. In any carbonate solution, the equation shows that CO₂ tension is a function of both the base and pH. A sodium acetate-acetic acid buffer solution was prepared with a pH of 4.46. This was then bubbled with pure CO₂ and left in an open beaker. 2 hours later, the addition of saturated barium hydroxide solution formed a precipitate, indicating that some CO₂ remained in solution. When another sample was boiled and tested after cooling, it formed no precipitate.

A second sodium acetate-acetic acid buffer mixture at pH 3.8 was bubbled with CO₂ and likewise left in an open beaker. The next day addition of barium hydroxide solution formed no precipitate. As Johnston (1915) states that the solubility product constant for BaCO₃ is $7 \times 10^{-9}$, and enough barium hydroxide was added to make the solution strongly alkaline, it is clear that the discernible solubility limit for carbon dioxide is between the two acidities tried. The solubility of CO₂ is, then, extremely small unless conditions permit its ionization, and it is really the solubility of H₂CO₃ which determines the capacity of a solution for this gas.

**SUMMARY**

The large amount of CO₂ in the ocean is significant to the fixation and use of energy by organisms. It occurs as H₂CO₃, HCO⁻₃, and CO⁻₃, the quantities of each depending upon the pH and excess base. Titration curves at different CO₂ tensions differ in a regular manner. They also vary considerably from titration curves for pure carbonate solutions. This difference is assignable to the fact that sea water contains other weak acids, whose amount and behavior is not yet known. Near the neutral range, however, these other acids together produce an effect corresponding to an acid with dissociation constant $k = n \times 10^{-8}$.

Because it is a mixture of weak acids and their salts, and because
some of the acids are not volatile, the pH of sea water may be
varied by the addition of acid or alkali and the change fixed at
any CO₂ tension. This CO₂ tension must be established in the
solution, however, by prolonged bubbling until the equilibrium
is reached.

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