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# Seawater Alkalinity Determination by the pH Method[1]

Charles Culberson, R. M. Pytkowicz, and J. E. Hawley

*Department of Oceanography*
*Oregon State University*
*Corvallis, Oregon 97331*

## ABSTRACT

The coefficient $f_H$, used in the seawater alkalinity method of Anderson and Robinson (1946), has been redetermined at $25°C$. We have found that $f_H = 0.741 \pm 0.005$ for salinities between $30°/oo$ and $41°/oo$. The effect of the formation of $HSO_4^-$ and HF of $f_H$ and on the hydrogen-ion concentration is discussed; the apparent dissociation constants of $HSO_4^-$ and HF are given for the salinities $26.7°/oo$ and $34.6°/oo$ at $25°C$.

*Introduction.* This work was performed to increase the accuracy of the method of Anderson and Robinson (1946) for determining the total alkalinity of seawater and to provide an interpretation of the term $f_H$, which appears in their equation for the alkalinity.

In the method of Anderson and Robinson, 25 or 30 ml of 0.01 N HCl are added to 100 ml of seawater. The alkalinity is calculated from the following equation (Anderson and Robinson 1946), using the measured pH of the acidified seawater and a tabulated value of $f_H$, which is an empirical coefficient that is related to the activity coefficient of hydrogen ions:

$$TA = \frac{1000}{V_s} V \cdot N - \frac{1000}{V_s} (V_s + V) \frac{a_H}{f_H}. \tag{1}$$

TA = total alkalinity in meq/l at $25°C$; $V_s$ = volume of seawater in ml; V = volume of HCl; N = normality of HCl; $a_H = 10^{-pH}$.

*Meaning of $f_H$.* The activity of an ion (I) can be represented in two equivalent ways: $a_I = (f_I)_F(I)_F$ or $a_I = (f_I)_T(I)_T$ (Pytkowicz et al. 1966). The subscripts F and T refer to the free species and the total (free plus complexed) species, respectively, and f is the activity coefficient. Garrels (1967) showed that free-

activity coefficients of single ions in seawater can be estimated by the mean-salt method. The ionic strength of a mixture of 30 ml of 0.01 N HCl and 100 ml of 34.6⁰/₀₀ seawater is 0.51. For this ionic strength, the mean-salt method yields $(f_H)_F = 0.9$.

The term $a_H/f_H$ in eq. (1) represents $(H^+)_T$ because it is the excess hydrogen-ion concentration over that necessary to titrate the anions of weak acids, regardless of the form in which $H^+$ occurs. Therefore, $f_H$ as determined in this work is actually $(f_H)_T$. Its value, 0.74, is smaller than $(f_H)_F = 0.9$, indicating that $H^+$ reacts with bases present in acidified seawater. The most likely bases are $SO_4^=$ (Disteche and Disteche 1967) and $F^-$ (Dyrssen 1965). If $SO_4^=$ and $F^-$ are the only bases present at pH's between 3 and 4 after the removal of carbon dioxide, then

$$(H^+)_T = a_H/(f_H)_T = (H^+)_F + (HSO_4^-)_T + (HF)_T. \qquad (2)$$

*Determination of $f_H$.* Eq. (1) indicates that, at constant volume and alkalinity, $a_H$ is a linear function of N if $f_H$ is independent of the pH. The value of $f_H$ can be calculated from the slope of a graph of $a_H$ versus N.

HCl solutions with normalities ranging from 0.0087 to 0.014 were prepared; 30 ml of acid were added to 100 ml of seawater, and the solutions were purged of carbon dioxide by bubbling for five minutes with water-saturated carbon dioxide-free air. The potentials of the seawater samples, which had been acidified with HCl of varying normality, were measured with a glass electrode, saturated calomel electrode pair (Beckman #40498 and 39170), and the potentiometric circuit described by Kester and Pytkowicz (1967).

The electrodes were standardized with NBS buffers 185-d (pH = 4.008 at 25°C) and 186-I-b, 186-II-b (pH = 7.413 at 25°C). The pH was calculated from the equation

$$pH = 4.008 - \frac{E_s - E_{4.008}}{58.91}. \qquad (3)$$

$E_s$ and $E_{4.008}$ are the potentials measured in the seawater and in the pH = 4.008 buffer. The slope of the glass-electrode response, 58.91 mv/pH, was determined from potential measurements in the two buffers.

Measurements were made at 25.00 ± 0.05°C for salinities of 29.78, 34.55, and 40.87⁰/₀₀. At each salinity, $f_H$ was calculated from a linear least-squares fit of $a_H$ versus N. Graphs of $a_H$ versus N were linear over the pH range studied (pH values between 3.0 and 4.1); therefore, $f_H$ is a constant in this pH range.

The final pH data and a comparison of our values with those of Anderson and Robinson (1946) and of Bruneau et al. (1953) are presented in Table I. The differences between the three sets of values for $f_H$ are due to several fac-

Table I. Experimental results and calculated values of $f_H$ at $25°$ C.

| HCl (mM) | pH | | |
|---|---|---|---|
| | 29.78⁰/₀₀ | 34.55⁰/₀₀* | 40.87⁰/₀₀ |
| 8.70 | 3.570 | 4.091 | |
| | 3.570 | 4.099 | |
| 8.98 | 3.500 | 3.902 | |
| | 3.498 | 3.894 | |
| 9.75 | 3.351 | 3.603 | |
| | 3.351 | 3.594 | |
| 10.32 | | | 4.052 |
| | | | 4.046 |
| 10.81 | 3.204 | 3.365 | 3.760 |
| | 3.200 | 3.364 | 3.755 |
| 11.86 | 3.091 | 3.209 | 3.451 |
| | 3.091 | 3.210 | 3.453 |
| 12.89 | 3.004 | 3.098 | 3.275 |
| | 3.004 | 3.100 | 3.278 |
| 13.96 | | | 3.151 |
| | | | 3.184 |
| | $f_H$ | | |
| Culberson, et al. . . . . . . . . . . . . | 0.746 | 0.741 | 0.737 |
| Anderson and Robinson (1946) . | 0.754 | 0.757 | 0.762 |
| Bruneau et al. (1953) . . . . . . . . | | 0.81 | |

* Filtered (0.45 $\mu$) seawater from a depth of 1500 m off the Oregon coast. The 40.87⁰/₀₀ seawater was prepared by evaporation, the 29.78⁰/₀₀ seawater by dilution with distilled water. Duplicate experiments were made at each acid normality.

tors. Anderson and Robinson did not remove carbon dioxide from their solutions and neglected the effect of the ionization of $H_2CO_3$ on the pH; also, four of the twelve samples analyzed by them were artificial seawaters that did not contain fluoride. It will be shown later that fluoride affects the value of $f_H$ in seawater. These two effects increased Anderson and Robinson's (1946) values of $f_H$ relative to ours. We cannot explain the difference between our values for $f_H$ and the value given by Bruneau et al.; part of the difference may be due to differences in the pH values assigned to the standard buffers.

*Apparent Dissociation Constants of $HSO_4^-$ and HF.* The apparent dissociation constants of $HSO_4^-$ and HF in seawater are defined by

$$K'_{HSO_4} = \frac{a_H (SO_4^=)_T}{(HSO_4^=)_T} \quad \text{and} \quad K'_{HF} = \frac{a_H (F^-)_T}{(HF)_T}; \qquad (4)$$

$K'_{HSO_4}$ and $K'_{HF}$ were determined at $25°$C for salinities of 26.7⁰/₀₀ (equivalent to 30 ml of acid plus 100 ml of 34.6⁰/₀₀ seawater) and 34.6⁰/₀₀. It has been

assumed that $(f_H)_F$ is a function of ionic strength and does not depend on the composition of the solution.

We determined $K'_{HSO4}$ by titrating a $NaCl-MgCl_2-CaCl_2-HCl$ solution, having the ionic strength of seawater, with a $Na_2SO_4$ solution of the same ionic strength, thus holding $(f_H)_F$ constant. In the absence of fluoride, eqs (2) and (4) give

$$K'_{HSO4} = \frac{(SO_4^=)_T}{(H^+)_T/a_H - 1/(f_H)_F}. \tag{5}$$

$(f_H)_F$ was determined from the ratio $a_H/(H^+)_T$ when $(SO_4^=)_T = 0$, and $K'_{HSO4}$ was calculated from the measured pH when the concentrations of sodium, magnesium, calcium, and sulfate ions were equal to those in seawater.

The method used to determine $K'_{HF}$ was similar to that used for $K'_{HSO4}$. A $NaCl-Na_2SO_4-MgCl_2-CaCl_2-HCl$ solution, having the ionic strength of seawater and the sodium, magnesium, calcium, and sulfate concentrations of seawater, was titrated with a $NaF$ solution. In the presence of $SO_4^=$ and $F^-$, eq. (2) can be rearranged to give

$$K'_{HF} = \frac{(F^-)_T + (HF)_T}{(H^+)_T/a_H - 1/(f_H)_F - (SO_4^=)_T/K'_{HSO4}} - a_H. \tag{6}$$

The ratio $(SO_4^=)_T/K'_{HSO4}$ was constant at the pH of the experiments (pH = 3.9), and the term $1/(f_H)_F + (SO_4)_T/K'_{HSO4}$ was calculated from the measured pH before fluoride was added.

The experimental data used to calculate $K'_{HSO4}$ and $K'_{HF}$ and the values of these two constants are presented in Tables II and III. Using our values for $(f_H)_F$, $K'_{HSO4}$, and $K'_{HF}$ at 26.7 °/oo salinity, we obtained $(f_H)_T = 0.724$. The measured value is $(f_H)_T = 0.741$. The difference between the measured

Table II. Calculated values of $K'_{HSO4}$ at 25 °C.

| S °/oo | $f_{H_{free}}$ | Weight Cl⁻ soln. (g) | Vol $SO_4^=$ soln. (ml) | $H_T^+$ mM | pH | $K'_{HSO4} \times 10^2$ |
|--------|--------|--------|--------|--------|--------|--------|
| 26.7 | 0.965 | 100.21* | 10.08** | 0.929 | 3.166 | 6.67 |
| 26.7 | 0.969 | 99.98 | 10.04 | 1.909 | 2.850 | 6.69 |
| 34.6 | 0.989 | 100.41 | 9.12 | 0.481 | 3.452 | 8.03 |
| 34.6 | 1.006 | 100.48 | 9.14 | 0.956 | 3.145 | 8.28 |
| 34.6 | 1.022 | 99.97 | 9.13 | 1.901 | 2.842 | 8.17 |

\* Composition of chloride solutions (mM).
26.7°/oo: NaCl, 349.7; MgCl₂, 44.4; CaCl₂, 8.6. Density 1.0143 in air at 25°C.
34.6°/oo: NaCl, 458.8; MgCl₂, 58.3; CaCl₂, 11.3. Density 1.0198 in air at 25°C.
\*\* Concentration of Na₂SO₄ solutions (mM).
26.7°/oo: Na₂SO₄, 236.1; effective ionic strength, 0.51, density 1.0252 in air.
34.6°/oo: Na₂SO₄, 334.6; effective ionic strength, 0.66, density 1.0373 in air.
The effective ionic strength of the Na₂SO₄ solutions was calculated with the association constant for NaSO₄⁻ determined by Pytkowicz and Kester (1969).

Table III. Calculated values of $K'_{HF}$ at $25°$ C.

| S‰ | Volume seawater (ml) | Volume NaF(ml) (0.1433 M) | pH | $K'_{HF} \times 10^3$ |
|---|---|---|---|---|
| 26.7 | 137.4* | 0.000 | 3.8982 | – |
| | | 0.080 | 3.9105 | 2.02 |
| | | 0.160 | 3.9226 | 2.00 |
| | | 0.240 | 3.9336 | 2.06 |
| | | 0.320 | 3.9446 | 2.08 |
| | | 0.400 | 3.9556 | 2.08 |
| | | 0.480 | 3.9658 | 2.10 |
| | | 0.560 | 3.9766 | 2.08 |
| | | | | $2.06 \pm 0.03$ |
| 34.6 | 148.1** | 0.000 | 3.8121 | – |
| | | 0.080 | 3.8209 | 2.66 |
| | | 0.160 | 3.8307 | 2.51 |
| | | 0.240 | 3.8395 | 2.52 |
| | | 0.320 | 3.8488 | 2.47 |
| | | 0.400 | 3.8578 | 2.46 |
| | | 0.480 | 3.8666 | 2.46 |
| | | | | $2.51 \pm 0.05$ |
| 34.6 | 135.9*** | 0.000 | 3.8158 | – |
| | | 0.080 | 3.8265 | 2.37 |
| | | 0.160 | 3.8363 | 2.47 |
| | | 0.240 | 3.8466 | 2.43 |
| | | 0.320 | 3.8565 | 2.43 |
| | | 0.400 | 3.8656 | 2.45 |
| | | 0.480 | 3.8755 | 2.42 |
| | | | | $2.43 \pm 0.02$ |

\* Composition of artificial seawater (mM): NaCl, 325.4; $Na_2SO_4$, 21.9; $MgCl_2$, 41.4; $CaCl_2$, 8.02; HCl, 0.1714.
\*\* Composition of artificial seawater (mM): NaCl, 423.5; $Na_2SO_4$, 28.5; $MgCl_2$, 53.8; $CaCl_2$, 10.5; HCl, 0.2094.
\*\*\* Composition of seawater same as in \*\* except HCl = 0.2080.

and calculated values of $(f_H)_T$ is probably due to errors in the estimation of $(f_H)_F$ and in the determination of $K'_{HSO_4}$ and $K'_{HF}$.

Our values for $(f_H)_F$ and $(f_H)_T$ can be used to calculate the amount of hydrogen ion that is complexed as $HSO_4^-$ and HF. At $34.6‰$ and $25°C$, we have calculated that

$$(H^+)_F = 0.74\,(H^+)_T = 0.74\,[(H^+)_F + (HSO_4^-)_T + (HF)_T].$$

Most of the difference between $(H^+)_F$ and $(H^+)_T$ is due to $HSO_4^-$, since $(HF)_T$ is only $2\%$ of $(H^+)_T$. The ratio $(H^+)_F/[(H^+)_F + (HSO_4^-)_T + (HF)_T]$ $= 0.74$ is constant for pH $> 3$ and may be applied to seawater of normal pH (pH $= 8$).

McIntyre (1965) and Dyrssen and Sillen (1967) proposed the use of $(H^+)_F$ instead of $a_H$ to describe acid-base equilibria in seawater. They suggested that $(H^+)_F$ be set equal to the amount of strong acid, $(H^+)_T$, added to carbonate-free seawater. Our data show that $(H^+)_F \neq (H^+)_T$, and, if $(H^+)_F$ is used as a variable in seawater, that $(H^+)_T$ must be corrected for the amount of $HSO_4^-$ and HF formed.

*Application of the Method to Seawater.* The proposed modified method of Anderson and Robinson (1946) consists of (i) adding 30 ml of 0.01 N HCl to 100 ml of seawater, (ii) driving off the carbon dioxide by purging for five minutes with water-saturated air, and (iii) measuring the final pH. The total alkalinity is calculated from eq. (1), using our value of $f_H = 0.741 \pm 0.005$. The method requires about seven minutes per sample. The precision $(2\sigma)$ has been estimated to be $\pm 0.008$ meq/l by combining the standard deviations from sets of replicates containing 9, 5, 3, and 3 samples.

We tested the accuracy of this method in the following way. Alkalinity-free seawater was prepared by acidifying a seawater sample (31.5°/oo) with HCl, purging the carbon dioxide with water-saturated carbon dioxide-free air, and adjusting the pH to 6.5 with NaOH. 2.514 meq/l of $Na_2CO_3$ was then added to the alkalinity-free seawater. Four replicate measurements of the alkalinity of this seawater by our modification of the Anderson and Robinson method gave 2.519, 2.519, 2.520, and 2.522 meq/l. The average recovery was 100.24°/o.

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