Alkalinity and total carbonate in sea water. A plea for p-T-independent data

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ABSTRACT

It is shown, by a practical example, how Gran's graphical method can be applied to an emf titration of a sea water sample with acid. From a single emf titration one may determine both the total alkalinity, A_t, and the total carbonate concentration, C_t. These quantities, if expressed in the unit M_w = mole/kg sea water, are both independent of p and T of the sample *in situ* and during the titration, which is an advantage in comparison with the traditional determination of pH only, or of pH and A_t.

The use of normalized values A_n and C_n, referred to a normal total halogenide concentration X_n, is suggested; A_n seems more convenient than the specific alkalinity used earlier. By studies of the variation of A_t and C_t with space and time one might follow chemical changes in a sea water mass, especially dissolution of, or losses of, $CaCO_3$ and CO_2, and ion exchange with clay minerals.

The chemical composition of sea water is affected by many processes: water is removed by evaporation and freezing, and added by rainfall, melting, and outflow of fresh water from the continents. Carbon dioxide is removed or added, by exchange with the air, and by biological activity. Calcium carbonate is dissolved or precipitated, etc. There may also be exchange of ions between sea water and sediments or suspended substances, especially aluminosilicates (SILLÉN 1959, GARRELS 1965, HOLLAND 1965). Considerable additions of soluble or suspended substances come from volcanic, biological, and industrial activity, and from rainfall.

One reason for attempting to map variations in space and time of the composition of sea water is that in this way one can get a better grasp of the processes mentioned.

Symbols

A_n = $A_t X_n/X_t$, normalized alkalinity (5)

A_t = $[HC^-] + 2[C^{2-}] + [B^-] + [OH^-] - [H^+]$, total alkalinity (4)

B_t = $[B^-] + [HB]$, total borate concentration (2)

C_n = $C_t X_n/X_t$, normalized carbonate concentration (5)

C_t = $[H_2C] + [HC^-] + [C^{2-}]$, total carbonate concentration (3)

E = emf. in cell: reference electrode/solution/glass electrode

E_0 = constant, eqn (7)

E_1, E_2, E_3, arbitrary constants

F = 1 Faraday (charge of 1 mol electrons)

F_1 = function, calculated from E and v by means of (9), and used for finding v_3 by means of (15)

F_2 = function, calculated from E and v by means of (10) and used for finding v_1 by means of (20)

F_3 = function calculated from E and v by means of (11) and used for finding v_2 by means of (21)

H = excess H^+ (over H_2C and HB), (12), in M_w

H_T = excess H^+ in acid added from buret, in M

k = $RTF^{-1} \ln 10$ (8)

K_a = $[H^+][HC^-]/[H_2C]$, first acidity constant of H_2CO_3 (19)

M = concentration unit, mol/liter

M_w = concentration unit, mol/kg solution (usually sea water)

p = pressure; $p(CO_2)$ = partial pressure of CO_2

P_1 = first equivalence point (corresponding to a solution of HC^- and HB)

P_2 = second equivalence point (corresponding to a solution of H_2C and HB)

"pH" = the reading of a pH-meter = $pH_0 - \log [H^+]$ (23)

pH_0 = constant, including various unknown quantities

R = gas constant

T = absolute temperature

v_0 = volume of original sea water sample

v = volume of acid added

v_1 = volume of acid added at P_1

v_2 = volume of acid added at P_2

w_0 = weight of original sea water sample

w = weight of acid added; w_1 at P_1; w_2 at P_2

X_n = total halogenide concentration in "normal sea water" = 0.54671 $\mathbf{M}_w$ (1 a)

X_t = $[Cl^-] + [Br^-]$, total halogenide concentration (1)

ΔA_n etc. = increase in A_n etc.

ϱ = density of sea water

$[A^+]$ = concentration of ion A^+, mol/kg sea water

$\{A^+\}$ = activity of ion A^+ on a scale defined so that $\{A^+\}/[A^+] \to 1$ as the composition of the solution approaches to that of normal sea water

$[HB] = [B(OH)_3]$

$[B^-] = [B(OH)_4^-]$

$[H_2C] = [H_2CO_3] + [CO_2]$

$[HC^-] = [HCO_3^-]$

$[C^{2-}] = [CO_3^{2-}]$

Note on concentrations and activities

Out of all possible activity scales that can be used for ions in an aqueous solution, the one based on infinitely dilute solutions has perhaps been overemphasized in the past. On this scale, the activity $\{A\}$ of an ion approaches to its concentration $[A]$ (on, say, the molarity or molality scale) so that $\{A\}/[A] \to 1$ as the composition of the solution approaches that of pure water.

The "operational" definition of pH (e.g. BATES & GUGGENHEIM 1960, BATES 1964), from the emf of a cell: calomel electrode/solution/H_2, is an attempt to approach to $pH = -\log \{H^+\}$ on this scale. However, especially at ionic concentrations >0.1 M the result is uncertain because of our ignorance on the behavior of liquid junction potentials and individual ionic activity coefficients.

In recent work on ionic equilibria it has often proved convenient to *define activity in terms of a salt medium* (such as 0.5 m NaCl, or 3 M $NaClO_4$) so that for each species $\{A\}/[A] \to 1$ as the composition of the solution approaches to the pure salt medium.

The advantage is that the results of measurements are better defined. If the reference cell is based on the same ionic medium, the liquid junction potential is an easily determined function of $[H^+]$ which can be neglected except in very acidic or alkaline solutions (BIEDERMANN & SILLÉN, 1952). (If the reference electrode is based on some other medium, this only shifts the emf by a constant, which cancels out in the calculations.) The activity correction is usually negligible so that the activity is practically equal to the concentration, and one may use concentrations (= activities) directly in the equations for the emf, and in the equilibrium constants. The latter may be called "stoichiometric constants" but are really also activity constants, on the scale defined.

In this paper we shall use the latter type of activity scale, and define activities based on the salt medium, "normal sea water". In our general equations, the concentrations will be given with the unit $\mathbf{M}_w$ = mol per kg solution, so that the total concentrations of various constituents do not vary with varying p and T. (We shall occasionally give one concentration, H_T, with the unit M = mol/liter).

Main constituents

By and large, the ratios between the concentrations of the main ionic constituents in sea water keep reasonably constant so that the variations in water content may be characterized by a single quantity, traditionally either the chlorinity or the salinity.

The *chlorinity* is defined as the mass of Cl^- (in grams) that is equivalent to the amount of Ag^+ that is precipitated on addition of excess Ag^+ to 1 kg of sea water. It is determined by titration of a known amount of sea water with Ag^+ solution. The so-called salinity is usually a secondary quantity, ultimately defined on the basis of chlorinity and Knudsen's equation: salinity (‰) = 0.030 + 1.8050 × chlorinity (‰).

The average composition of sea water is

near that of the "normal water" which is distributed from the Hydrographic Laboratory at Copenhagen and has 19.374 ‰ chlorinity (35 ‰ salinity). "Normal water" has a density ϱ of 1.02769 g/cm³ at 5°C and 1.02336 g/cm³ at 25°C. The major ionic concentrations, expressed in the unit mM_w (millimole/kg sea water) are: 468.04 mM_w Na^+, 53.27 mM_w Mg^{2+}, 10.33 mM_w Ca^{2+}, 10.00 mM_w K^+, 545.88 mM_w Cl^-, 28.20 mM_w SO_4^{2-}. All these are non-protolyzed at the pH of sea water ($\approx$8.1), as are also the 0.83 mM_w Br^-, $\approx$0.10 mM_w Sr^{2+} and 0.07 mM_w F^-.

We shall denote the total halogenide concentration by X_t

$$X_t = [Cl^-] + [Br^-] \tag{1}$$

and that in "normal water" by

$$X_n = 0.54671\ M_w \tag{1a}$$

Protolytic species

In addition, sea water contains carbonate ($\approx$2.4 mM_w) and borate (0.43 mM_w) in various steps of protonation. In the following, we shall write for convenience HB for $B(OH)_3$, B^- for $B(OH)_4^-$, H_2C for the sum of H_2CO_3 and CO_2, HC^- for HCO_3^-, and C^{2-} for CO_3^{2-}. Moreover we shall write

$$B_t = [HB] + [B^-] \tag{2}$$

$$C_t = [H_2C] + [HC^-] + [C^{2-}] \tag{3}$$

These are the main protolytes in the bulk of sea water. Other protolytic species may be neglected: 0.0023 mM_w phosphate is much smaller than B_t and C_t, fluoride does not protolyze in the range of interest, and if $[Si(OH)_4]$ is $\approx$ 0.1 mM_w, then $[SiO(OH)_3^-]$ is negligible at the pH of sea water. (In anoxic sea water, one may have to consider also the concentrations of phosphate ions, $SH^- + H_2S$, and $NH_4^+ + NH_3$.)

The concentrations of the protolytic species are traditionally characterized by two measured quantities, namely the total alkalinity (A_t) and pH. A_t is determined by adding excess acid, boiling off all H_2C, and titrating back to pH $\approx$6, so that all C has been transformed to H_2C, and removed, and all B to HB. The acid consumption then corresponds to

$$A_t = [HC^-] + 2[C^{2-}] + [B^-](+ [OH^-] - [H^+]) \tag{4}$$

in the original sea water. It is usually expressed in mM, or with the unit 10^{-3} M. We shall express it in mM_w, which makes little difference in the numerical values.

Barnes (1959) suggests this method to be the best one, but other procedures have also been used. Anderson & Robinson (1946) and Bruneau, Jerlov & Koczy (1953) measured the pH values, using a glass electrode, after adding two exact amounts of acid (0.25 or $\approx$0.42 mmol HCl) to 100 ml of sea water, and others have used indicators. Hood *et al.* (1963) used a direct emf titration technique, but the details are not known to us. Tsurikova (1962) has compared various methods and recommends a direct titration of 10 ml of sea water with 0.1 M HCl, using a mixture (methylene blue + methyl red) as indicator. The method was recommended in 1944 by S. V. Bruevich and S. K. Demenchonok.

The measurement of pH used to be made by means of a pH color indicator but is nowadays often made by determining the emf between a glass electrode in the sea water sample, and a reference electrode. Even at ordinary temperatures and pressures, the exact meaning of the "pH" measured in this way is not too well theoretically defined, as indicated above. Additional technical difficulties are involved in the definition and measurement of the pH value of sea water *in situ*, e.g. at 200 atm pressure, and 4°C, or in computation of the value *in situ* from the pH measured on board a ship.

Moreover, the value of "pH" is not an ideal parameter for following small changes in the chemical composition of sea water. Even if a certain mass of water were to remain unchanged chemically, its pH (but not its alkalinity A_t on the M_w scale) changes if it moves to places with other values for p and T.

If one wants to know the concentrations of various ions, or the corresponding equilibrium pressure of CO_2, a common procedure is to calculate these quantities from the measured "pH" and A_t values, using tables and equations given by Buch (1951). If one wants to follow the chemical changes in sea water, it would have seemed preferable to measure directly, instead of pH, some variable that is independent of p and T.

Logarithmic diagram and equivalence points on titration

Fig. 1 gives the logarithms of the concentrations of various protolytic species, plotted as

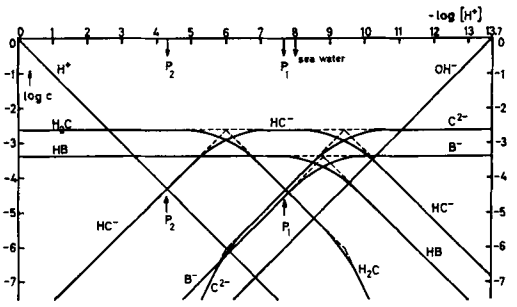

FIG. 1. Logarithmic diagram for protolytes in sea water, assuming log $B_t = -3.37$, log $C_t = -2.62$ and pK_a values: H_2C −6.0, HC^- −9.4, HB −8.8. The diagram gives log C for various species, as functions of $-\log [H^+]$. P_1 and P_2 are the two equivalence points in titration with acid.

functions of $-\log [H^+]$. We have assumed that, like in average sea water, log $B_t = -3.37$ and log $C_t = -2.62$. Moreover we have used the log K_a values: H_2C −6.0, HC^- −9.4, HB −8.8, which may be representative for the equilibrium constants in this medium at average temperatures and chlorinities. The relative positions of the curves in Fig. 1 should not change very much for reasonable changes in chlorinity, temperature and pressure. The value of log $[H^+]$ of sea water is around −8.0 ("pH" ≈ 8.1) so that the main protolytic species are HC^- and HB, with smaller amounts of C^{2-} and HB^- and still smaller of H_2C.

If H^+ is added by titration, there will be two equivalence points (points of minimum buffer capacity) as seen from Fig. 1. The first, P_1, corresponds to a solution of only HC^- and HB, for which we have the "proton condition" (compare for instance SILLÉN 1959*a*):

$$[H_2C]\,(+[H^+]) = [C^{2-}] + [B^-]\,(+[OH^-]).$$

P_1 is slightly to the left of the intersection point of the H_2C and C^{2-} lines.

The second equivalence point, P_2, corresponds to a solution of only H_2C + HB, and is at the intersection point $[H^+] = [HC^-]$, all other protolytic species being negligible.

In a recent paper (DYRSSEN 1965) one of us has shown that these two equivalence points come out very clearly by an ordinary emf titration with a glass electrode, especially if the data are plotted using GRAN's method (1952). The details of the procedure are indicated at the end of this paper.

If we denote by v_1 the volume of acid needed to reach P_1, and by v_2 that needed to reach P_2, then v_2 obviously corresponds to the total alkalinity A_t and $(v_2 - v_1)$ to the total carbonate concentration, C_t. Neither of these is dependent on p or T, if one uses mmol/kg sea water as the concentration unit.

To characterize the state of the acid-base systems in sea water at a certain point in space-time, it is then not necessary to measure "pH" *in situ*. One need only filter the water *in situ*, bring the water sample to the laboratory under such precautions that neither CO_2 nor $CaCO_3$ are lost, and determine A_t and C_t by an emf titration at whatever temperature one prefers in the laboratory (4°, 10°, 25°C).

Normalizing A and C

One can eliminate the influence of variations in water content by giving numbers that are proportional to the ratios A_t/X_t and C_t/X_t. The chlorinity is determined by Ag^+ titration of a given amount of sea water, which can also be made potentiometrically. Gran plots have been shown to be helpful here, too (DYRSSEN and JAGNER 1966).

The ratio A_t/X_t has been used repeatedly by oceanographers and is termed the "specific alkalinity". We would think, however, that for various mass balance calculations it might sometimes more convenient to use instead normalized values.

$$A_n = A_t X_n/X_t;\; C_n = C_t X_n/X_t \qquad (5)$$

In sea water of "normal" composition, A_n and C_n would then simply be equal to A_t and C_t. The ratios A_n and C_n would, of course, be the same for a certain sample of sea water, and independent of p and T, even if A_t, C_t, and X_t were to be expressed on a volume scale, such as mol/liter.

Changes in A_t and C_t on certain chemical reactions

Now let us see how the most important chemical changes would affect A_t and C_t:

Chemical reaction	ΔA_t	ΔC_t	$\Delta(A_t - C_t)$	$\Delta(A_t - 2C_t)$	
1) n_1 mol $CaCO_3$ dissolved or $(-n_1)$ mol $CaCO_3$ precipitated	$+2n_1$	$+n_1$	$+n_1$	—	
2) n_2 mol CO_2 added or $(-n_2)$ mol CO_2 lost	—	$+n_2$	$-n_2$	$-2n_2$	
3) n_3 mol H^+ from solution exp l equivalent amounts of K^+, Na^+ or $\frac{1}{2}Ca^{2+}$ from aluminosilicates	$+n_3$	—	$+n_3$	$+n_3$	
added effect	$2n_1 + n_3$	$n_1 + n_2$	$n_1 - n_2 + n_3$	$-2n_2 + n_3$	(6)

Other processes than these—the reactions of N, P and S compounds for example—may probably be neglected except in stagnant (anoxic) waters.

If one could map the variations of A_t and C_t with time and space, they could thus be correlated to the processes mentioned. Obviously, two quantities, ΔA_t and ΔC_t, from acidimetric titrations, could not give us all three values n_1, n_2 and n_3. If the third process concerned were only an exchange $2H^+ - Ca^{2+}$, then a process with $n_3 = x$ and $n_3 = 2x$ would be equivalent to one with $n_1 = x$, as far as the solution is concerned, although there would be small differences in the sediment records. If other cations than Ca^{2+} take part in process 3, accurate analyses for the variations of $[Ca^{2+}]$ might indicate whether also process 3 is important.

Additional information from titration data

As a byproduct of an emf titration as described, one could calculate the true $[H^+]$ in the sea water in question, and moreover find the equilibrium constant $[H^+][HCO_3^-]/[H_2CO_3]$ in the medium of that chlorinity and at laboratory temperature. A comparison of these values with those calculated from traditionally accepted equilibrium constants might give food for thought.

If one wants to know the concentrations of individual species (H_2C, B^-, H^+ etc), or the equilibrium $p(CO_2)$ for the original sample *in situ*, one could proceed in the opposite direction to the traditional one and calculate them from A_t, C_t, and the equilibrium constants at the p and T *in situ*. These calculations could later be repeated with the same A_t and C_t and improved values for the equilibrium constants, if desirable.

Procedure, calculation and example

Sea water should be sampled in the usual way by drawing it through a filter which removes suspended particles and organisms, if any. It should be handled throughout so that losses of CO_2 and $CaCO_3$ are avoided. If, in exceptional cases, the solution were to be slightly turbid from $CaCO_3$ when brought to the laboratory, the $CaCO_3$ should not be separated before titration.

After the sample has been brought to the temperature set for titration, a measured amount, say v_0 ml (or w_0 grams), of the sample is brought into a vessel with a glass electrode and a reference electrode. The sample is then titrated with a solution which contains strong acid, H_T M, in a salt medium similar to that of sea water. E is measured for a series of values of v, the total volume (in ml) of the titrant added. (Alternatively H_T may be given in M_w, and the added weight w of acid measured).

Since, with this arrangement, the liquid junction potentials can be neglected or assumed constant (see above), the relationship between E and $[H^+]$ is

$$E = E_0 + k \log [H^+]; \; [H^+] = 10^{(E-E_0)/k} \qquad (7)$$

where

$$k = RTF^{-1} \ln 10, \text{ e.g. } 59.16 \text{ mV at } 25°C \qquad (8)$$

From the curve $E(v)$, the approximate positions of P_1 and P_2 are obvious (see e.g. Fig. 2). We may find accurate values by means of the auxiliary functions F_1, F_2 and F_3, which are calculated from E and v as described below. The procedure is theoretically explained under "proof".

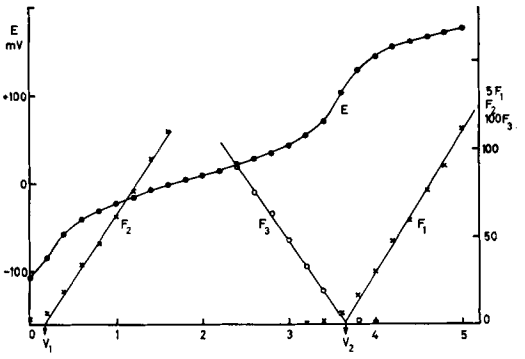

FIG. 2. Plot of data for titration in table 1. Emf. E as a function of added volume v of acid. F_1, F_2 and F_3 are auxiliary functions plotted for finding the equivalence points P_1 and P_2.

For the points after P_2 we plot

$$F_1 = (v_0 + v)\, 10^{(E - E_1)/k} \tag{9}$$

versus v where E_1 is an arbitrary constant like E_2 and E_3 below. The linear extension of $F_1(v)$ intersects the v axis at v_2. (Compare eq. 15 below.) Using this value for v_2 we plot, for values of v between v_1 and $\frac{1}{2}(v_1 + v_2)$

$$F_2 = (v_2 - v)\, 10^{(E - E_2)/k} \tag{10}$$

The linear extension of F_2 intersects the v axis at v_1 (compare eq. 20 below). Finally with this value for v_1 we may plot

$$F_3 = (v - v_1)\, 10^{(E_3 - E)/k} \tag{11}$$

The linear extension of F_3 intersects the v axis at v_2, which is a check of the first value for v_2 (compare eq. 21 below).

Proof. We may assume that the sea water and the mixture have the same density ϱ, within the experimental accuracy. A similar and still simpler treatment can be made for additions from a weight buret (when v, v_1 and v_2 are replaced by w, w_1 and w_2) or by means of a coulometer.

At any point of the titration, the H^+ excess over P_2 ($= H_2C$ and HB) is, in M_w,

$$H = [H^+] - [OH^-] - [HC^-] - 2[C^{2-}] - [B^-] \tag{12}$$

The total excess amount of H^+ is, by analytical definition, in millimols

$$\varrho(v_0 + v)\, H = -\varrho v_0 A_t + v H_T = (v - v_2)\, H_T \tag{13}$$

The last equality in (13) follows since $H = 0$ for $v = v_2$.

In the last part of the titration, after P_2, $H \approx [H^+]$ so that (13) gives

$$\varrho(v_0 + v)\, [H^+] \approx (v - v_2)\, H_T \tag{14}$$

Combining (14) with (9) and (7) we find

$$F_1 \approx (v - v_2)\, H_T \cdot 10^{(E_0 - E_1)/k} \cdot \varrho^{-1} = \text{constant} \cdot (v - v_2) \tag{15}$$

In the range between P_1 and P_2 we may, in practice, neglect all terms in (12) except $[HC^-]$ so that (13) gives

$$\varrho(v_0 + v)\, [HC^-] \approx (v_2 - v)\, H_T \tag{16}$$

Since we have found that $(v_2 - v_1)$ corresponds to C_t we have

$$\varrho v_0 C_t = \varrho(v_0 + v)\, ([H_2C] + [HC^-]) = (v_2 - v_1)\, H_T \tag{17}$$

From (16) and (17) we find

$$\varrho(v_0 + v)\, [H_2C] \approx (v - v_1)\, H_T \tag{18}$$

Now, the equilibrium law gives

$$[H^+]\, [HC^-] = K_a [H_2C] \tag{19}$$

or, inserting (7), (16) and (18) into (19)

$$10^{(E - E_0)/k} (v_2 - v) \approx K_a (v - v_1) \tag{19a}$$

Combining (19a) with (10) and (11) we find

$$F_2 \approx 10^{(E_0 - E_2)/k} \cdot K_a (v - v_1) = \text{constant} \cdot (v - v_1) \tag{20}$$

$$F_3 \approx K_a^{-1} 10^{(E_3 - E_0)/k} \cdot (v_2 - v) = \text{constant} \cdot (v_2 - v) \tag{21}$$

Equations (15), (20) and (21) give F_1, F_2 and F_3 as functions of v, and justify the procedure described. The approximations involved are quite good. As is seen F_1, F_2 and F_3 are proportional to the amounts of H^+, H_2C, and HC^- present in the solution. Of course, the concentrations in our equations from (7) on refer to the solution during titration, not to the original sea water.

The values for E_1, E_2 and E_3 are immaterial, and F_1, F_2 and F_3 may be multiplied by convenient scale factors.

TABLE 1. *Titration of 150 ml sea water at 14°C (salinity 34.80 ‰) with v ml (0.1000 M HCl, 0.4483 M NaCl). Emf = E mV between a glass electrode and a saturated calomel electrode. Plots of $F_1 - F_3$ gave (Fig. 2) $v_1 = 0.17$ ml, $v_2 = 3.65$ ml. Average $E_0 = 350.3$ mV, $-\log K_a = -6.011$, $\log [H^+]$ in sea water $= -8.016$.*

v	E	$F_1 - F_3$	eq. (24)	$[H^+]$ eq. (14)	E_0 eq. (7)	$-\log [H^+]$ eq. (7)	$-\log K_a$ eq. (25)
		F_2					
0	−106.6	2.8				8.016	
0.2	− 83.7	6.6				7.614	
0.4	− 56.9	18.4				7.144	
0.6	− 40.0	34.0				6.847	
0.8	− 30.9	46.0				6.688	
1	− 21.8	61.5				6.528	
1.2	− 14.7	75.6				6.404	6.028
1.4	− 7.2	94.2				6.272	6.010
1.6	− 1.0	110.0				6.163	6.007
1.8	+ 5.0					6.058	6.003
2	+ 9.9					5.972	6.017
2.2	+ 15.3		F_3			5.877	6.023
2.4	+ 22.6		0.895			5.749	6.000
2.6	+ 29.1		0.750			5.635	5.999
2.8	+ 35.3	F_1	0.632			5.526	
3.0	+ 43.8	0.103	0.482			5.377	
3.2	+ 55.4	0.165	0.327			5.174	
3.4	+ 70.3	0.301	0.190			4.912	
3.6	+103.8	1.17	0.052			4.325	
3.8	+129.4	3.27	0.020			3.875	
4	+144.1	5.95	0.011	0.000234	(351.1)	3.631[a]	
4.2	+155.7	9.51		0.000363	(351.8)	3.440[a]	
4.4	+161.4	11.9		0.000492	350.0	3.308[a]	
4.6	+167.8	15.4		0.000621	350.5	3.206[a]	
4.8	+171.6	18.1		0.000749	349.8	3.126[a]	
5	+176.8	22.3		0.000877	351.0	3.057[a]	

[a] Calculation from $[H^+]$, eq. (14).

If the potentiometer gives direct readings in "pH", one may plot instead

$$F_1 = (v_0 + v) \cdot 10^{-\text{"pH"}};\ F_2 = (v_2 - v) \cdot 10^{-\text{"pH"}};$$
$$F_3 = (v - v_1) \cdot 10^{-\text{"pH"}} \qquad (22)$$

This follows from the relationship

$$\text{"pH"} = \text{pH}_0 - \log [H^+] \qquad (23)$$

where pH_0 is a constant containing the liquid junction potential, the ratio between the two activity scales, and systematic errors in electrodes etc.

If $v < v_0$, one may also, for F_1, plot simply $10^{-\text{"pH"}}$ or antilog $((E - E_1)/k)$.

For the Gran plot it does not matter whether the "pH" values have any connection with those that are defined by the IUPAC-NBS scale (BATES and GUGGENHEIM 1960, BATES 1964). However, it is desirable that the potentiometer can be read to 0.01 pH unit (0.6 mV) or better.

Table 1 and Fig. 2 are taken from the same titration as described by DYRSSEN (1965). The sea water sample, 150 ml ($= v_0$) or 154 g ($= w_0 =$ 150 ϱ) was titrated with 0.1000 M ($= H_T$) HCl, containing also 0.4483 M NaCl. A more sophisticated mixture of inert ions in the acid would have done no harm, as long as the excess $[H^+]$ is known, but did not seem necessary here.

The first two columns in Table 1 give the volume v of HCl added, and the measured E. (Radiometer pHM4, saturated calomel reference electrode.) Columns 3–5 give the functions to be plotted:

$$F_1 = 10^{(E-100)/57};\ F_2 = (v_2 - v) \cdot 10^{(E+100)/57};$$
$$F_3 = (v - v_1) \cdot 10^{-E/57} \qquad (24)$$

If we compare (24) with (9), (10) and (11) we see that the values $E_1 = 100$, $E_2 = -100$ and $E_3 = 0$ mV have been used. The expression for F has been simplified since $(v_0 + v)$ is practically constant. In Fig. 2, scale factors are used. The number 57 is the value for k at 14°C, the temperature of that particular experiment. The plots give $v_2 = 3.65$ ml and $v_1 = 0.17$ ml. Since $v_0 = 150$ ml and $H_T = 0.1000$ M we find

$$A_t = 3.65 \cdot 100/150\, \varrho = 2.37\ \mathrm{mM}_w;$$
$$(A_t - C_t) = 0.17 \cdot 100/150\, \varrho = 0.11\ \mathrm{mM}_w$$

and

$$C_t = 3.48 \cdot 100/150\, \varrho = 2.26\ \mathrm{mM}_w \qquad (25)$$

After a certain number of such experiments it may come out that P_1 and P_2 each time occur practically at the same two E values, say E_{P_1} and E_{P_2}. One may then simply, in the majority of titrations, search for the values for v at E_{P_1} and E_{P_2}. Not too seldom a check with a Gran diagram should however be made since reference electrodes may change.

Calculation of $[H^+]$ *and* K_a. From the points after P_2 one can calculate directly $[H^+] = \varrho H_T(v - v_2)/(v_0 + v)$ and hence $E_0 = E - k \log [H^+]$ (7). Using this value for E_0 and (7) one may then calculate log $[H^+]$ for other points, including the first, corresponding to sea water. The value for log $K_a(H_2CO_3)$ may be found from

$$\log K_a = \log ([H^+]\,[HCO_3^-]/[H_2CO_3]) = \log [H^+] + \log ((v_2 - v)/(v - v_1)) \qquad (26)$$

If this type of titration develops into a routine procedure, it will probably prove expedient to feed the measured values (E, v) into a computer and let it calculate the "best" values for A_t, C_t, $[H^+]$ and $K_a(H_2CO_3)$. Of course, the electronic computer could also calculate A_n and C_n.

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ЩЕЛОЧИ И ПОЛНАЯ УГЛЕКИСЛАЯ СОЛЬ В МОРСКОЙ ВОДЕ. ДОВОД ДЛЯ НЕЗАВИСИМОСТИ ДАННЫХ ОТ Р-Т.

На фактическом примере показано, как графический метод Czan'a может быть применен к едс-титрованию пробы морской воды, содержащей кислоту. Из одного едс-титрования можно определить полную концентрацию как щелочи A_t, так и углекислой соли C_t. Эти величины, выраженные в единицах M_w=моль/кг, морской воды не зависят от давления и температуры при взятии ее и во время титрования, что является преимуществом по сравнению с традиционным определением только pH или pH и A_t. Предлагается использование нормализованных величин C_n и A_n, отнесенных к нормальной полной концентрации галогенов X_n. A_n оказывается более удобной чем удельная щелочность, использовавшаяся ранее. Изучая изменения A_n и C_n в пространстве и во времени можно следить за химическими изменениями в массе морской воды, особенно за растворением или потерями $CaCO_3$ и CO_3 и обменом ионов с минералами ила.