

by the liquid junctions. Besides, the effect of pressure on these junctions would have to be taken into account, and the treatment of results based on single ion activity determination is open to criticism.

However, since most of the oceanographic data refer to paH measurements, we have tried to measure paH at atmospheric pressure in mixtures of HCl + NaCl or KCl + MgSO₄ + MgCl₂ + CaCl₂. Saturated KCl agar-agar junctions were used with calomel electrodes as inner and outer electrodes of the glass cell. Stable and reproducible results have been obtained in KCl with 0.01 HCl + 0.09 KCl in the reference compartment. The value indicated on Fig. 9 for $\log a_{H^+}$ in 0.01 HCl + 0.09 KCl was checked with a hydrogen electrode—calomel electrode cell, and is close to the value reported in Harned and Owen (10), 3.898. The hydrogen ion activity in HCl + KCl was first measured, and the effect of the added salts was investigated either with 0.01 HCl + 0.09 KCl as inner solution or with 0.01 HCl + 0.5/n - 0.01 KCl, n being equal on both sides of the glass electrode. Trying to measure a_{H^+} in HCl + NaCl with 0.1 HCl as inner solution resulted in erratic information. Reproducible data could only be obtained by systematically using KCl + HCl at the same ionic strength as inner solution.

The curves giving $\log a_{H^+}$ in HCl + NaCl in presence of Mg and Ca salts have been determined by taking 0.5/n NaCl - 0.01 HCl for inner solutions and

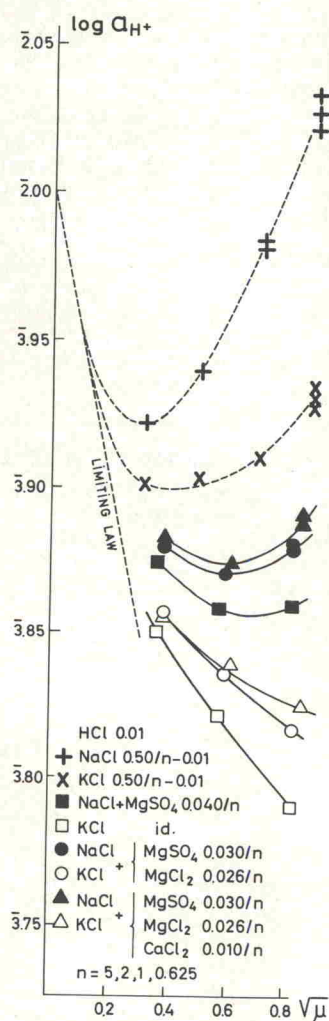


Fig. 9. Hydrogen ion activity ($\log a_{H^+}$), in 0.01 HCl + NaCl or KCl, in presence or not of MgSO₄, MgCl₂, CaCl₂ as a function of $\sqrt{\mu}$ (glass electrode with calomel electrodes and sat. KCl agar-agar salt bridges).

making n equal in both compartments. If one takes $c_{H^+} = c_{HCl}$, $\log y_{H^+}$ at $\mu = 0.75$ is 1.887 and one then can assume that it nearly has the same value in sea water. Anderson and Robinson (14) estimate $\log y_{H^+}$ equal to 1.880 in sea water (Cl = 20.0%) acidified to pH 3.3-3.9 with HCl, which is not too far from our value for $\log y_{H^+}$.

Evaluation of apparent dissociation constants $y_{H^+}k^{c(1)} = K^{c(1)}$ and $y_{H^+}k^{c(2)} = K^{c(2)}$ of carbonic acid in sea water at 1 atm and 1000 kg. cm⁻².—The apparent constants used in oceanography are defined as $K^{c(1)} = a_{H^+} \times [HCO_3^-]_T/[CO_2] = y_{H^+}k^{c(1)}$ and $K^{c(2)} = a_{H^+} \times [CO_3^{=}]_T/[HCO_3^-]_T = y_{H^+}k^{c(2)}$, where T refers to total concentrations. Since $\gamma_m = y_c/do$ (Eq. [7]) it follows that $pK^{m(1)(2)} = pK^{c(1)(2)} - 0.001$ at 1 atm.

According to Lyman (13), $pK^{c(1)} = 6.00$ and $pK^{c(2)} = 9.12$ at 22°C, Cl % = 20.0. Taking our values $pk^{c(1)1} = 5.89$, $pk^{c(2)1} = 9.015$ valid for artificial sea water in the pmH_1 interval 7.9-8.5, and $-\log y_{H^+} = 0.11$, gives $pK^{c(1)} = 6.00$ and $pK^{c(2)} = 9.125$ which is in good agreement. Since $pk^{c(1)}$ has been determined at pmH_1 5.0 where obviously HCO₃⁻ trapping by Mg and Ca is very small or inexistent (see Fig. 6A), but where the effect of SO₄⁼ can be measured, and since $pk^{c(1)}$ fits with the $pK^{c(1)}$ value given by Lyman, one comes to the conclusion that at alkaline pH, HCO₃⁻ trapping by Mg and Ca must be small in sea water, or that the HCO₃⁻ bound to Mg or Ca cannot be distinguished from that linked to Na. The problem is however not completely solved since in more concentrated buffers ($[CO_3^{=}] + [HCO_3^-] = 0.05 - 0.09$) HCO₃⁻ binding by Ca and Mg is obvious at pmH_1 7.0. Further analysis of these results and more experiments will be needed to decide whether or not HCO₃⁻ trapping persists in the alkaline range when CO₃⁼ binding reaches its maximum, and to find out how it depends on the buffer concentration.

To estimate the effect of pressure on $pK^{c(1)}$ and $pK^{c(2)}$, the pressure dependence of γ_{H^+} needs to be known. It cannot be calculated in media as complex as sea water. Since however this uncertainty affects both $pK^{c(1)}$ and paH identically, it has no bearing on the determination of the ratios $[CO_3^{=}]_T/[HCO_3^-]_T$, $[CO_3^{=}]_T/[CO_2]$ and $[HCO_3^-]_T/[CO_2]$ needed in oceanographic calculations to compute $[CO_2]$, $[HCO_3^-]_T$, $[CO_3^{=}]_T$ from paH , $pK^{c(1)}$, $pK^{c(2)}$, and $\Sigma CO_2 = [CO_2] + [HCO_3^-]_T + [CO_3^{=}]_T$. The simplest assumption, which is to neglect the effect of pressure on γ_{H^+} , leads to admit that $\Delta pK^{m(1)(2)}/\Delta p = \Delta pk^{m(1)(2)}/\Delta p$, so that in natural sea water at 1000 kg. cm⁻², $pK^{m(1)}$ and $pK^{m(2)}$ would, respectively, be equal to 6.00 - 0.314 and 9.125 - 0.178 (see p. 336) whereas $pK^{c(1)}$ and $pk^{c(2)}$ would become: 6.00 - (0.314 + 0.017) and 9.125 - (0.178 + 0.017), between pmH_1 8.0 and 8.5.

According to Buch and Gripenberg (16), the change of $pK^{m(1)}$ and $pK^{m(2)}$ with pressure are, respectively, 0.480 and 0.180 at 1000 bars, or 0.470 and 0.176 at 1000 kg. cm⁻². Their values were based on $\Delta V_1^\circ = -28.0$ cm³ mole⁻¹ for the first ionization step of carbonic acid and $\Delta V_1^\circ = -10.5$ cm³ mole⁻¹ for the second step assuming that the HCO₃⁻ ion would behave as acetic acid. Curiously enough our data fit almost exactly for $K^{c(2)}$, although the reasons of the small effect of pressure on $K^{c(2)}$ are completely different from what these authors thought them to be.

As we already indicated, $pk^{c(2)}$ and $pK^{c(2)}$ either on the molar or molal scale, determined in artificial sea water without boric acid at pressure p will give correct estimates for $[HCO_3^-]_T$ and $[CO_3^{=}]_T$ in the pmH_1 range 8.0-8.5, and it is theoretically possible, taking the boric acid effect into consideration, to calculate the pmH , pcH , or paH of a given surface sea water sample brought to pressure p , or at the corresponding depth. It is however much more easy to read $\Delta pmH/\Delta p$ from Fig. 5, or to use Table I where we have given the paH shifts on the molar scale in natural sea water

Table I. *paH* at 1 atm and 1000 bar in natural sea water, molar scale*, Cl %_o 20.0

<i>paH</i> at 1 atm	7.5	7.6	7.7	7.8	7.9	8.0
<i>paH</i> at 1000 bars Buch and Gripenberg (16)	7.15	7.29	7.43	7.55	7.67	7.78
This paper (a)	7.19	7.30	7.41	7.52	7.63	7.74
(b)	7.20	7.31	7.42	7.535	7.65	
<i>paH</i> at 1 atm	8.1	8.2	8.3	8.4	8.5	8.6
<i>paH</i> at 1000 bars Buch and Gripenberg (16)	7.89	8.00	8.10	8.20	8.30	—
This paper	7.85	7.95	8.05	8.155	8.255	8.355

* $\log \gamma_{H^+CH^+} = \log \gamma_{H^+mH^+} + 0.016$ at 1000 bars (c, molar scale, m, molal scale); $\log \gamma_{H^+}$ is assumed not to vary with pressure; $-\log \gamma_{H_2O} = 0.114$ and $-\log \gamma_{H_2O} = 0.11$.

predicted on the basis of Buch and Gripenberg's (16) estimates of $pK''_{(2)}$ and $pK''_{(1)}$ at 1000 bars and our experimental rounded off data.

The two series of values from *paH* 7.5 to 8.0 reflect the scattering of the results of Fig. 5; to obtain set (a), 0.3 mv where subtracted from curve 6' to take into account the difference between the results in artificial and natural sea water; set (b) corresponds to curve 3 between 7.5 and 7.9. To adapt these values to other types of water small corrections will have to be made to take into account differences in salinity, SO_4^{2-} , Mg, Ca, and boric acid content.

The set of ionization functions and apparent dissociation constants based on the experiments described in this paper is given in Table II.

It is important to keep in mind that the ionization functions k' , k'' , and also K'' in Table II, can only be used to interpret emf measurements made with one particular type of reference half-cell. If other cells are used corrections have to be made affecting *pmH* and pK' identically.

Conclusions

A coherent set of ionization functions has been established on the molal and the molar concentration scales, from 1 atm to 1000 kg. cm^{-2} and at 22°C for

carbonic acid in NaCl (KCl) over a wide range of ionic strengths, in the presence of Mg^{++} , Ca^{++} , and SO_4^{2-} ions, and in sea water. It allows the use of *pmH* or *pcH* measurements with a junctionless glass electrode cell and ΣCO_2 determinations to calculate the concentrations of CO_2 , HCO_3^- , CO_3^{2-} (free and bound to Na, Mg, and Ca). Data are also available to take into account the increased dissociation of boric acid in natural sea water at high pressure. Corrections are given for different types of reference half-cells.

In situ paH, *pcH*, or *pmH* values at any ocean depth have been determined for one type of surface water (Atlantic Cl = 20.0‰) and can simply be read from the experimental curve giving $\Delta pmH/\Delta p$ as a function of *pmH*, at 1 atm and 22°C, in the *pmH* interval 5.0-9.0. The data can be used at any other temperature if one assumes that the temperature coefficient of the ionization functions is independent of pressure or the pressure coefficient is independent of temperature. This assumption however plausible, remains to be proven experimentally. Small corrections for differences in salinity, sulfate, B, Mg, Ca concentrations will have to be established for other water types.

Detailed calculations will be given in a following paper and will be used for the quantitative interpretation of direct *in situ pcH* or *pmH* measurement at great ocean depths (5, 6).

The apparent mean activity coefficient of HCl has been measured in NaCl solutions in the presence of Mg^{++} , Ca^{++} , and SO_4^{2-} at atmospheric pressure and at 1000 kg. cm^{-2} , and also γ_{H^+} at 1 atm. It is thus theoretically possible to calculate $\gamma_{HCO_3^-}$ and $\gamma_{CO_3^{2-}}$ in the various bicarbonate and carbonate buffers investigated including sea water, since γ_{CO_2} is known with rather good precision (9, 15).

The determination of γ_{H^+} in NaCl in the presence of Mg^{++} , Ca^{++} , SO_4^{2-} allows correlation of the ionization functions obtained with junctionless glass electrode cells with the so-called apparent dissociation constants widely used in oceanography to calculate $[CO_3^{2-}]_{total}$ and $[HCO_3^-]_{total}$. The results show that the apparent second dissociation constant is pH dependant with a rather broad minimum between *pmH*₁ 7.9 and 8.5, where the mean value of $pK''_{(2)}$ is 9.125 at 1 atm and 22°C. Since $pK''_{(1)} = 6.00$ at this temperature and pressure, both these values are in agreement with the data of Lyman (13).

Table II. Ionization functions and apparent dissociation constants for carbonic acid in sea water (Cl 20.0 ‰) at 22°C valid between *paH* 8.1 and 8.6^a

Ionization functions	1 atm				1000 bar			
	$pK'_{(1)}$		$pK'_{(2)}$		$pK'_{(1)}$		$pK'_{(2)}$	
$pK' = -\log \frac{[H^+][R^-]}{[HR]}$	c	m	c	m	c	m	c	m
	5.89	5.885	9.49	9.485	5.553	5.565	9.19	9.202
	5.89	5.885	9.49	9.485	5.55	5.565	9.19	9.20
Apparent ionization functions ^b	$pK''_{(1)} = pK'_{(1)}$		$pK''_{(2)}$		$pK''_{(1)} = pK'_{(1)}$		$pK''_{(2)}$	
$pK'' = -\log \frac{[H^+][R^-]_T}{[HR]_T}$	5.89	5.885	9.015	9.01	5.553	5.565	8.817	8.829
	5.89	5.885	9.015	9.01	5.55	5.565	8.82	8.83
Apparent oceanogr. dissociation constants	$pK''_{(1)}$		$pK''_{(2)}$		$pK''_{(1)}$		$pK''_{(2)}$	
$pK'' = -\log \frac{a_{H^+} \times [R^-]_T}{[HR]_T}$	6.00	6.00	9.125	9.125	5.663	5.68	8.927	8.944
($pK''_{m_1} = pK''_{c_1} - 0.001$)	6.00	(-0.001)	9.125	(-0.001)	5.66	(-0.001)	8.93	(-0.001)
	6.00	6.00	9.125	9.125	5.66	5.68	8.93	8.94
	$pK'_{(1)}, pK''_{(1)}, pK''_{(1)}$		$pK'_{(2)}$		$pK'_{(2)}$		$pK''_{(2)}, pK''_{(2)}$	
	c	m	c	m	c	m	c	m
Ionization functions and dissociation constants shift at 1000 bars	0.320				0.283		0.181	
	+0.017 ^c				+0.017		+0.017	
	0.337	0.320			0.300	0.283	0.198	0.181

^a $\log \gamma_{H^+}$ is assumed not to vary with pressure; the second row of data corresponds to rounded off values; c and m indicate the molar and molal concentration scale respectively.

^b T indicates total concentrations.

^c 0.017 = $\log d_{1000}/d_1$, where d is the density.