

The Determination of Dissociation Constants of Carbonic Acid in Synthetic Sea Water in the Salinity Range of 20–40 ‰ and Temperature Range of 5–30°C

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The dissociation constants of carbonic acid have been determined by potentiometric titrations in synthetic sea water covering a salinity range of 20–40 ‰ and a temperature range of 5–30°C. Corresponding values of pK_w have also been determined. The activity scale is chosen so that the activity coefficient approaches unity when the concentrations of H^+ , OH^- , $H_2CO_3 + CO_2$, HCO_3^- , and CO_3^{2-} approach zero in synthetic sea water of a certain salinity. The concentration unit is M_w , mol per kg solution.

Chemical analysis of the carbonate system in sea water involves the determination of the total concentrations of CO_3^{2-} , HCO_3^- , and dissolved CO_2 , including such species as ion-pairs with the major cations (*e.g.* $MgCO_3$ and $MgHCO_3^+$) and hydrated forms (*e.g.* H_2CO_3). No methods are available for direct determination of all these concentrations in a sample of sea water. However, with knowledge of the dissociation constants of carbonic acid, they may be computed from values of two or three of the parameters pH, alkalinity, total carbonate content or equilibrium pressure of carbon dioxide of a sample. Methods have been reported for measurement of these parameters with good accuracy and precision (Refs. 1–4). An evaluation of different methods for chemical analysis of the carbonate system in sea water is given in a review by Park.⁵ Tables of dissociation constants of carbonic acid determined for the purpose of analysis of the carbonate system in sea water have been published by Buch^{6–8} and Lyman.⁹ They used different activity scales for H^+ (both based on infinite diluted water solutions) and for H_2O , H_2CO_3 , and CO_2 . Therefore a direct comparison between the values of both sets of constants is difficult, and, for a certain pH (corrected to the proper scale) and alkalinity, each set of constants will not give the same calculated concentrations of the carbonate species. A redetermination therefore seemed to be desirable.

Dyrssen and Sillén suggested¹⁰ that the dissociation constants of carbonic acid should be determined with the activity of all the species defined in the same activity scale. The logical choice is then to define the activity scale for $X = H^+$, OH^- , $H_2CO_3 + CO_2$, HCO_3^- , and CO_3^{2-} so that the activity coefficient $f_x = \{X\}/[X]$ approaches unity as $[X]$ approaches zero in sea water of a given salinity. This means that the activity of H_2O at each salinity is unity and that every salt solution is treated as an independent solvent. However, for most oceanographic measurements of the carbonate system the salinity will be in the range of 35 ‰, and the corrections for the salinity will then be quite small. The choice of activity scale is further elucidated in Ref. 11.

This article describes the fairly elaborate technique that was used to produce a new set of dissociation constants of carbonic acid together with values of the ionic product of water. These constants are both thermodynamically well defined and applicable without corrections to practical analytical work. The technique can be used for the determination of acidity constants in media that differ considerably from dilute aqueous solutions, *e.g.* body fluids and mixed electrolyte-organic solutions.

SYMBOLS AND UNITS

The concentration unit used in the present work is $M_w = \text{mol per kg solution}$, a temperature and pressure independent concentration unit suggested by Dyrssen and Sillén.¹⁰ The concentrations of solutions added from burets are, however, given in $M = \text{mol per litre of solution}$. Emf values are given in millivolts. H_2CO_3 denotes the sum of hydrated and unhydrated carbon dioxide in solution.

LETAGROP stands for "finding the pit", a computer program used for the calculation of the titration data (see below).

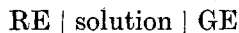
Notations used in the text are listed below.

B	total concentration of $B = H_2CO_3$ given in the input to LETAGROP.
B_0	B in the starting solutions.
B_{tot}	total concentration of B adjusted for systematic error by $B_{\text{tot}} = f_B B$.
f_B	adjustable parameter in LETAGROP defined by $B_{\text{tot}} = f_B B$.
b	free concentration of B , $b = [H_2CO_3]$.
C_{HX}	concentration of monobasic weak acid HX given in the input to LETAGROP.
E	measured emf.
E_0	a constant in $E = E_0 + (RT \ln 10/F) \log h + E_j$.
E_j	liquid junction potential.
H_{calc}	excess concentration of H^+ over H_2O and H_2CO_3 calculated by eqn. (10).
H_{tot}	excess analytical concentration of H^+ over H_2O and H_2CO_3 .
H_0	H_{tot} in the starting solutions.
H_T	excess analytical concentration of H^+ over H_2O in buret solutions (= titre of hydrochloric acid, given in M).
δH_0	adjustable parameter in LETAGROP defined in eqn. (9).
h	free concentration of H^+ , $h = [H^+]$.

K_{1c}	first dissociation constant of carbonic acid, $K_{1c} = [H^+][HCO_3^-]/[H_2CO_3]$.
K_{2c}	second dissociation constant of carbonic acid, $K_{2c} = [H^+][CO_3^{2-}]/[HCO_3^-]$.
K_{HX}	acidity constant of monobasic weak acid HX given in the input to LETAGROP.
K_w	ionic product of water, $K_w = [H^+][OH^-]$.
m_0	weight of starting solutions.
n_{CO_2}	number of mol of carbon dioxide.
P_{CO_2}	equilibrium partial pressure of carbon dioxide.
t_{HCl}	titre of hydrochloric acid in buret solutions (in M).
t_{OH}	titre of sodium hydroxide in buret solutions (in M).
T	temperature in K.
v_e	equivalence volume of buret solution (in ml).
V	volume of equilibrium solutions.
v_T	volume of buret solutions.
σ	standard deviation of parameters as defined in Ref. 24 obtained in the output from LETAGROP.
$\sigma(H)$	standard deviation of H_{tot} as defined in Ref. 24 obtained in the output from LETAGROP.

CHOICE OF EXPERIMENTAL CONDITIONS

The experiments for determination of the dissociation constants of carbonic acid were carried out as potentiometric titrations. The total carbonate concentration ($0.002 M_w$) was held approximately constant during the titration and the total hydrogen concentration (analytical excess of H^+ over H_2O) was varied by adding hydrochloric acid from a buret. Since carbon dioxide can leave the solution at high total hydrogen concentrations the titrations were performed in a closed titration vessel filled to 99–99.5 % of its volume with equilibrium solution. Acid was added from a microburet, the total volume added being 0.2 % of the total volume of the titration vessel. With this arrangement the amount of carbon dioxide leaving the solution during a titration was very small and the total carbonate concentration was nearly constant. The effect of possible escape of carbon dioxide is treated below. Ionic strengths of the synthetic sea water media used varied in the range $0.4 M_w$ to $0.8 M_w$ (corresponding to salinities from 20 to 40 ‰) and titrations were performed at temperatures from 5 to 30°C. The cell used for measuring h is conveniently written as



where GE denotes a glass electrode and RE a reference half cell; RE = ionic medium titrated saturated with $AgCl|AgCl, Ag$.

Emf of this cell can, in the log h -range studied, be written

$$E = E_0 + (RT \ln 10/F) \log h \quad (1)$$

where E_0 is a constant characteristic of the electrodes used. The validity of this equation will be discussed below. The initial value of $-\log h$ was 9 and

the final value was about 3, the excess acid being used to evaluate E_0 in eqn. (1).

EXPERIMENTAL

Chemicals and solutions. The *synthetic sea water media* were prepared (mainly following Sillén^{12,13}) with compositions similar to the main composition of sea water of corresponding salinity. Compositions of "normal sea water" and synthetic sea-water used in this work are listed in Table 1. As seen from this table K^+ of "normal" sea water has been

Table 1. Main ionic composition¹⁰ in mol per kg sea water of "normal" sea water distributed from I.A.P.S.O., Standard Sea Water Service, Charlottenlund Slot, Denmark, with chlorinity 19.374‰ corresponding to a salinity of 35.000‰ and the synthetic sea water medium of 35‰ salinity used in this work.

Cation	"Normal" sea water	Synthetic sea water	Anion	"Normal" sea water	Synthetic sea water
Na ⁺	468.04	478.0	Cl ⁻	545.88	550.0
Mg ²⁺	53.27	54.0	SO ₄ ²⁻	28.20	28.0
Ca ²⁺	10.33	10.0	Br ⁻	0.83	—
K ⁺	10.00	—	F ⁻	0.07	—
Sr ²⁺	0.10	—	HCO ₃ ⁻	2.40	—
Equivalent sum of cations	605.44	606.0	B(OH) ₃ + B(OH) ₄ ⁻	0.43	—
			Equivalent sum of anions	605.62	606.0

replaced by Na⁺. Furthermore, minor constituents like Sr²⁺, Br⁻, F⁻ and B(OH)₃ + B(OH)₄⁻ have also been excluded. For the salinities 20, 25, 30, and 40‰ the listed concentrations were reduced by 4/7, 5/7 and 6/7 or increased by 8/7. The solutions were prepared from weighed amounts of dried NaCl, Na₂SO₄, and stock solutions of magnesium and calcium chlorides. Chloride concentrations in the stock solutions were checked by a chlorinity titration technique developed by Jagner and Årén.¹⁴

Carbonate was added to the ionic medium from a stock solution of sodium carbonate and hydrogen carbonate. In the starting equilibrium solution the total carbonate content was about 2.0 mM_w and the analytical excess hydrogen concentration over H₂O about 1.3 mM_w (corresponding to 1.3 mM_w HCO₃⁻ and 0.7 mM_w CO₃²⁻). The carbonate was added very carefully to the ionic medium to avoid a sudden pH-change that may disturb the glass electrode function. The initial titration solution becomes supersaturated with regard to calcium carbonate. To avoid precipitation of calcium carbonate the addition of carbonate was carried out with vigorous stirring within 2 h before the titration started. The hydrochloric acid (Merck Titrisol[®]) was 2 M and standardized against Tl₂CO₃ using the same microburet as that used in the carbonate titrations. All reagents were Merck *p.a.* grade and the water used to prepare the solutions was doubly distilled deionized water.

Purity of the medium. To estimate the amount of weak protolytic impurities present in the ionic media used a procedure was followed similar to the titration method described by Ciavatta.¹⁵ A solution of 250 ml ionic medium containing about 0.125 mmol HCl was deaerated for 2 h with a CO₂-free nitrogen stream and transferred to the argon-filled titration vessel described under Apparatus. The solution was then titrated with 0.2 M NaOH and back-titrated with 0.2 M HCl. For each titration Gran¹⁶ functions were plotted against *v* ml titrant. The intersections of these functions with the *v*-axis (Fig. 1 in Part I of Ref. 11) corresponded to an impurity of weak protolytes of 15–25 μmol per

kg solution. A full discussion of the medium purity is given in Ref. 11. One reason for careful investigation of the impurity concentration in the salt media is that in the LETAGROP calculation (see below) a better fit of experimental data from carbonate titrations was achieved when introducing $C_{\text{HX}} = 2.0 \times 10^{-5} \text{ M}_w$. With this parameter fixed in the calculations and the parameter K_{HX} varied the program came out with $K_{\text{HX}} \approx 10^{-5} \text{ M}_w$ for most titrations treated.

APPARATUS

The titration vessel is illustrated in Fig. 1. The volume of the reaction vessel (Quickfit FV 250) is 250 ml. The titration vessel was placed in a paraffin oil thermostat bath, which held temperatures between 5 and 30°C within 0.05°C.

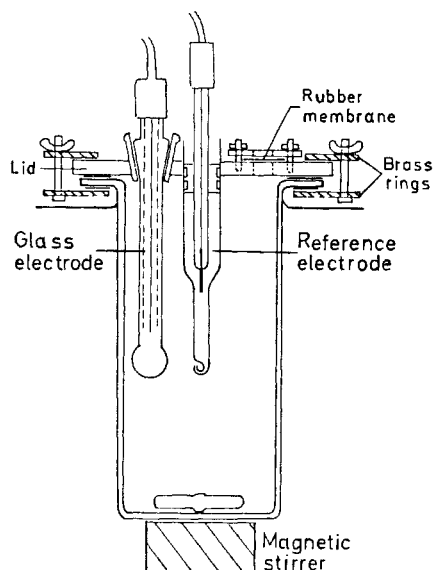


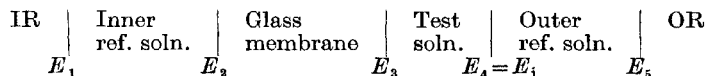
Fig. 1. Titration vessel.

The buret was an Agla syringe microburet of 0.5 ml capacity with a micrometer screw. It was mounted in a stand which permitted vertical motion. The buret tip was a platinum needle which was run through the flexible rubber membrane during titration. The tip was allowed to dip into the solution when adding reagent but was pulled out of the solution (but not the membrane) after each addition to avoid leakage of reagent from the tip during the emf measurements.

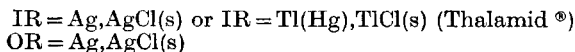
The circuit for measuring the emf of the glass-reference electrode cell used included a digital voltmeter (Solartron LM 1867) with 10 μV resolution and a voltage follower circuit connected to the input of the voltmeter. The follower circuit including a high quality operational amplifier (Philbrick SP2A) serves as a current amplifier (or impedance transformer) with a voltage amplification equal to 1.0000. This circuit allowed for rapid glass electrode measurements, which are impossible without a current amplifier because of the necessity of using the input RC-filter of this type of digital voltmeter.

EMF MEASUREMENTS

A more detailed diagram of the cell used is



IR and OR denotes the solid phases of the two reference half cells, which in the experiments were



The measured emf, E , is the algebraic sum of the potential differences $E_1 - E_5$ existing at the phase boundaries in the cell, and we assume the equation

$$E = E_0 + (RT \ln 10/F) \log h + E_j \quad (2)$$

to be valid. For precise measurements of h with the cell three conditions must be fulfilled: (a) E_1 , E_2 , and E_5 must remain constant during the experiment, (b) for E_3 the equation

$$E_3 = \text{const} + (RT \ln 10/F) \log h \quad (3)$$

must be valid, (c) the liquid junction potential E_j must be known. E_0 is the sum of E_1 , E_2 , E_5 , and the constant term of the equation for E_3 . In a well designed cell one can normally trust the constancy of E_0 . E_j can, except in very acid or alkaline solutions, be neglected if the test and reference cell solutions as here are based on the same ionic medium.¹⁷ The dependence of E_3 on $\log h$, *i.e.* the validity of eqn. (3), must be tested for each glass electrode if precise values of h are to be measured.

The *saltbridge* designed for this investigation is illustrated in Fig. 1. The upper part is an internally drilled glass tube with 13.0 mm inner diameter. Teflon flanges glued to the Ag, AgCl-electrode glass stem fit into this tube. The end of the lower part is J-shaped and forms the liquid junction. This junction may be renewed by pressing the stem with the flanges down. The Ag, AgCl-electrodes used in the reference electrodes were prepared according to Brown.¹⁸

Glass electrodes for use in the equilibrium titrations were checked for "Nernstian behaviour" according to eqn. (3) and long term stability. A test procedure with the hydrogen electrode as described by Olin¹⁹ was adopted. The hydrogen electrodes were prepared according to Bates.²⁰ The extensive work in selecting good glass electrodes is fully described in Ref. 11. For the electrodes finally chosen (Jena type U, Schott & Genossen, Mainz, W. Germany) it was found that the emf against the hydrogen electrode was constant to within ± 0.1 mV in the range $-2.1 < \log h < 8.5$ and the sodium error was about 0.3 mV ($0.005 \log h$ -units) for $\log h = -9.0$ at 25°C increasing slightly at lower temperatures.

It is important that $\log h$ is not changed more than about 0.3 units on each addition of strong acid or base in the test procedure, as for large rapid changes in $\log h$ there is a risk that the electrode function is disturbed. In spite of the capriciousness of the glass electrodes it would appear that more difficulties would be encountered in using a hydrogen electrode that removes carbon dioxide continuously. Buch,^{7,8} using the hydrogen electrode, tried to cancel this effect with a system of wash bottles, whereas Lyman⁹ used the glass electrode.

Precise potentiometric measurements with cells involving high resistance glass electrodes in solution chemistry work have not been reported in literature until recently.²¹ The time-consuming check procedures for testing of long term stability and Nernstian behaviour, often with disappointing results and rejection of several electrodes, may explain the preference of the hydrogen electrode over the glass electrode although the latter has several advantages. The increased use of computer processed measuring systems in many laboratories making these check procedures more convenient may change this attitude.

TITRATIONS FOR DETERMINATION OF K_w

The experiments for purity control of ionic media could be designed for the determination of K_w , the ionic product of water, in the medium investigated. Such experiments were performed as three successive potentiometric titrations in an initially deaerated "pure" ionic medium solution in a closed titration vessel:

- (1) Titration with 0.2 M HCl to $h \approx 2 \times 10^{-4} M_w$.
- (2) Titration with 0.2 M NaOH to $[OH^-] \approx 2 \times 10^{-4} M_w$.
- (3) Backtitration with 0.2 M HCl to $h \approx 2 \times 10^{-4} M_w$.

The equivalence points were evaluated with Gran¹⁶ diagrams; in all, five equivalence points were determined in each experiment (three with excess H^+ , two with excess OH^-). The following equations are then used for the calculation of E_0 and pK_w .

$$E = E_0 + (RT \ln 10/F) \log h = E_0 + (RT \ln 10/F) \log K_w - (RT \ln 10/F) \log [OH^-] \quad (4)$$

In the regions with excess of H^+

$$[H^+] = h = (v_T - v_e)t_{HCl}/(m_0 + v_T) \quad (5)$$

In regions with excess of OH^-

$$[OH^-] = (v_T - v_e)t_{OH}/(m_0 + v_T) \quad (6)$$

The concentration of OH^- cannot be raised to more than about $2 \times 10^{-4} M_w$ in a sea water medium because of the low solubility of $Mg(OH)_2$. Furthermore the sodium error of the glass electrode makes it unsuitable for measurements at higher OH^- -concentrations. These pK_w -determinations were performed to obtain chemically reasonable values for K_w to be used in the LETAGROP computer program as will be discussed in the next section. The choice of value of the parameter C_{HX} in LETAGROP is also based on values obtained in these experiments.

Values of K_w were determined for 35 ‰ synthetic sea water of six temperatures from 5 to 30°C and at five salinities from 20 to 40 ‰ at 25°C. Ex-

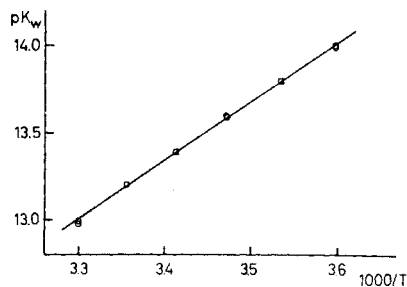
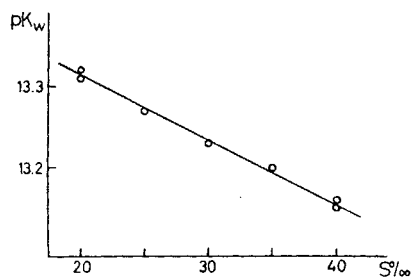


Fig. 2a. Plot of experimental values of pK_w at 25°C against salinity. Fig. 2b. Plot of experimental values of pK_w at 35 ‰ salinity against $1/T$.

perimental values of pK_w are plotted in Figs. 2a and 2b. Details of the calculation of pK_w as well as tables with experimental and interpolated values of pK_w are given in Ref. 11.

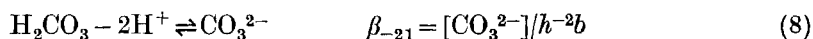
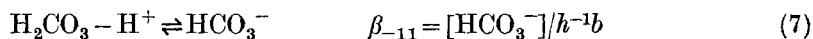
CALCULATIONS AND RESULTS

For each titration 30–40 (v_T, E)-values (“titration points”) were collected in the $\log h$ range $-9 < \log h < -3$. These primary data were processed with an IBM 360/65 computer using the generalized least squares program LETAGROP written by Sillén *et al.* in the recent Fortran-version ETITR.^{22,23} With known experimental parameters and a certain model chosen for the chemical system investigated by potentiometric titrations this program finds “best” values of the stability constants for the most reasonable species in this system. The program can also be used to adjust and refine experimental parameters like E_0 and the total concentrations of the chemical system studied.²³

In this case the species formed between carbonate ions and protons are quite well established, and a fixed model can therefore be used. This increases the possibility of refining both the stability constants and some experimental parameters.

Titration were performed so that $H_0, B_0,$ and E_0 could be refined with a LETAGROP treatment. Therefore these parameters only had to be approximately known for each experiment (in principle the treatment constitutes an analytical determination of alkalinity, total carbonate, and pH of the initial solution). Thus it was not necessary to prepare equilibrium solutions from deaerated carbon dioxide free ionic medium solutions since carbon dioxide is one of the components of the chemical system studied. Approximate values of $H_0, B_0,$ and E_0 for each experiment were determined using a Gran method designed for determination of alkalinity and total carbonate by Dyrssen and Sillén.¹⁰

The final LETAGROP calculation for each titration was carried out assuming no other species present in the solutions than $H^+, OH^-, CO_3^{2-}, HCO_3^-$, and H_2CO_3 . This may be justified as long as the free concentrations of sulphate, magnesium, and calcium ions remain constant in the solution titrated and no carbon dioxide leaves the solution. The experimental conditions are so chosen that these conditions are very closely fulfilled. H^+ and H_2CO_3 have been chosen as components which may seem strange at first. H_2CO_3 is, however, a predominating species over a large range of the titration whereas CO_3^{2-} is not predominating in any region of the titration. The equilibria and stability constants can be written with the notations $[H^+] = h$, and $[H_2CO_3] = b$



The relations between the dissociation constants of carbonic acid and these constants are

$$pK_{1c} = -\log \beta_{-11} \quad \text{and} \quad pK_{2c} = \log \beta_{-11} - \log \beta_{-21}$$

The equations used by the program in these calculations are eqn. (1) and

$$H_{\text{tot}} = v_{\text{T}}H_{\text{T}}/(m_0 + v_{\text{T}}) + m_0(H_0 + \delta H_0)/(m_0 + v_{\text{T}}) \quad (9)$$

$$H_{\text{calc}} = h - K_{\text{w}}h^{-1} - \beta_{-11}h^{-1}b - 2\beta_{-21}h^{-2}b - K_{\text{HX}}C_{\text{HX}}m_0/[(m_0 + v_{\text{T}})(K_{\text{HX}} + h)] \quad (10)$$

$$B_{\text{tot}} = f_{\text{B}}B = b + \beta_{-11}h^{-1}b + \beta_{-21}h^{-2}b \quad (11)$$

Each titration was treated separately and the error squares sum $U = \sum(H_{\text{calc}} - H_{\text{tot}})^2$ was minimized. The equilibrium constants K_{HX} , β_{-11} , and β_{-21} were adjusted in the calculations and K_{w} was held constant. The adjustable parameters are E_0 , δH_0 , f_{B} , and C_{HX} ; however, C_{HX} (see purity of medium above) was not adjusted during the calculation.

Changes in the liquid junction potential have been neglected because of the low values of h and $[\text{OH}^-]$ in the titrations. The ionic product of water, K_{w} , was independently determined as described above.

The values of $\log \beta_{-11}$, $\log \beta_{-21}$, and $\text{p}K_{\text{aC}}$ with their standard deviations (given as 3σ) and the standard deviation in H , $\sigma(H)$, defined as in Ref. 24, are given in Ref. 11. Experimental data and some calculated values for a representative titration are listed in Table 2. In this example and for most

Table 2. Experimental data (computer output from LETAGROP) for a titration at 20°C and 35‰ salinity. For each titration point are given V_{T} = the volume of buret solution with $H_{\text{T}} = 1.990$ M added to 248.1 g solution, E = measured emf in millivolts, H_{tot} as calculated from eqn. (9) in mM_{w} , $\log h$ calculated from eqn. (1), $Z = (H_{\text{tot}} - h + [\text{OH}^-])/B_{\text{tot}}$ and $\Delta Z = 10^3(H_{\text{calc}} - H_{\text{tot}})/B_{\text{tot}}$. H_{calc} and B_{tot} are calculated from eqns. (10) and (11).

V_{T}	E	H_{tot}	$\log h$	Z	ΔZ
0.000	-954.50	-2.61	-8.716	-1.347	-0.12
0.016	-946.83	-2.49	-8.584	-1.281	0.26
0.032	-937.99	-2.36	-8.432	-1.215	-0.31
0.048	-926.71	-2.23	-8.238	-1.148	-0.08
0.060	-915.34	-2.13	-8.043	-1.099	0.09
0.068	-905.28	-2.07	-7.870	-1.066	0.11
0.076	-892.05	-2.00	-7.642	-1.033	0.48
0.084	-876.72	-1.94	-7.379	-1.000	0.20
0.092	-862.52	-1.88	-7.135	-0.967	0.27
0.104	-846.90	-1.78	-6.866	-0.917	0.33
0.116	-835.98	-1.68	-6.678	-0.868	-0.39
0.128	-827.43	-1.59	-6.531	-0.818	-0.94
0.144	-817.98	-1.46	-6.369	-0.752	-0.56
0.164	-808.17	-1.30	-6.200	-0.670	-0.94
0.188	-797.53	-1.11	-6.017	-0.571	0.82
0.212	-787.57	-0.91	-5.846	-0.472	0.94
0.232	-779.14	-0.75	-5.701	-0.389	0.47
0.248	-771.92	-0.62	-5.577	-0.323	0.09
0.264	-763.85	-0.50	-5.438	-0.258	-0.05
0.276	-756.93	-0.40	-5.319	-0.209	-0.38
0.288	-748.67	-0.30	-5.177	-0.160	-0.28
0.300	-738.20	-0.21	-4.997	-0.112	-0.03
0.308	-729.24	-0.14	-4.843	-0.082	-0.22
0.316	-717.41	-0.08	-4.640	-0.053	-0.02
0.324	-701.96	-0.02	-4.374	-0.030	0.34

Table 2. Continued.

0.332	-685.99	0.05	-4.100	-0.016	0.09
0.344	-668.28	0.14	-3.795	-0.008	0.14
0.356	-657.04	0.24	-3.602	-0.005	-0.25
0.368	-649.03	0.34	-3.464	-0.003	-0.30
0.380	-642.84	0.43	-3.358	-0.003	0.13
0.392	-637.91	0.53	-3.273	-0.002	-0.14
0.408	-632.48	0.66	-3.180	-0.002	0.23

$$U = \sum(H_{\text{calc}} - H_{\text{tot}})^2 = 2.00 \times 10^{-5} \text{ mM}^2.$$

$$\sigma(H) = 0.00088 \text{ mM}.$$

"Best values" calculated: $K_{\text{HX}} = (6.8 \pm 1.4) \times 10^6$, $\beta_{-11} = (1.222 \pm 0.003) \times 10^{-6}$, $\beta_{-11} = (1.142 \pm 0.007) \times 10^{-15}$.

$$H_0 = -2.615 \text{ mM}_w, B_0 = 1.941 \text{ mM}_w, E_0 = (-447.54 \pm 0.03) \text{ mV}.$$

Values of $K_w = 4.1 \times 10^{-14}$ and $C_{\text{HX}} = 0.02 \text{ mM}_w$ were not adjusted.

titrations a random scattering of numerically small values around zero was found for the quantity $(H_{\text{calc}} - H_{\text{tot}})/B_{\text{tot}}$, which is the "error" in H_{tot} divided by B_{tot} in each titration point. The low values of this quantity and thereby of $\sigma(H)$ in each titration indicates good internal precision in each titration. Double determinations for each salinity and temperature generally gave values for each constant differing in the order of 3σ for each constant.

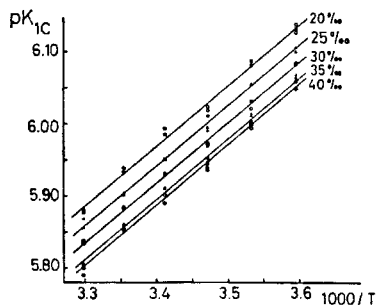


Fig. 3a. Plot of experimental values of pK_{1C} at various salinities against $1/T$. The fitting of the lines is described in Ref. 11.

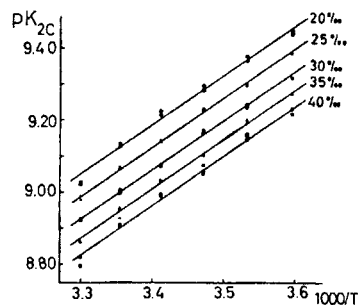


Fig. 3b. Plot of experimental values of pK_{2C} at various salinities against $1/T$. The fitting of the lines is described in Ref. 11.

In Figs. 3a and 3b values of pK_{1C} and pK_{2C} are plotted against $1/T$. In Figs. 4a and 4b the values are plotted against salinity. The fitting of the lines in Figs. 3 and 4 is described in Ref. 11 where also tables of interpolated values are given.

The accuracy of the equilibrium constants may be lower than the precision in each determination. Errors in the emf measurements and consequently in $\log h$ are likely to be very small and errors caused by drift are relatively easy to detect with the high resolution of the emf measuring circuit used in this work. Errors in H_{tot} are not as easy to detect during experiments. Two sources of error will be indicated. Small volumes of hydrochloric acid may be by capillary

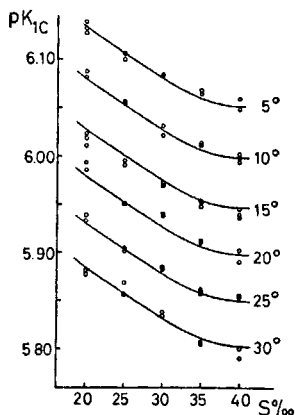


Fig. 4a. Plot of experimental values of pK_{1C} at various temperatures against salinity. Curves correspond to values obtained from the lines in Fig. 3a.

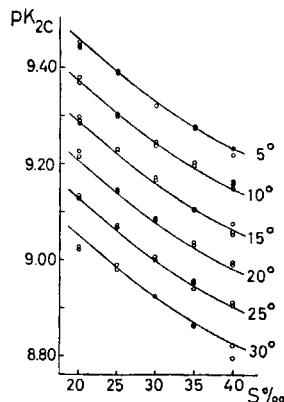


Fig. 4b. Plot of experimental values of pK_{2C} at various temperatures against salinity. Curves correspond to values obtained from the lines in Fig. 3b.

forces have leaked out of the microburet syringe. Since additions are almost equal and performed with equal time intervals this leaking may give an error corresponding to a too low value of H_T , the titre of the hydrochloric acid used. The values of pK_{1C} and pK_{2C} computed may have decreased by 0.002–0.005 log units as a consequence of this error in H_T . The presence of a small gas volume in contact with the solution may introduce an error in H_{tot} , discussed in the next section, since some carbon dioxide (equal to H_2CO_3 in the calculations) may leave the solution into the gas phase.

Note on the use of HALTAFALL and LETAGROP for estimation of the effect of systematic errors. The computer program HALTAFALL^{25,26} calculates free concentrations of all species assumed in a certain model of a chemical system when total concentrations of the components and stability constants are given as data input to the program. Thus it can be used to simulate titration curves by increase or decrease of total concentrations in each new titration point. In this work titration curves corresponding to experimental carbonate titrations were simulated using the total concentrations used in the experiments and suitable constants. Values of $\log h$ for each titration point were transformed to emf-values E according to eqn. (1) with certain values chosen for E_0 and T . The (v_T, E) values obtained for a simulated titration curve may now be treated with LETAGROP to find best values of pK_{1C} and pK_{2C} . The effect of a small change in some experimental condition on the values of pK_{1C} and pK_{2C} found in a LETAGROP treatment of experimental data can be estimated as follows. Input data to a HALTAFALL calculation are given so that they correspond to the actual change in experimental parameters. The (v_T, E) values obtained in this HALTAFALL calculation are subsequently treated in LETAGROP to obtain "best" values of pK_{1C} and pK_{2C} . The procedure will be exemplified in three examples where a simulated curve including some "error" is compared to an "error-free" curve, referred to as the original titration.

Example 1. An acid impurity HX with $[HX]_{\text{tot}} = 2 \times 10^{-5}$ M and $K_{\text{HX}} = 1.0 \times 10^{-5}$ is added to the original input to HALTAFALL. In the subsequent LETAGROP treatment no acid impurity is assumed. The "best" fit gives a pK_1 -value 0.009 log units lower and an unchanged pK_2 -value as compared to the original titration. The value of B_0 is also changed. When $C_{\text{HX}} = 2 \times 10^{-5}$ M was given in the input data to LETAGROP the original values of pK_{1c} , pK_{2c} , and B_0 were obtained and K_{HX} came out with the value 1.02×10^{-5} . The values are of course dependent on the choice of range of H_{tot} and the number of points, but in this case a H_{tot} -range and number of points corresponding to experimental titrations were used.

Example 2. There is a "drift" in E_0 , constantly decreasing during the titration, to a value 0.3 mV lower than the original value. From each E -value in the original titration numbers were subtracted corresponding to the "drift". LETAGROP treatment shows very slight differences in calculated values of pK_{1c} and pK_{2c} . The values were lower than the original by 0.001 and 0.003 log units, while the value for E_0 was 0.15 mV lower than the original. Although the shifts in E_0 for the last points of the titration as compared to the original are about 0.30 mV, the value of 3σ for E_0 calculated in LETAGROP is only 0.04 mV, a somewhat optimistic value. The value of $\sigma(H)$ for this treatment was, however, considerably increased.

Example 3. In this case the assumption was made that carbon dioxide leaves the solution of 250 ml to a 2 ml gas volume, a reasonable approximation of an experimental titration. Equilibrium for distribution of carbon dioxide between solution and gas phase is assumed. The relations $[\text{CO}_2]_{\text{aq}}/P_{\text{CO}_2} = 0.03 \text{ M}_w/\text{atm}$ ²⁷ and $P_{\text{CO}_2}V = n_{\text{CO}_2}RT$ are used to calculate the amount of carbon dioxide present in the gas phase assuming constant total pressure for every titration point. This amount, expressed as $[\text{CO}_2]_{\text{aq}}$ in the 250 ml solution, is subtracted from B_{tot} and twice this value from H_{tot} in each titration point where carbon dioxide (H_2CO_3 in the calculations) is present. The treatment implies some simplification but is rather reasonable. When the simulated curve, obtained by HALTAFALL, is treated with LETAGROP the "best" fit gives a pK_1 -value 0.005 log units higher and an unchanged pK_2 -value as compared with the original titration.

This method for estimating the quantitative effect of certain changes in experimental conditions on calculated equilibrium constants is relatively convenient and may save some time when designing experiments for equilibrium studies of chemical systems in solutions. The versatility of HALTAFALL-calculations when designing methods for quantitative analysis in solutions has been demonstrated by Jagner²⁸ and for testing reasonable models of chemical systems by Wahlberg.²⁹

DISCUSSION

A direct comparison of the present set of constants with those of Buch⁶⁻⁸ and Lyman⁹ is difficult since different activity scales are used. The differences are discussed elsewhere.³⁰ For the precise determination of the carbonate species in a sample of sea water from pH and some other measurable parameter (*e.g.* total alkalinity or carbon dioxide pressure) it is necessary to measure pH

on a pH-scale that is consistent with the activity scale used in the determination of the present set of constants. In a separate work³¹ it is shown how pH values on such a scale can be assigned to buffer solutions containing "tris" (2-amino-2-hydroxymethylpropane-1,3-diol) in synthetic sea water. It is also shown that errors due to liquid junction potentials can be kept quite small if such buffer solutions are used in the pH determination of a sea water sample. Differences in the values of the dissociation constants of carbonic acid determined in synthetic sea water and in sodium chloride media of corresponding ionic strengths are treated elsewhere.³²

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