

A METHOD FOR CALCULATING THE *IN SITU* pH
OF SEAWATER

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ABSTRACT

A method is presented for the accurate calculation of *in situ* pH from surface measurements on sampled seawater, based on the assumption that total CO₂, total alkalinity, and total boron are invariant with respect to temperature and pressure when expressed in eq/kg units. Sample calculation on a model seawater is presented, and it is shown that the "average temperature coefficient" of the pH of seawater is a function of salinity, pH, and alkalinity of the water.

Gieskes (1969) has presented an approximate method for the estimation of the temperature effect on the pH of seawater. His method, based on a number of approximations, yields an "average temperature coefficient" of 0.0114 pH units/°C. I wish to present a method for the accurate calculation of the *in situ* pH of normal seawater, given the temperature and pressure at the depth of collection. This method is based on a few assumptions that are justifiable for open ocean seawater.

METHOD

The following assumptions are made:

1. Total alkalinity (TA) in eq/kg units is invariant with respect to temperature and pressure.
2. ΣCO_2 , namely dissolved CO₂, carbonic acid, bicarbonates, and carbonates in eq/kg units is invariant with respect to temperature and pressure.
3. Total boron (TB) in eq/kg units is invariant with respect to temperature and pressure.
4. The alkalinity of seawater (TA) is equal to the carbonate alkalinity (CA), borate alkalinity (BA), and the concentration of the hydroxyl ion (OH⁻) minus the concentration of the hydrogen ion (H⁺).

Namely:

$$\text{TA} = \text{CA} + \text{BA} + (\text{OH}^-) - (\text{H}^+). \quad (1)$$

The last assumption clearly implies that we are considering here only open ocean sea-

water in which the only protolytic species are the carbonate, borate, and water. For seawater with appreciable amounts of sulfide or ammonia, equation (1) should be modified.

In the normal range of seawater, equation (1) can be practically reduced to:

$$\text{TA} = \text{CA} + \text{BA}. \quad (2)$$

An analysis of the error involved in this approximation is discussed below.

The protolytic species of seawater are related to the pH of the seawater by the following two equations: (Skirrow 1965)

$$\text{CA} = \Sigma \text{CO}_2 \frac{a\text{HK}'_1 + 2\text{K}'_1\text{K}'_2}{a\text{H}^2 + a\text{HK}'_1 + \text{K}'_1\text{K}'_2}, \quad (3)$$

$$\text{BA} = \text{TB} \frac{\text{K}_\text{B}}{a\text{H} + \text{K}_\text{B}}, \quad (4)$$

where K'_1 , K'_2 , K_B are Lyman's apparent dissociation constants (Lyman 1956) and $a\text{H}$ is the activity of the hydrogen ion based on the National Bureau of Standards scale.

Equations (2), (3), and (4) can be combined yielding:

$$\begin{aligned} \text{TA} = \Sigma \text{CO}_2 \frac{a\text{HK}'_1 + 2\text{K}'_1\text{K}'_2}{a\text{H}^2 + a\text{HK}'_1 + \text{K}'_1\text{K}'_2} \\ + \text{TB} \frac{\text{K}_\text{B}}{a\text{H} + \text{K}_\text{B}}. \end{aligned} \quad (5)$$

Of the seven parameters in equation (5), TA, ΣCO_2 , TB, $a\text{H}$, K'_1 , K'_2 , and K_B , the first three are invariant with respect to temperature and pressure, while the three constants are known for any given temperature and pressure (Lyman 1956; Culbertson and Pytkowicz 1968).

Hence, if the invariant quantities are known, equation (5) can be solved for pH ($a\text{H}$) for any given set of K values. This equation is basically a third order equation and can be solved by standard procedures. A different approach has been used here: an iteration procedure on a digital computer. The program assumes an initial value for pH which is tested in equation (5) for equality of its two sides. If the two sides of the equation are not equal,

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TABLE 1. Some in situ pH values derived by the iteration method

Surface condition				In situ condition				In situ condition			
Cl (%)	TA (meq/kg)	T (°C)	pH	T (°C)	P (atm)	pH	Temp coefficient ($\Delta pH/^\circ C$)	T (°C)	P (atm)	pH	Temp coefficient ($\Delta pH/^\circ C$)
4	2.5	20	7.500	0	1	7.665	0.0082	10	1	7.580	0.0080
	2.5	20	8.000	0	1	8.209	0.0104	10	1	8.108	0.0108
	2.5	20	8.500	0	1	8.734	0.0117	10	1	8.624	0.0124
19	2.5	20	7.500	0	1	7.697	0.0098	10	1	7.583	0.0083
	2.5	20	8.000	0	1	8.213	0.0106	10	1	8.102	0.0102
	2.5	20	8.500	0	1	8.721	0.0110	10	1	8.607	0.0107
19	0.5	20	7.500	0	1	7.687	0.0093	10	1	7.589	0.0089
	0.5	20	8.000	0	1	8.206	0.0103	10	1	8.101	0.0101
	0.5	20	8.500	0	1	8.709	0.0104	10	1	8.603	0.0103
19*	2.5	20	7.500	0	1,000	7.240	—	10	1,000	7.181	—
	2.5	20	8.000	0	1,000	7.812	—	10	1,000	7.736	—
	2.5	20	8.500	0	1,000	8.339	—	10	1,000	8.259	—

* These calculations were carried out by applying polynomial approximations to the K values. Calculated pH values are accurate to within ± 0.005 pH unit.

the pH is incremented until the real pH is approached to within a specified error.

To make such a computation, one must know TA, TB, and ΣCO_2 . Total borate can be estimated from the chlorinity of seawater using the relationship of Culkin (1965).

$$TB \text{ (g/kg)} = Cl \text{ (\%)} \times 0.237, \quad (6)$$

or

$$TB \text{ (meq/kg)} = \frac{Cl \text{ (\%)} \times 0.237}{10.8}. \quad (7)$$

Total alkalinity and total CO_2 can be obtained by measuring them directly or by measuring any pair of the carbonate system such as pH and ΣCO_2 , pCO_2 and ΣCO_2 , and so forth (Park 1969).

Once the values of TA, ΣCO_2 , and TB are known, one can use the iteration method to calculate the pH for any given K'_1 , K'_2 , and K_B , namely for any temperature and pressure conditions.

RESULTS

Using the above computation method, I have generated tables for the "average temperature coefficient of pH of seawater"; Table 1 is a sample. These calculations assume a model seawater with certain values of chlorinity, alkalinity, and pH at

20C as indicated. Equation (5) was then solved for pH at 0 and 10C by the iteration method using Lyman's K values. For the high-pressure calculation, the apparent dissociation constants were modified according to Culberson and Pytkowicz (1968). The average temperature coefficient was calculated by dividing the pH difference by the temperature span.

It is clear from Table 1 that the average temperature coefficient is not constant. It depends on the salinity, pH, and total alkalinity of seawater, as one would expect.

For normal seawater, the variations will be about $\pm 0.003 \Delta pH/^\circ C$, which may result in an error of ± 0.06 pH unit for a 20C temperature difference. The dependence on alkalinity, however, is small and for normal seawater the pH error for a 20C span will be no larger than 0.01 pH unit, if one assumes that TA is constant at 2.5 meq/kg.

This calculation agrees well with the values reported by Buch and Nynäs (1939) as given by Harvey (1960), even though their values are based on Buch's dissociation constants (Buch 1938).

I stated above that in the normal oceanic range equation (2) can replace equation (1) with sufficient accuracy. To test this statement, I have carried out similar calcu-

lations in which the terms (H^+) and $-(OH^-)$ have been added to equation (5). These values were computed from the pH value during the iteration procedure. Namely, we have assumed as a first approximation that

$$(H^+) = (aH^+). \quad (8)$$

This refinement changed the values of the average temperature coefficient by no more than 0.0002, which might cause an error of 0.004 pH units for a 20C span. Hence, for all practical purposes equation (5) can be used.

DISCUSSION

It is evident from these results that the temperature coefficient of the pH of seawater is not a constant value. For precision calculations, one should avoid using an average temperature coefficient that is only a linear approximation to a nonlinear phenomenon. An accurate procedure would be to determine ΣCO_2 , CA, and TB on board ship and then to derive the *in situ* pH by using equation (5) and the *in situ* K values.

In his paper, Gieskes (1969) presented both theoretical and experimental values for the average temperature coefficient of the pH of seawater. Experimental data were produced to confirm his derivation that the temperature coefficient of seawater can be represented, within the oceanographic range, by $0.0114 \pm 0.001 (\Delta pH/^\circ C)$ independent of pH , salinity, and temperature. My results do not agree with this conclusion and I am unable to explain the discrepancy. My calculations, though based on Lyman's constants, agree also with the

results of Buch and Nynäs. I can only assume that this conflict is a result of disagreement between published constants and Gieskes' measured results. This apparent conflict however, clearly indicates the need for more experimental data on the temperature dependence of the pH of seawater.

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