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ABSTRACT

The effect of pressure on the dissociation of carbonic acid has been investigated over a wide range of pH (pH 5.1-9.6) and ionic strength (0-1.0) in NaCl and KCl, using junctionless glass electrode cell measurements. At 22°C, $\Delta V_1^\circ = -25.4 \text{ cm}^3 \text{ mole}^{-1}$ and $-25.6 \text{ cm}^3 \text{ mole}^{-1}$ for the first and second ionization steps, respectively. The directly measured pmH or pCH shifts induced by pressure in sea water between pH 5.1 and 9.1 are explained by the enhanced dissociation of H₂CO₃, HCO₃⁻, CaCO₃, and MgCO₃, the effect of SO₄⁼ and the interference of boric acid ($\Delta V_1^\circ = -32.1 \text{ cm}^3 \text{ mole}^{-1}$). Values of the ionization functions $k'_{(1)} = [\text{H}^+][\text{HR}^-]/[\text{H}_2\text{R}]$ and $k'_{(2)} = [\text{H}^+][\text{R}^-]/[\text{HR}^-]$ of carbonic acid, valid in natural seawater, have been determined at 22°C, at 1 atm and at 1000 bars together with the apparent dissociation constants ($pK''_{(1)}$ and $pK''_{(2)}$) used in oceanography to calculate $[\text{CO}_3^{=}]_{\text{total}}$, $[\text{HCO}_3^-]_{\text{total}}$ from *in situ* pH values. Corrections are given for different types of reference half-cells, and an approach toward the absolute values of $pK_{(1)}$ and $pK_{(2)}$ in sea water is indicated.

The effect of pressure (p) on the dissociation constant (K) of a weak electrolyte (HR) is related to the corresponding volume change (ΔV) for the ionization reaction $\text{HR} \rightleftharpoons \text{H}^+ + \text{R}^-$ by the equation

$$\left(\frac{\partial \ln K}{\partial p} \right)_{m,T} = \frac{-\Delta V}{RT} \quad [1]$$

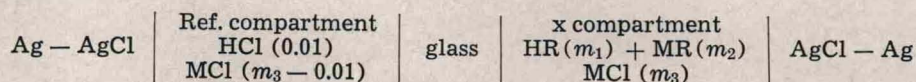
Data are available for ΔV_1° at atmospheric pressure, zero salt concentration, and zero weak electrolyte concentration for carbonic acid calculated from density

and SO₄⁼ ions and boric acid is investigated to interpret the data obtained with natural sea water samples (4) and from direct *in situ* determinations (5, 6).

Theoretical

The theory underlying the determination of dissociation constants as a function of pressure has been discussed in previous papers (3, 4).

The buffered cell used for the present determinations is of the type:



where M represents Na or K.

The emf (E) at pressure 1, or p , is expressed by:

$$E_{1,p} F/2.3 RT = \log (m_{\text{H}^+})^{\text{ref}_{1,p}} - \log (m_{\text{H}^+})^{x_{1,p}} + 2 \log \frac{(\gamma_{\text{HCl}})^{\text{ref}_{1,p}}}{(\gamma_{\text{HCl}})^{x_{1,p}}} \quad [2]$$

For an acid HR of the strength of carbonic acid $\log K^m = \log (m_{\text{H}^+} + m_1/m_2) + 2 \log \gamma_A$; $2 \log \gamma_A = \log (\gamma_{\text{H}^+} + \gamma_{\text{R}^-}/\gamma_{\text{HR}})$; $m_{\text{H}^+} + m_1/m_2 = k^m$ and:

$$(E_1 - E_p) F/2.3 RT = \log \frac{K^m_p}{K^m_1} + 2 \log \frac{\gamma_{A1}}{\gamma_{Ap}} + 2 \log \frac{(\gamma_{\text{HCl}})^{\text{ref}_1}}{(\gamma_{\text{HCl}})^{\text{ref}_p}} - 2 \log \frac{(\gamma_{\text{HCl}})^{x_1}}{(\gamma_{\text{HCl}})^{x_p}} \quad [3]$$

The terms in γ_{HCl} cancel each other at infinite dilution of the weak electrolyte, but if m_1 and m_2 are small and if the salt effect of the weak acid is small, cancellation practically occurs for finite values of m_1 and m_2 .

Equation [3] then simplifies to

$$(E_1 - E_p) F/2.3 RT = \log \frac{K^m_p}{K^m_1} + 2 \log \frac{\gamma_{A1}}{\gamma_{Ap}} = \log \frac{k^m_p}{k^m_1} \quad [4]$$

measurements, conductivity, and glass electrode determinations:

Reaction	Density, 25°C $-\Delta V_p^\circ$ ($p = 1 \text{ atm}$) $\text{cm}^3 \text{ mole}^{-1}$	Conductivity, 25°C $-\Delta V_p^\circ$ ($p = 1 \text{ atm}$) $\text{cm}^3 \text{ mole}^{-1}$	Glass electrode, 22°C $-\Delta V_p^\circ$ ($p = 1 \text{ atm}$) $\text{cm}^3 \text{ mole}^{-1}$
H ₂ CO ₃ → HCO ₃ ⁻ + H ⁺	29.0 (1)	26.5 (2)	26.6 (3) (unbuffered cell) 25.5 (3) (buffered cell) 25.4 (this paper; buffered cell)
HCO ₃ ⁻ → CO ₃ ⁼ + H ⁺	27.8 (1)	—	25.6 (this paper; buffered cell)

The ΔV_1° values from glass electrode measurements published in our earlier papers (3, 4) were obtained by extrapolation of ΔV_1 to zero KCl concentration over a limited ionic strength range (0-0.1).

In view of the interest in precise knowledge of the effect of pressure on the dissociation of carbonic acid for oceanographic work, the present paper deals with the determination between 1 and 1000 atm of the dissociation constants $K_{(1)}$ and $K_{(2)}$ and the ionization functions $k_{(1)}$, $k_{(2)}$ ($k_{(1)} = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2]$, $k_{(2)} = [\text{H}^+][\text{CO}_3^{=}] / [\text{HCO}_3^-]$) in presence of NaCl or KCl, over a wide ionic strength range (0-0.8), at various buffer ratios (pH 5.1-9.6). The effect of Ca⁺⁺, Mg⁺⁺,

the primes indicating that k' is only known approximately because of the former assumptions.

In the case of carbonic acid, extrapolation of $(E_1 - E_p) F/2.3 RT$ as a function of $\sqrt{\mu}$ leads easily to $\log K^{m_p}/K^{m_1}$ and a double extrapolation first to zero weak acid concentrations at a given μ , and then to zero KCl or NaCl concentration, is not required.

It can be shown (7) that $\Delta V_1 = 1.016 \times (E_1 - E_{1000})$ if ΔV_1 is expressed in $\text{cm}^3 \text{mole}^{-1}$, E in millivolts, p in kg. cm^{-2} . E_{1000} is measured on the tangent of $E_1 - E_p = f(p)$ drawn through $p = 1 \text{ atm}$. For carbonic acid, $E_1 - E_p = \Delta E_p$ is a linear function of p up to 1000 kg. cm^{-2} , so that E_{1000} corresponds to the emf effectively measured at 1000 kg. cm^{-2} .

Concentrations (m) and activity coefficients (γ) are given on the molal scale (mole per kg of pure solvent) in Eq. [1]-[4].

If the concentrations are expressed on the molar scale (mole per liter solution, c) the following classical equations ([5]-[10]) can be used to relate c , m , the corresponding activity coefficients, y and γ , the density (d) of the solution and of pure water (d_o), M_i the molecular weight of solute i , the dissociation constants and ionization functions K^c , k^c , K^m , k^m

$$m_i = c_i / (d - \sum c_i M_i / 1000) \quad [5]$$

$$c_i = m_i d / (1 + \sum m_i M_i / 1000) \quad [5']$$

$$\gamma = y [(d - \sum c_i M_i / 1000) / d_o] \quad [6]$$

$$m \gamma d_o = c y \quad [7]$$

$$K^m = K^c / d_o; k^m = k^c (1 + \sum m_i M_i / 1000) / d \quad [8]$$

$$\log K^{m_p} / K^{m_1} = \log K^c_p / K^c_1 - \log d_{op} / d_{o1} \quad [9]$$

$$\log k^{m_p} / k^{m_1} = \log k^c_p / k^c_1 - \log d_p / d_1 \quad [9']$$

Combining [7] and [2] gives

$$\frac{(m\gamma)^{\text{ref}}_{1,p}}{(m\gamma)^{x_{1,p}}} = \frac{(cy)^{\text{ref}}_{1,p}}{(cy)^{x_{1,p}}} \quad [10]$$

If the activity coefficients can be made to cancel in both ref and x compartments of the glass electrode, $(E_1 - E_p) F/2.3 RT$ will be equal to $\log k^{m_p} / k^{m_1}$ and extrapolate to $\log K^{m_p} / K^{m_1}$ as a function of μ (Eq. [4]) whatever the concentration scale used.

In aqueous solutions $d_p/d_1 = d_{op}/d_{o1} = 1.04$ at 1000 atm, $\log d_{1000}/d_1 = 0.017$, and it is thus easy to use $(E_1 - E_{1000})$ to calculate the ratios of the dissociation constants and ionization functions either on the c or the m scale.

When the absolute values of k^{m_1} , k^c_1 are required, Eq. [5], [5'], and [6] can be used to calculate either ionization function from the results obtained on the c or the m scale, respectively.

In practice, if the highest precision is not required, $c \approx m$ at 0.1M. At concentrations where the correction to calculate m from c is more important, the densities in the x and ref compartments of the glass electrode are nearly equal when the buffer concentration is small compared with the NaCl or KCl concentrations, and only m_{H^+} needs be computed in the reference solution, since $m_{Cl^-} = m_{Cl^-}^{\text{ref}}$.

In the present paper, concentrations referring to the gross composition of the solutions are indicated on the molar scale, and to simplify the symbol M referring to molarity is omitted (0.5 NaCl means 0.5M NaCl). The hydrogen ion stoichiometric concentration $[H^+]$ is represented by $pcH = -\log [H^+]$ on the c -scale and pmH on the m -scale, the hydrogen ion activity a_{H^+} by $paH = -\log a_{H^+}$ and if the distinction between pcH , pmH , paH is irrelevant, the symbol pH is used; subscripts p , 1, 1000 indicate pressure p , 1 atm, 1000 kg. cm^{-2} (ex.: pmH_1 , pmH_{1000}); $\Delta E_{1000} = E_1 - E_{1000}$ in millivolts (mv).

Experimental

The equipment described in 1962 (7) is used. It is important in the experiments involving equilibration

with either pure CO_2 or mixtures of CO_2 and nitrogen to saturate the silicone oil used in the glass electrode cell and to fill the cell with pipettes containing a controlled gas phase (3).

The glass electrode is made from Corning 015 glass, when no sodium error is to be expected. A commercial electrode, E.I.L.¹ n° 18331 unsensitive toward Na^+ at alkaline pH is used whenever necessary.

Corrections for asymmetry potential shift with pressure is made as described earlier (3, 4, 7). When both cell compartments contain the same solution ΔE_{1000} is generally between 0 and ± 1.0 mv. Higher values indicate defective Ag-AgCl electrodes.

Highest grade reagents (Merck) and air-free bi-distilled water (Pyrex) are used.

Results

First ionization function and first dissociation constant of carbonic acid in bicarbonate buffer in presence of NaCl or KCl, at $p = 1 \text{ atm}$ and $p = 1000 \text{ kg. cm}^{-2}$.—Figure 1 shows ΔE_{1000} in mv as a function of $\sqrt{\mu}$ for various bicarbonate buffers at different buffer ratios, in presence of NaCl or KCl. Extrapolation to zero ionic strength gives 25.0 mv corresponding to $-\Delta V_1^\circ = 25.4 \text{ cm}^3 \text{mole}^{-1}$, in agreement with our previous experiments (4).

Figure 2 gives the ionization function $pk^{c(1)} = -\log k^{c(1)}$ and $pK^{c(1)} = -\log K^{c(1)} = pk^{c(1)} + \frac{1.01 \sqrt{\mu}}{1 + \sqrt{\mu}}$ as a function of μ at $p = 1 \text{ atm}$ and $pK^{c(1)p} / \log d_p/d_1$ at $p = 1000 \text{ kg. cm}^{-2}$ ($\log d_p/d_1 = 0.017$).

The absolute values of $pK^{c(1)}$ (6.38) and $pk^{c(1)}$ are in good agreement with the data of Harned and Davis (8) and of Harned and Bonner (9) ($pK^{m(1)} = 6.3809$ at 20° and 6.3519 at 25°C).

The concentration ratios $[\text{HCO}_3^-]/[\text{CO}_2]$ are computed from the equations of these authors and the same extrapolation function is found to fit our results and theirs. The $2 \log (y_{\text{HCl}})^{\text{ref}} / (y_{\text{HCl}})^x$ term in Eq. [1] (c scale) is calculated from the values of γ_{HCl} in NaCl and KCl taken from Harned and Owen (10). It is assumed that γ_{HCl} in the x compartment is only affected by the ionic strength, and the ratio of the activity coefficients is also supposed to be valid on the molar scale. At $\mu \geq 0.5$, γ_{HCl} practically cancels in both compartments.

At $\mu = 0.75$, $pk^{m(1)} = pk^{c(1)} - 0.007 = 5.995$. The correction is -0.005 , -0.0057 , -0.0065 , -0.0073 ,

¹ Electronic Instruments Limited, Richmond, Surrey, England.

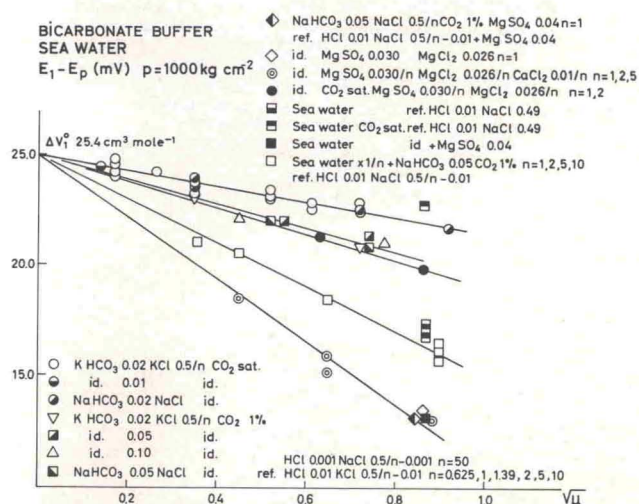


Fig. 1. Glass electrode emf shifts at 22°C produced by pressure (1000 kg. cm^{-2}) in bicarbonate buffers, at different buffer ratios, as a function of $\sqrt{\mu}$, in NaCl, KCl, in presence of Mg^{++} , Ca^{++} , SO_4^- ions, and in sea water.

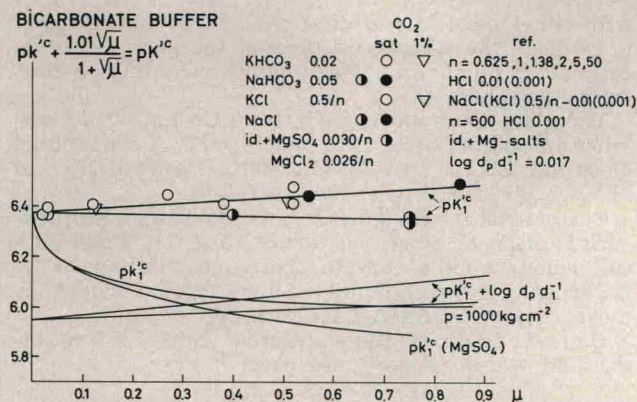


Fig. 2. First ionization function ($k'_{(1)}$) of carbonic acid and as a function of μ at atm pressure and 1000 kg.cm⁻² in NaCl and KCl at 22°C. Effect of MgSO₄ + MgCl₂.

-0.0081, -0.009 at μ 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, respectively (calculated from the density of NaCl solutions), and at $\mu = 0$, it is equal to -0.001.

Second ionization function and second ionization constant of carbonic acid in carbonate buffer in presence of NaCl or KCl, at $p = 1$ atm and $p = 1000$ kg. cm⁻².—Figure 3 gives ΔE_{1000} in mv, as a function of $\sqrt{\mu}$ for carbonate buffer in presence of NaCl or KCl.

Extrapolation to zero ionic strength gives 25.1 mv or $-\Delta V_1^0 = 25.6$ cm³ mole⁻¹, which is practically the same result obtained in bicarbonate buffers. The value calculated by Owen and Brinkley (1) from density determinations is 27.8 cm³ mole⁻¹.

Figure 4 shows the ionization function $pk'^c_{(2)}$ as a function of $\sqrt{\mu}$ at $p = 1$ atm, $pk'^c_{(2)p} + \log d_p/d_1$ at $p = 1000$ kg. cm⁻²; the results in 0.5 and 0.8 NaCl do not depend on the buffer ratio and are identical either with NaHCO₃ 0.08 + Na₂CO₃ 0.01 or with NaHCO₃ 0.025 + Na₂CO₃ 0.025. $pk'^c_{(2)} = 10.37$ corresponds to the values published by Harned and Scholes (11) ($pK^m_{(2)} = 10.377$ at 20°C, 10.329 at 25°C) who extrapolate their data between $\mu = 0.15$ and 0.

At $\mu = 0.75$, $pk'^m_{(2)1} = 9.60 - 0.007$ in NaCl.

Effect of buffer ratio on the ionization of carbonic acid at 1000 kg. cm⁻² in NaCl and KCl solutions.—Figures 1 and 3 show that, at a given buffer ratio, ΔE_{1000} extrapolates linearly to the same value at $\mu = 0$, and that a change in the buffer concentration has the

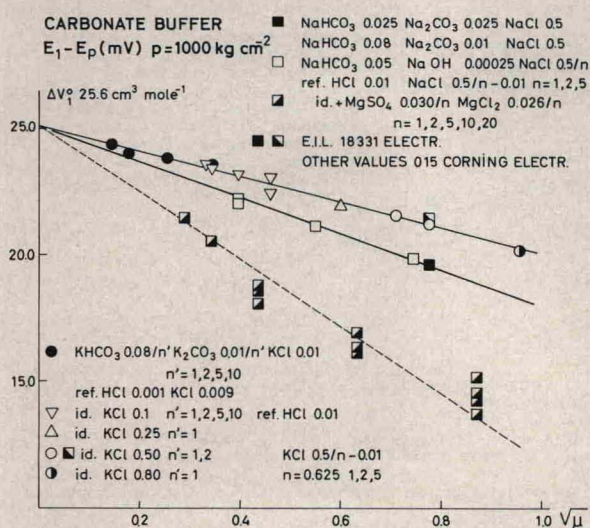


Fig. 3. Glass electrode emf shifts at 22°C, produced by pressure (1000 kg.cm⁻²) in carbonate buffers, at different buffer ratios, as a function of $\sqrt{\mu}$, in NaCl or KCl, in presence of Mg⁺⁺, Ca⁺⁺, SO₄⁻, and in sea water.

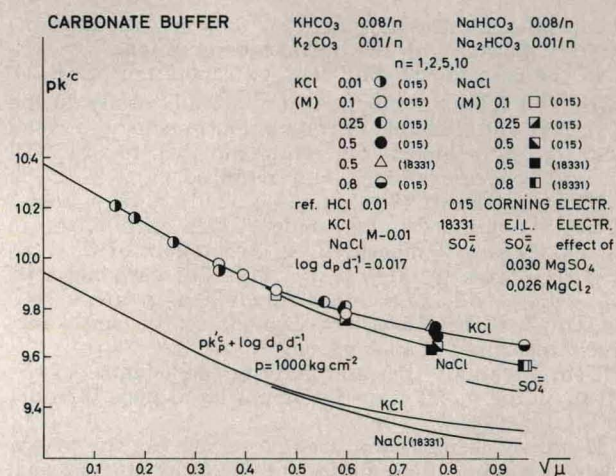


Fig. 4. Second ionization function ($k'_{(2)}$) of carbonic acid as a function of $\sqrt{\mu}$ at atm pressure and 1000 kg.cm⁻² in NaCl and KCl at 22°C. Sulfate effect of 0.030 MgSO₄ (+0.026 MgCl₂).

same effect as the corresponding μ change produced by an increase of the NaCl or KCl concentration. It is therefore easy to obtain a graphical estimate of ΔE_{1000} at a chosen ionic strength, even from isolated values measured at another ionic strength.

Curves 1 and 1' from Fig. 5 give ΔE_{1000} at $\mu = 0.75$ (ionic strength of sea water at Cl‰ = 20.0) as a function of pmH_1 , in NaCl and KCl. The emf shifts depend only slightly on the total CO₂ concentration in the range investigated ([HCO₃⁻] + [CO₃⁼]) between 0.09 and 0.0025; arrows indicate the values at 0.0025 in Fig. 5).

The reason for the difference between the results in NaCl and KCl at $pmH_1 \approx 8.5$ is, we believe to be correlated with the fact that, at 1 atm, the curves giving $pk'_{(2)}$ as a function of $\sqrt{\mu}$ (Fig. 3) demonstrate the greater tendency for carbonate ions to associate with Na than with K. Ion pairs like Na⁺ - CO₃⁼ or Na⁺ - NaCO₃⁻ will dissociate under pressure, and free CO₃⁼ ions, hitherto masked for the carbonic acid equilibrium, will modify the buffer ratio, so that the pmH shift induced by pressure can be expected to be smaller than in a medium where association is less important or inexistent. We will see that magnesium and calcium ions which have a much larger tendency to form ion pairs with CO₃⁼ than sodium ions also have a much larger lowering effect on the emf changes produced by pressure in carbonate buffers.

Since K⁺ or Na⁺ may also form ions pairs with HCO₃⁻, a complete analysis of curves 1 and 1' appears to be far from easy and would require the knowledge of $pk'_{(1)(2)}$ and $\Delta pk'_{(1)(2)}/\Delta p$ in absence of any ionic association; the dissociation constants of NaCO₃⁻ and NaHCO₃ would have to be taken into account and also the equilibrium $2HCO_3^- \rightleftharpoons CO_3^{=2} + H_2CO_3$, which is displaced when CO₃⁼ or HCO₃⁻ is released in the solution. Besides the salt effect of NaCl or KCl would have to be known.

There is however no difficulty in considering that in the ionization functions $k'_{(1)}$ and $k'_{(2)}$, determined at atmospheric pressure or at 1000 kg. cm⁻², [CO₃⁼] and [HCO₃⁻] refer to the total concentration of CO₃⁼ and HCO₃⁻, ions present either as free ions or forming ion pairs with Na or K.

In the pmH_1 interval 8.5-9.5 the thus defined $pk'_{(2)1000}$ can be measured without ambiguity from curves 1 and 1' of Fig. 5 since ΔE_{1000} is constant. The buffer ratio and the term $2 \log \gamma_{A1}/\gamma_{Ap}$ in Eq. [3] are constant, the mean activity coefficient being referred to the total concentrations of free and masked ions. $\log k'^m_{(2)1000}/k'^m_{(2)1}$ is therefore equal to 0.315 ($\Delta E_{1000} = 19.0$ mv) and 0.350 ($\Delta E_{1000} = 20.8$ mv) in NaCl and KCl, respectively.

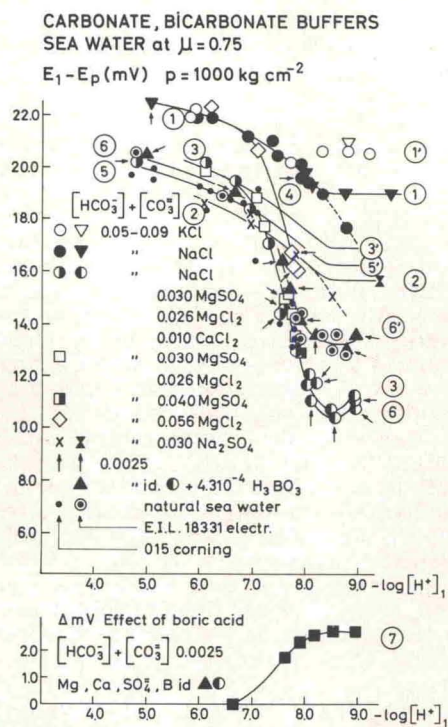


Fig. 5. Glass electrode emf shifts at 22°C produced by pressure (1000 kg.cm⁻²) in bicarbonate, carbonate buffers, and sea water at $\mu = 0.75$, as a function of $pmH = -\log m_H$ measured at atm pressure. Curve 1, NaHCO₃, Na₂CO₃, CO₂ ([HCO₃⁻] + [CO₃⁼]) 0.05 - 0.09 and 0.0025 (arrow) in 0.5 NaCl. Curve 1', KHCO₃, K₂CO₃, CO₂ ([HCO₃⁻] + [CO₃⁼]) 0.05 - 0.09 in 0.5 KCl. Curve 2, NaHCO₃, Na₂CO₃, CO₂ ([HCO₃⁻] + [CO₃⁼]) 0.05 - 0.09 in 0.5 NaCl; effect of Na₂SO₄ (0.030). Curve 3, NaHCO₃, Na₂CO₃, CO₂ ([HCO₃⁻] + [CO₃⁼]) 0.05 - 0.09 in 0.5 NaCl; effect of MgSO₄ (0.030), MgCl₂ (0.026), CaCl₂ (0.01) (Precipitates are obtained at pH > 8.0). Arrows indicate results for [HCO₃⁻] + [CO₃⁼] = 0.0025 (see also curve segments 6). Curve 3', NaHCO₃, Na₂CO₃, CO₂ ([HCO₃⁻] + [CO₃⁼]) 0.05 - 0.09 in 0.5 NaCl; SO₄⁼ effect of MgSO₄ (0.030). Curve 4, NaHCO₃, Na₂CO₃, CO₂ ([HCO₃⁻] + [CO₃⁼]) 0.05 - 0.09 and 0.025 (arrows); effect of MgCl₂ (0.056). Curve 5, Natural sea water Cl %_o ≈ 19.5 (Atlantic), corrected at Cl %_o 20.0 ($\mu = 0.75$). Curve 5', Natural sea water; SO₄⁼ effect. Curve 6, Artificial sea water: [HCO₃⁻] + [CO₃⁼] = 0.0025; 0.030 MgSO₄, 0.026 MgCl₂, 0.010 CaCl₂, 0.5 NaCl (with or without boric acid in the acid range). Curve 6', Artificial sea water with boric acid (4.3 10⁻⁴) (alkaline range). Curve 7, Effect of boric acid; smoothed difference in mv between ($E_1 - E_{1000}$) in artificial sea water without boric acid (see curves 3 and 6) and ($E_1 - E_{1000}$) in the same with 4.3 10⁻⁴ boric acid (see curves 6 and 6').

Inspection of curve 1 further indicates that the results at $pmH_1 \leq 7.00$ are identical in KCl and NaCl. If one again assumes that the bicarbonate concentration corresponds to the sum of the free HCO₃⁻ ions and the undissociated sodium or potassium bicarbonate, $\log k'^{m(1)1000}/k'^{m(1)1}$ is equal to 0.359 ($\Delta E_{1000} = 21.0$ mv) at $pmH_1 7.0$, 0.376 at $pmH_1 6.0$, and 0.385 at $pmH_1 5.0$. Here the term $2 \log \gamma_{A1}/\gamma_{Ap}$ in Eq. [3] is not constant and depends on the buffer ratio.

The question that remains to be answered concerns the choice of suitable values for $pk'_{(1)1000}$ and $pk'_{(2)1000}$ in the pmH_1 range 7.0-8.5, where the emf changes induced by pressure depend on both ionization functions.

If we consider a solution containing NaCl and NaHCO₃ at atmospheric pressure, its $pmH_1 = \frac{1}{2}(pk'^{m(1)1} + pk'^{m(2)1})$; at $\mu = 0.75$, one finds $pmH_1 \approx 7.8 = \frac{1}{2}(6.0 + 9.6)$ and $[CO_2] = [CO_3^{=}]$. At $pmH_1 = 7.8$, $\Delta E_{1000} = 20.0$ mv, and simple considerations show that $[CO_2]$ will remain equal to $[CO_3^{=}]$ if $2.3 RT/F \log k'^{m(1)1000}/k'^{m(1)1}$ and $2.3 RT/F \log k'^{m(2)1000}/k'^{m(2)1}$ are taken symmetric with respect to $\Delta E_{1000} = 20.0$ mv.

For instance, 21.0 and 19.0 mv read at $pmH_1 7.0$ and 8.5 on curve 1 of Fig. 5. In that case the equilibrium $2HCO_3^- \rightleftharpoons CO_3^{=} + H_2CO_3$ is shifted. Thus, at $pmH_1 = 7.8$, if $[HCO_3^-] + [CO_3^{=}] = 0.05$, 6.10^{-5} HCO₃⁻ is formed at 1000 kg. cm⁻² at the expense of 3.10^{-5} CO₂ and 3.10^{-5} CO₃⁼, which corresponds to a 4% change of the initial CO₂ and CO₃⁼ concentrations. At $pmH_1 7.0$ and 8.5, the change of either [CO₂] and [HCO₃⁻] or [CO₃⁼] and [HCO₃⁻] is negligible when pressure is applied. If one could assume $2.3 RT/F \log k'^{m(1)1000}/k'^{m(1)1}$ and $2.3 RT/F \log k'^{m(2)1000}/k'^{m(2)1}$ to be equal to ΔE_{1000} read on curve 1 at any pmH_1 between 5.0 and 9.0, the CO₂, HCO₃⁻, CO₃⁼ concentrations would remain constant at any pressure. This is what happens at infinite dilution where $\Delta V^o_{(1)1} = \Delta V^o_{(2)1}$.

In KCl, if one neglects the slight minimum at $pmH_1 7.8$, $2.3 RT/F \log k'^{m(1)1000}/k'^{m(1)1}$ and $2.3 RT/F \log k'^{m(2)1000}/k'^{m(2)1}$ are equal within ± 0.25 mv over the range 7.0-9.0. However, this is an oversimplification since the minimum at 7.8 could be explained by the release of CO₃⁼ and HCO₃⁻ from ion pairs. HCO₃⁻ behaves as a base at $pmH_1 < 7.8$ and as an acid at $pmH_1 > 7.8$, whereas the release of CO₃⁼ always results in lowering the hydrogen ion concentration.

The choice of the values of $pk'^{m(1)1000}$ at $pmH_1 7.0$ and $pk'^{m(2)1000}$ at $pmH_1 8.5$ to be used in the pmH_1 interval 7.0-8.5 remains questionable, even in KCl, but there is no other alternative unless reliable values for $pk'^{m(1)}$ and $pk'^{m(2)}$ become available in absence of any ionic association. However, at the alkaline end of the pmH_1 interval 7.0-8.5, $pk'^{m(1)}$ needs not to be known with great precision to calculate [HCO₃⁻] or [CO₃⁼]. At $pmH_1 8.0$, an error of 0.02 ($\Delta E \approx 1.2$ mv) in $pk'^{m(1)1000}$ affects [CO₂] by 2% and [HCO₃⁻] and [CO₃⁼] by only 0.1%.

The separate salt effect of NaCl on $2.3 RT/F \log k'^{m(1)1000}/k'^{m(1)1}$ can be estimated at $pmH_1 < 5.0$ since curve 1 in Fig. 5 seems to reach a plateau in the acid range and since ΔE_{1000} is known at 0 ionic strength (25.0 mv). Thus, for the salt effect, one finds 25.0 - 22.6 = 2.4 mv. This value fits with the fact that $2 \Delta E_{1000} = 23.6$ mv at $\mu = 0.75$ in a solution containing only NaCl and saturated with CO₂. At $\mu = 0$, $2 \Delta E_{1000} = 26.2$ mv (3) and the difference 26.2 - 23.6 = 2.6 mv.

It seems reasonable to assume that the difference between ΔV^o_1 found in pure CO₂ solutions and in bicarbonate buffer at 0 ionic strength might be related to the existence of NaHCO₃ ion pairs even when the concentration of NaHCO₃ becomes very small. The same effect occurs in other buffer systems investigated with the glass electrode technique: ΔV^o_1 is always found to be smaller in buffers than in the corresponding pure acid (3), and the explanation given above might be general.

Finally, one will notice (Fig. 5, dotted part of curves 1 and 2) that Corning 015 electrodes display an alkaline error in presence of NaCl at 1000 kg. cm⁻² at $pmH_1 > 8.25$, although no such error can be detected even at 8.75 at atmospheric pressure.

Ionization of carbonic acid in presence of Mg⁺⁺, Ca⁺⁺, and SO₄⁼ in NaCl solutions, at concentrations found in sea water, at 1 atm and 1000 kg. cm⁻² and at different buffer ratios ($\mu = 0.75$).—When Ca or Mg salts are added to carbonate and bicarbonate buffers, it is well known [see Garrels, Thompson, and Siever (12)] that MgCO₃ and CaCO₃ ion pairs are formed and that the trapping of HCO₃⁻ ions is also to be considered. The dissociation of carbonic acid can still be described by the ionization functions $k'_{(1)}$ and $k'_{(2)}$ where [CO₃⁼] and [HCO₃⁻] refer to the free carbonate and bicarbonate ions (plus those bound to Na as seen in the preceding section), but it is also useful to define apparent ionization functions $k''_{(2)} = [H^+][CO_3^{=}]/[HCO_3^-]$, $k''_{(1)} = [H^+][HCO_3^-]/[CO_2]$ where [CO₃⁼]_T and [HCO₃⁻]_T correspond to the total amount of carbonate and bicarbonate. We will call $k'_{(2)}$ and $k'_{(1)}$ true ionization functions.

True and apparent ionization functions of carbonic acid in presence of Mg^{++} , Ca^{++} and $SO_4^{=}$, in NaCl solutions at 1 atm ($\mu = 0.75$).—Figure 6 gives the pmH_1 changes (in mv) produced when $MgCl_2$, curve 4; $MgCl_2 + MgSO_4$, curve 3; $MgCl_2 + MgSO_4 + CaCl_2$, curve 2; Na_2SO_4 , curve 1 are added to bicarbonate and carbonate buffers at atmospheric pressure, as a function of pmH_1 measured in the solutions containing the added salts. The reference 0.01 HCl + 0.49 NaCl solution has the same salt composition as the buffer under test it is assumed that $m_{H^+} = m_{HCl}$ and that the mean activity coefficient of HCl is the same in both compartments. The added salts are tested at concentrations normally found in sea water ($Cl\%_o = 20.0$).

Effect of $SO_4^{=}$ on the true ionization functions $k'_{(1)1}$ and $k'_{(2)1}$.—Inspection of Fig. 6 shows that the effect of $SO_4^{=}$ ions can be distinguished from the effect of Ca and Mg.

$MgCl_2$ at $pmH_1 < 6.0$ obviously does not modify $k'_{(1)1}$ which is thus the same as in pure bicarbonate solutions at the same ionic strength. The ordinate difference between curves 3 and 4 in Fig. 6 shows but little variations over the pmH_1 interval considered and allows one to calculate $pk'^{c(1)1}$ and $pk'^{c(2)1}$. Thus for the investigated buffers ($MgSO_4$ 0.030, $[HCO_3^-] + [CO_3^{=}]$ between 0.0025 and 0.09) $pk'^{c(1)1} = 5.89$ and $pk'^{c(2)1} = 9.49$ at $\mu = 0.75$ (see Fig. 2 and curve segment in Fig. 4); $pk''^{m(1)1} = 5.89 - 0.005$ and $pk''^{m(2)1} = 9.49 - 0.005$. The correction for the change of concentration scale is somewhat smaller than in pure NaCl solutions and is based on a total salt content of 36.4g and the corresponding density of sea water 1.025 at 22°C (13).

Effect of Ca and Mg and the apparent ionization functions $k''_{(1)}$ and $k''_{(2)}$.—The shape of the curves of

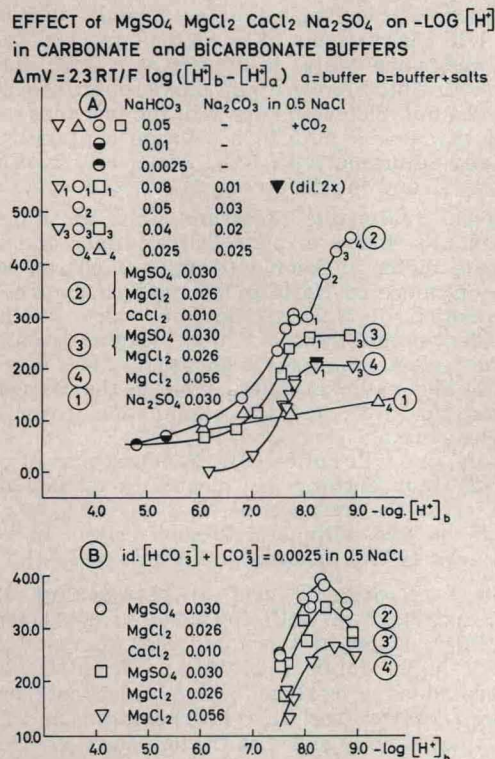


Fig. 6. Glass electrode emf shifts produced by the addition of $MgSO_4$, $MgCl_2$, $CaCl_2$, Na_2SO_4 to bicarbonate and carbonate buffers at atmospheric pressure. A. $[HCO_3^-] + [CO_3^{=}]$ 0.05 - 0.09 in 0.5 NaCl: Curve 1, effect of Na_2SO_4 (0.030); Curve 2, effect of $MgSO_4$ (0.030), $MgCl_2$ (0.026), and $CaCl_2$ (0.010). Precipitates are obtained at points 2, 3, and 4; result at pmH 4.8 corresponds to $[HCO_3^-] + [CO_3^{=}]$ 0.0025; Curve 3, effect of $MgSO_4$ (0.030) and $MgCl_2$ (0.026); Curve 4, effect of $MgCl_2$ (0.056). B. $[HCO_3^-] + [CO_3^{=}] = 0.0025$. (2'), (3'), (4') same as (2), (3), (4).

Fig. 6 which give the emf shifts resulting from the addition of Ca and Mg salts to bicarbonate and carbonate buffers can be understood if one bears in mind that removing a constant amount of $CO_3^{=}$ produces a pmH shift which is maximum at $pmH = \frac{1}{2}(pk'^{m(1)} + pk'^{m(2)})$. When the trapped $CO_3^{=}$ is a function of the initial $CO_3^{=}$ concentration, the maximum is broadened and shifted toward a more alkaline pmH . Removing HCO_3^- produces no shift at $pmH = \frac{1}{2}(pk'^{m(1)} + pk'^{m(2)})$, but results in an acidification or an alkalization at more acid or more alkaline pmH values; HCO_3^- trapping is evident in Fig. 6 in the acid range especially when $CaCl_2$ is added to the more concentrated buffers already containing $MgSO_4$ and $MgCl_2$, but the same operation produces a precipitate at $pmH > 8.1$. No precipitates are observed in the diluted buffers. The data gathered in Fig. 6 can be used to calculate the dissociation constants of $MgCO_3$, $CaCO_3$, $MgHCO_3^+$, and $CaHCO_3^+$ as Garrels *et al.* (12) have done from paH determinations on bicarbonate and carbonate buffers before and after addition of $CaCl_2$ and $MgCl_2$. This problem, which involves lengthy calculations, is quite beyond the scope of the present paper and will not be dealt with.

However, at $pmH_1 \approx 8.0$, Fig. 6 makes it possible to evaluate the apparent second ionization function of carbonic acid, $k''_{(2)}$, in presence of Ca^{++} , Mg^{++} , and $SO_4^{=}$ ions.

For buffers where $[HCO_3^-] + [CO_3^{=}] = 0.0025$, the emf shift due to the addition of 0.030 $MgSO_4$, 0.026 $MgCl_2$, and 0.010 $CaCl_2$ is equal to 38.0 mv at $pmH_1 \approx 8.3$. With $pk'^{c(2)1} = 9.67$ in the pure buffer, this leads to $pk''^{c(2)1} = 9.67 - 0.65 = 9.02$ at $\mu = 0.73$; at $\mu = 0.75$, $pk''^{c(2)1} = 9.015$.

More refined calculations taking into account the true ionization functions $k'^{c(1)}$ (5.89) and $k'^{c(2)}$ (9.49), the equilibrium $2HCO_3^- \rightleftharpoons CO_3^{=} + H_2CO_3$ which is displaced when $CO_3^{=}$ is removed, give a mean value of 9.015 ± 0.015 at $\mu = 0.75$ in the pmH_1 interval 7.9-8.5, with a minimum at 8.3 where $pk''^{c(2)1} = 9.00$. On the molal scale $pk''^{m(2)} = 9.015 - 0.005$, again at $\mu = 0.75$.

The agreement between the directly evaluated value of $pk''^{c(2)1}$ and the calculated one, implies that, in first approximation, HCO_3^- -trapping by Mg^{++} and Ca^{++} must be very small at $pmH_1 \approx 8.0$. Trapping of HCO_3^- to a greater extent than Na ions do, would lead to an apparent lowering of $pk'^{c(1)}$ and also affect $pk''^{c(2)1}$ but in a more complicated way, depending on pH. This problem will not be discussed here, and it will be assumed that between pmH_1 7.9 and 8.5 it is not necessary to introduce a first apparent ionization function, or that $pk'^{c(1)} = pk'^{c(1)}$ in buffers where $[CO_3^{=}] + [HCO_3^-] = 0.0025$.

Since $pk''^{c(2)1} - pk'^{c(2)1} = 0.48$, $[CO_3^{=}]_T \approx 3 [CO_3^{=}]$ and $[Mg - CaCO_3] \approx 2 [CO_3^{=}]$. At pmH_1 8.0 $[HCO_3^-] + [CO_3^{=}] = 0.0025$, $[CO_3^{=}] = 7.34 \cdot 10^{-5}$, $[Mg - CaCO_3] = 1.45 \cdot 10^{-4}$ or 0.22% of the total Ca and Mg concentrations, which is of the order of magnitude (0.28%) given by Garrels *et al.* (12, 15).

In buffers where $[CO_3^{=}] + [HCO_3^-] = 0.09$, $pk''^{c(2)1}$ at pmH_1 8.1 is found equal to 9.12 when directly evaluated from curve 2, Fig. 6A, and equal to 9.10 when calculated at $\mu = 0.84$, taking reaction $2HCO_3^- \rightleftharpoons CO_3^{=} + H_2CO_3$ into consideration and neglecting the possibility of HCO_3^- trapping in the alkaline range. The apparent ionization function $pk''^{c(2)1}$ is thus not only dependent on pH but also on the concentration of the buffering species. This remark is important and needs to be taken into consideration when dealing with data to be valid in natural sea water.

True and apparent ionization functions of carbonic acid, in presence of Mg^{++} , Ca^{++} , and $SO_4^{=}$, in NaCl solutions at 1000 kg. cm^{-2} ($\mu = 0.75$).—Comparison of curves 1 and 2 in Fig. 5 shows that ΔE_{1000} observed in pure buffer solutions is reduced by a constant amount in the presence of 0.030 Na_2SO_4 , between pmH_1 6 and 9.5 (the reference 0.01 HCl + 0.49 NaCl solution has

again the same salt composition as the buffer under test and m_{H^+} is assumed to be equal to m_{HCl} .

Curve 3 indicates that ΔE_{1000} drops progressively from 20.0 mv at $pmH_1 = 6.0$ to 13.1 mv at $pmH_1 = 7.9$ in 0.05 NaHCO₃ + 0.5 NaCl solutions containing 0.030 MgSO₄, 0.026 MgCl₂, and 0.010 CaCl₂ at various concentrations of CO₂.

At pH > 8.1 pressure has been applied to the solutions containing the precipitate (see p. 334). The reported emf shifts correspond to the measurements made during the second or third pressure run. The first run generally gives rather unstable values.

Nearly the same emf shifts are observed at pmH_1 7.8-7.9 with 0.04 MgSO₄ or 0.030 MgSO₄ + 0.026 MgCl₂ with or without 0.010 CaCl₂ (also see Fig. 1 and 3). Lowering of the total CO₂ concentration has not a great effect either. At $[CO_3^{=}] + [HCO_3^{-}] = 0.0025$, where no precipitates are observed, the results (indicated by arrows and curve segment 6 in Fig. 5) are about 0.3-0.4 mv lower than those obtained with buffers where $[CO_3^{=}] + [HCO_3^{-}]$ is between 0.09 and 0.05.

When both NaCl and Mg-Ca salt concentrations are reduced it can be seen from Fig. 1 and 3 that extrapolation to $\mu = 0$ again gives $-\Delta V_{01} = 25.4 \text{ cm}^3 \text{ mole}^{-1}$. The scattering of the results can be explained by the large pH dependence of ΔE_{1000} in the alkaline range.

Adding 0.056 MgCl₂ alone to 0.5 NaCl + 0.05 NaHCO₃, saturated with CO₂, has no or little effect on ΔE_{1000} observed in pure bicarbonate buffer (Fig. 5, curve 4). Between pmH_1 6.2 and 7.85, ΔE_{1000} falls from 22.3 mv to 16.0 mv. The 6.3 mv difference is nearly the same as the 6.5 mv value obtained with 0.030 MgSO₄ + 0.026 MgCl₂ for the same pmH_1 interval. The difference between curve 3 and 4 is obviously due to the sulfate ions, since the total Mg concentration is kept constant.

We already have noticed a similar effect of SO₄⁼ when 0.030 Na₂SO₄ is added to pure bicarbonate buffers (curves 1 and 2 in Fig. 5). The fact that MgSO₄ is less dissociated than Na₂SO₄ probably explains the difference in magnitude between the effects of 0.030 Na₂SO₄ and 0.030 MgSO₄. Since the ordinate difference between curve 4 and 3 is nearly constant, the SO₄⁼ effect of MgSO₄ practically must be constant over the whole pmH_1 range. This observation allows one to extrapolate curve 3 parallel to curves 2 and 1 in the alkaline range (curve 3') and to dissociate the SO₄⁼ effect from the more complicated Mg-Ca effect observed between 6.5 and 9.0.

To interpret the Mg-Ca effect, we will assume that the MgCO₃ and CaCO₃ ion pairs, formed at atmospheric pressure, further dissociate at higher pressures, liberating CO₃⁼ ions which alter the $[CO_2]/[CO_3^{=}]$ ratio of the buffer, eventually shift reaction $2HCO_3^{-} \rightleftharpoons CO_3^{=} + H_2CO_3$, and thus oppose the acidification induced by pressure and caused by the dissociation constants shifts. This assumption leads to the admission that $\log k^{m_{1000}}/k^{m_1}$, in presence of MgCl₂ has the same value, for each true ionization function, as found in pure bicarbonate buffer at the same pmH_1 and ionic strength, not only between pmH_1 5.5 and 7.0, but throughout the whole pmH_1 range. When MgSO₄ is substituted for part of the MgCl₂, $\log k^{m_{1000}}/k^{m_1}$ is lowered by an amount corresponding to the SO₄⁼ effect. One can then use the same arguments developed above and measure $pk'_{(1)}$ and $pk'_{(2)}$ at pmH_1 7.0 and 8.5, respectively, on curve 3 and 3'.

One thus finds that at $\mu = 0.75$, $[CO_3^{=}] + [HCO_3^{-}] = 0.0025$, $\log k^{m_{1000}}/k^{m_1} = 0.316$ (18.5 mv) for $k'_{(1)}$ and 0.283 (16.5 mv) for $k'_{(2)}$. In more concentrated buffers, these values become 0.325 (19.0 mv) and 0.290 (17.0 mv) at the same ionic strength and pmH_1 .

At pmH_1 8.5, Fig. 5 further allows to obtain a direct estimate of the effect of pressure on the apparent ionization function $pk''_{(2)}$. At $[HCO_3^{-}] + [CO_3^{=}] = 0.0025$, $\log k^{m_{(2)1000}}/k^{m_{(2)1}} = 0.178$ ($\Delta E_{1000} = 10.4$

mv). A more elaborate treatment using $pk^{m_{(1)1000}}$ and $pk^{m_{(2)1000}}$, taking into account the equilibrium $2HCO_3^{-} \rightleftharpoons CO_3^{=} + H_2CO_3$, the amount of MgCO₃ formed at atmospheric pressure, shows that $\log k^{m_{(2)1000}}/k^{m_{(2)1}}$ increases from 0.178 at pmH_1 8.5, to 0.187 at 8.0, 0.190 at 7.9, and 0.214 at 7.6. A mean value of 0.183 \pm 0.005 can be taken in the pmH_1 interval 8.0-8.5. The same value can be read from Fig. 5 at $pmH_1 = 8.5$ for the more concentrated buffers.

The effect of pressure on $pk''_{(1)}$ needs not be considered in the alkaline range since we have admitted that between pmH_1 7.9 and 8.5, $pk'_{(1)} = pk''_{(1)}$. At $pmH_1 \leq 7.0$, comparison of the curves of Fig. 5 and 6 for the more concentrated buffers, where HCO₃⁻ trapping by Ca⁺⁺ seems obvious, shows that pressure must have only a very small effect on the dissociation of any trapped HCO₃⁻ ions.

Dissociation of carbonic acid in natural sea water (Cl = 20‰) at high pressures; effect of boric acid.—The reference compartment of the glass electrode contains 0.49 NaCl, 0.01 HCl, 0.030 MgSO₄, 0.026 MgCl₂ and 0.010 CaCl₂.

The sea water samples come from the Atlantic Ocean (north of Spain, Cl ‰ = 19.5) and have been equilibrated with CO₂ + N₂ mixtures, or small amounts of Na₂CO₃ have been added to cover the 5.0-9.0 pmH_1 interval. The emf shifts produced by increasing pressure from 1 atm to 1000 kg. cm⁻² are corrected in Fig. 5 at $\mu = 0.75$ (Cl ‰ = 20.0). Scattering is higher than with artificial buffers; nevertheless, it is obvious that from pmH_1 5.0 to about 7.25 (curve 5), sea water follows the general pattern observed in bicarbonate buffers with added Mg, Ca, and sulfate ions. The quantitative agreement is good, although the data for natural sea water are about 0.3-0.4 mv below these for artificial sea water (arrows in Fig. 5). Extrapolation of the curve drawn in the acid range (curves 5 and 5'), parallel to curves 1, 2, 3', allows one to obtain $\log k^{m_{1000}}/k^{m_1}$ for the first and second dissociation step: 0.314 (18.3 mv) and 0.278 (16.3 mv), respectively, at $pmH_1 = 7.0$ and 8.5. This corresponds to the shift of the true ionization functions which are assumed to have the same value at 1 atm as the corresponding functions determined in artificial sea water (see above).

At pH > 7.25, the data for natural sea water progressively depart from the results in artificial sea water containing Mg⁺⁺, Ca⁺⁺, and SO₄⁼. At pH 8.5-9.0, ΔE_{1000} is about 3.0 mv higher in natural sea water and to nearly duplicate these results, 0.43 10^{-3} H₃BO₃ must be added, the pmH_1 being adjusted by the $[HCO_3^{-}]/[CO_3^{=}]$ ratio (curve 6', Fig. 5). The ordinate difference between curve 6' and the corresponding emf shifts observed in artificial sea water without boric acid is given by curve 7 which shows the effect of boric acid between pmH_1 6.5 and 9.0.

Preliminary experiments to investigate the effect of pressure on the dissociation of boric acid show that in NaCl 0.1, $\Delta V_{1'}$ extrapolates to $-29.0 \text{ cm}^3 \text{ mole}^{-1}$ at zero borate buffer (H₃BO₃ + borax) concentration, to $-30.7 \text{ cm}^3 \text{ mole}^{-1}$ in NaCl 0.01 and to $-31.4 \text{ cm}^3 \text{ mole}^{-1}$ in NaCl 0.001; $\Delta V_{1^0} = -32.1 \text{ cm}^3 \text{ mole}^{-1}$. In 0.5 NaCl + 0.030 MgSO₄ + 0.026 MgCl₂ and 0.010 CaCl₂, at pH 7.9, $\Delta V_{1'}$ is equal to $-23.1 \text{ cm}^3 \text{ mole}^{-1}$ (22.7 mv) at zero borate concentration, and the same value can be used at the boron concentration of sea water. Since in sea water $pk^{m_{(1)1}} = 8.605$ for boric acid ($pk^{c_{(1)1}} - \log y_{H^+} = pK^{c_{(1)1}} = 8.72$ [Lyman (13)], $pk^{m_{(1)1000}} = 8.605 - 0.39 = 8.215$). These values correspond fairly well to the pmH_1 at which curve 7 of Fig. 5 reaches a maximum. It is also easy to verify that at $pmH_1 = 8.353$ and $[HCO_3^{-}] + [CO_3^{=}] = 0.0025$, the increase in HCO₃⁻ concentration at 1000 kg. cm⁻² ($pmH_{1000} = 8.124$), calculated from the values of $pk^{m_{(2)}}$ and $pk^{m_{(1)}}$ for carbonic acid, obtained in artificial sea water without boric acid, corresponds to the decrease in H₃BO₃ concentration, estimated from $pk^{m_{(1)}}$ and

$pk^{m(1)1000}$ found for boric acid in sea water ($\Delta[\text{HCO}_3^-]_T = 0.39 \cdot 10^{-4}$; $\Delta[\text{H}_3\text{BO}_3] = 0.38 \cdot 10^{-4}$).

The interpretation of the pH changes induced by pressure in natural sea water is thus far from simple. The enhanced dissociation of carbonic acid observed in NaCl at the corresponding ionic strength is modified by the presence of sulfate ions, by the dissociation of MgCO_3 and CaCO_3 , and by the dissociation of boric acid. The two last effects are pH dependent, and reaction $\text{H}_3\text{BO}_3 + \text{CO}_3^{2-} \rightleftharpoons \text{HCO}_3^- + \text{H}_2\text{BO}_3^-$ must be considered.

Without going into the details of a quantitative analysis, it is immediately clear that the emf shifts observed at $pm\text{H}_1 > 8.0$ in artificial sea water containing boric acid or in natural sea water cannot be used for a direct estimation of $\Delta pk''_{(2)}/\Delta p$ for the second apparent ionization function; instead, $pk''_{(2)p}$ has to be taken equal to the corresponding function determined in artificial sea water without boric acid in order to calculate $[\text{CO}_3^{2-}]_T$ and $[\text{HCO}_3^-]_T$ at pressure p . In artificial sea water, in absence of boric acid, $\log k''_{m(2)1000}/k''_{m(2)1} = 0.183 \pm 0.005$ from $pm\text{H}_1$ 8.0 to 8.5; in natural sea water, since ΔE_{1000} is somewhat lower, $\log k''_{m(2)1000}/k''_{m(2)1}$ will be taken equal to 0.178 ± 0.005 in the same $pm\text{H}_1$ interval. If the greatest precision is required, the pH dependence of $\log k''_{m(2)1000}/k''_{m(2)1}$ must be taken into account (see p. 335). The value of $pk''_{(2)}$ at 1 atm found in artificial sea water without boric acid (9.01, see p. 334) is taken to be the same in natural sea water. The complete set of ionization functions which we believe to be valid in natural sea water at 1 atm and at 1000 bars, within our basic assumptions, is given in Table II.

Some of the results of Fig. 5 have been indicated in Fig. 1 together with data obtained with 0.01 HCl + 0.49 NaCl as reference half-cell, and which are in agreement with our earlier results (4). $\Delta E_{1000} = 16.7$ mv instead of 13.4 mv at $pm\text{H}_1$ 7.8; the difference of 3.3 mv is due to the effect of pressure on γ_{HCl} in the presence of $\text{MgSO}_4 + \text{MgCl}_2 + \text{CaCl}_2$ compared to γ_{HCl} in pure HCl or HCl + NaCl (see below). Dilution of sea water leads to erratic pressure-induced emf shifts, but sea water + 0.05 NaHCO_3 , CO_2 1% can be diluted, and the extrapolation of the results to $\mu = 0$ gives $\Delta V_1^\circ = -25.4 \text{ cm}^3 \text{ mole}^{-1}$ identical with the value found in pure bicarbonate (Fig. 1).

Apparent values of γ_{HCl} , y_{H^+} in HCl + NaCl in presence of Mg^{++} , Ca^{++} , SO_4^{2-} ; effect of pressure.—The apparent mean activity coefficient of 0.01 HCl on the molal scale in presence of 0.5/n — 0.01 NaCl, MgSO_4 , $\text{MgSO}_4 + \text{MgCl}_2$, $\text{MgSO}_4 + \text{MgCl}_2 + \text{CaCl}_2$ is given in Fig. 7 for several values of n assuming $m_{\text{H}^+} = m_{\text{HCl}}$. The reference half-cell was filled with HCl 0.01, NaCl 0.09. The data for pure NaCl or KCl + HCl solutions are taken from Harned and Owen (10), and control experiments show that our results fit these curves with an error not greater than ± 0.002 . From Eq. [6], $\log \gamma$ can be calculated from $\log \gamma$: in NaCl solutions at $\mu = 0.5$ $\log \gamma = \log y - 0.004$; the correction factor is -0.0047 , -0.0055 , -0.0063 , -0.0071 , -0.008 at $\mu = 0.6, 0.7, 0.8, 0.9, 1.0$, and -0.006 at $\mu = 0.75$. At $\mu = 0.75$ in sea water, the correction becomes -0.004 .

MgCl_2 alone has a much smaller effect on γ_{HCl} : addition of 0.056 MgCl_2 to 0.49 NaCl + 0.01 HCl makes $\log \gamma_{\text{HCl}}$ drop from 1.864 to 1.849.

The pressure dependency of γ_{HCl} in 0.01 HCl + 0.49 NaCl containing MgSO_4 , $\text{MgSO}_4 + \text{MgCl}_2$ is represented in Fig. 8 either with 0.01 HCl + 0.49 NaCl as reference half-cell or 0.1 HCl. It is clear that MgSO_4 is the main cause involved.

In the preceding sections, it has been assumed continuously that γ_{HCl} measured in 0.01 HCl + 0.49 NaCl + 0.030 MgSO_4 + 0.026 MgCl_2 + 0.010 CaCl_2 has the same value in carbonate and bicarbonate buffers containing the same salts, in the range $[\text{CO}_3^{2-}] + [\text{HCO}_3^-] = 0.09 - 0.0025$. That the specific salt effect

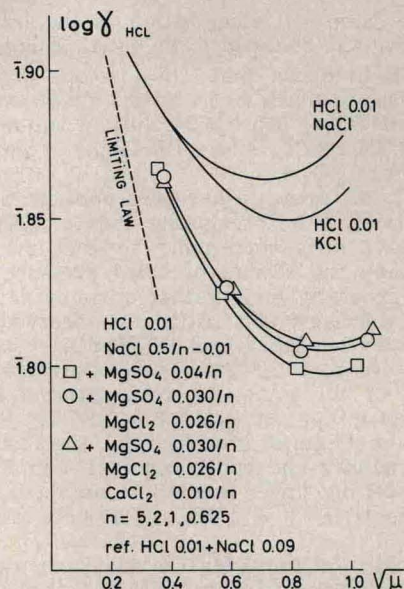


Fig. 7. Mean activity coefficient (γ_{HCl}) of HCl in NaCl, KCl; apparent values in presence of MgSO_4 , MgCl_2 , CaCl_2 as a function of $\sqrt{\mu}$.

of CO_2 , CO_3^{2-} , HCO_3^- is small, is demonstrated by Fig. 1, 2, 3, and 4, where it can be seen that changing the buffer concentration (at a given buffer ratio for Fig. 2 and 4) has about the same effect as changing the ionic strength. Comparison of the data of Fig. 5 further shows that lowering the $[\text{CO}_3^{2-}] + [\text{HCO}_3^-]$ concentration from 0.09 to 0.0025 has only a very small effect on ΔE_{1000} at a given ionic strength (0.75).

Figure 7 also indicates that γ_{HCl} is fairly independent of μ in the region of the ionic strength of sea water. Corrections for salinity differences are thus very small; corrections however have to be made to take into account the eventual difference in Cl^- content between both glass electrode compartments, in order to calculate $-\log [\text{H}^+]$, assuming γ_{HCl} to be equal in both solutions. Ordinary $pa\text{H}$ electrodes with liquid junctions at first sight appear to be simpler to use, since the exact composition of the reference glass electrode half-cell does not have to be known with precision. However, conventional $pa\text{H}$ electrodes display a much more sluggish response and great errors can be introduced

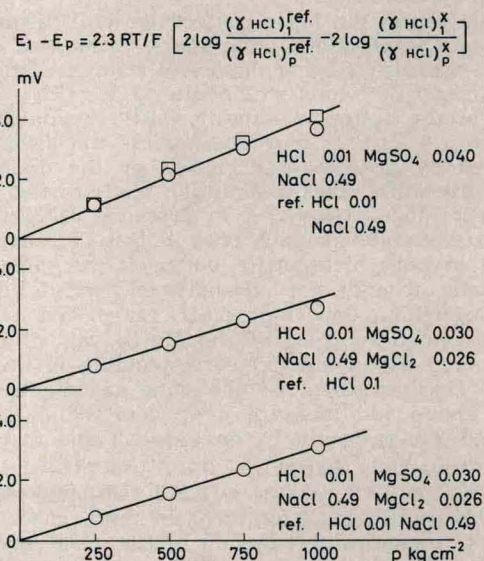


Fig. 8. Effect of pressure on $2 \log (\gamma_{\text{HCl}})_{1}^{\text{ref}} / (\gamma_{\text{HCl}})_{p}^{\text{ref}} - 2 \log (\gamma_{\text{HCl}})_{1}^{x} / (\gamma_{\text{HCl}})_{p}^{x}$, $2.3 \text{ RT}/F = E_1 - E_p$, where $^{\text{ref}}$ and x correspond to the inner and outer compartment of the glass electrode cell; effect of MgSO_4 and MgCl_2 .

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 + $MgSO_4$ + $MgCl_2$ + $CaCl_2$. 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

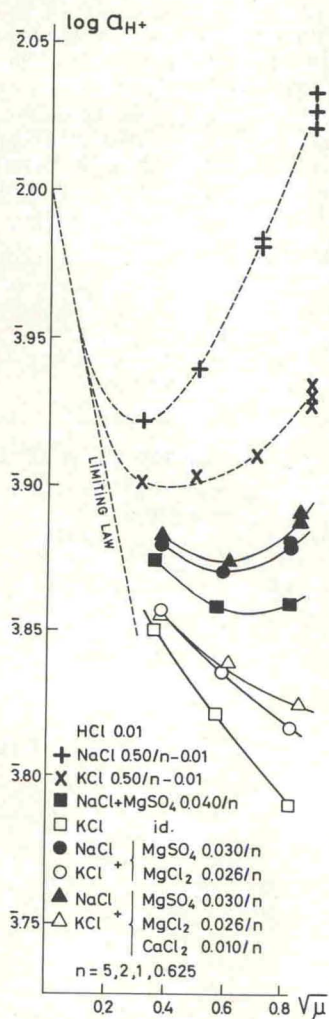


Fig. 9. Hydrogen ion activity ($\log a_{H^+}$), in 0.01 HCl + NaCl or KCl, in presence or not of $MgSO_4$, $MgCl_2$, $CaCl_2$ as a function of $\sqrt{\mu}$ (glass electrode with calomel electrodes and sat. KCl agar-agar salt bridges).

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 $\gamma_m = \gamma_c/\rho$ (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 HCO_3^- trapping by Mg and Ca is very small or inexistent (see Fig. 6A), but where the effect of $SO_4^{=}$ 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, HCO_3^- trapping by Mg and Ca must be small in sea water, or that the HCO_3^- 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 ($[CO_3^{=}] + [HCO_3^-] = 0.05 - 0.09$) HCO_3^- 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 HCO_3^- trapping persists in the alkaline range when $CO_3^{=}$ 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 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 $\Delta V_1^0 = -28.0$ cm^3 mole⁻¹ for the first ionization step of carbonic acid and $\Delta V_1^0 = -10.5$ cm^3 mole⁻¹ for the second step assuming that the HCO_3^- 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

* $\log y_{H^+}c_{H^+} = \log \gamma_{H^+}m_{H^+} + 0.016$ 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 $-\log y_{H_2O} = 0.11$.

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 y_{H^+} at 1 atm. It is thus theoretically possible to calculate $y_{HCO_3^-}$ and $y_{CO_3^{2-}}$ in the various bicarbonate and carbonate buffers investigated including sea water, since y_{CO_2} is known with rather good precision (9, 15).

The determination of y_{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
Ionization functions and dissociation constants shift at 1000 bars	$pk'_{(1)}, pk''_{(1)}, pK''_{(1)}$		$pk'_{(2)}, pK''_{(2)}$		$pk'_{(2)}$		$pk''_{(2)}, pK''_{(2)}$	
	c	m	c	m	c	m	c	m
	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.

If one admits that the pressure dependence of γ_{H^+} can be neglected, then the effect of pressure, compared with data from Buch and Gripenberg (16), shows fortuitous agreement for the second apparent dissociation constant in the pmH_1 interval 8.0-8.5 (on the molal scale at 1000 bars, $pK''_{(2)} = 0.181$ against 0.180), but the effect of pressure on the first constant is much less than that predicted by these authors (at 1000 bars, $pK''_{(1)} = 0.320$ instead of 0.480).

The comparison must be considered with caution since we do not know the absolute values of the ionization functions and apparent dissociation constants, but it shows that one cannot simply assume, as Buch and Gripenberg did, that H_2CO_3 dissociates at high pressure in sea water in the same manner as at zero ionic strength and that HCO_3^- behaves as acetic acid.

The reduced effect of pressure on the apparent second dissociation constant of carbonic acid in sea water at $pmH_1 > 8.0$ corresponds to an apparent volume change of $-10.6 \text{ cm}^3 \text{ mole}^{-1}$ instead of $-25.6 \text{ cm}^3 \text{ mole}^{-1}$ observed at 0 ionic strength. This can be understood by taking into consideration: 1° the effect of NaCl on the pressure dependence of the mean activity coefficient of H_2CO_3 and HCO_3^- ; 2° the effect of sulfate ions which does not depend on pH; and 3° the formation of $MgCO_3$ and $CaCO_3$ at atm pressure which dissociate under pressure, liberating CO_3^{2-} ions which alter the buffer ratio, the whole process being pH dependent.

The increased dissociation of boric acid, the result of which is again a function of the hydrogen ion concentration, explains why the pmH or pcH shift observed in sea water is progressively larger from pmH_1 7.0 to 9.0 than that predicted from the effect of pressure on the apparent ionization function of HCO_3^- , measured in artificial sea water without boric acid. Factors 1°, 2°, and 3°, on the contrary, really or apparently depress the effect of pressure on the ionization of carbonic acid. $MgCO_3$ and $CaCO_3$ thus appear to have a buffering action against hydrogen ion concentration changes induced by pressure in sea water although boric acid progressively and partially counteracts this effect at pmH_1 values greater than 7.0.

Starting from these considerations one might imagine that other buffer systems involving ion pairs or complex ions able to liberate anions capable of binding H^+ ions, could be prepared, where $\Delta pmH/\Delta p$ would be very small. Such media would be very useful in, for instance, the study of the specific effect of pressure on biological systems. Furthermore, if the effect of pressure on a given acid-base equilibrium is well known, changes produced by the pressure induced dissociation of added ion pairs offer a way to demonstrate their existence at atmospheric pressure.

The results which we have obtained at 1000 kg. cm^{-2} in pure carbonate and bicarbonate buffers in NaCl or KCl show, for example, that probably more ion pairs exist in NaCl than in KCl, in correlation with the difference observed for the corresponding ionization functions at atmospheric pressure. This observation might prove a clue to interpret the anomalies encountered when ΔV_1° is computed from glass electrode measurements by extrapolation at zero ionic strength (3). The values obtained in pure acid are always somewhat higher than in the corresponding buffers ($-26.5 \text{ cm}^3 \text{ mole}^{-1}$ in H_2CO_3 , $-25.4 \text{ cm}^3 \text{ mole}^{-1}$ in bicarbonate buffer, for example). This effect could be explained if ion pairs still exist at the highest dilutions which are practical for precise emf determinations.

ADDENDUM¹

Interpretation of the SO_4^{2-} -effect.—It has been assumed in the preceding pages that $m_{H^+} = m_{HCl} = 0.01$ in the reference half-cells containing 0.03 $MgSO_4$ and the effect of SO_4^{2-} ions on the observed emf values have therefore been interpreted as a change which affects $k'_{(1)}$, $k'_{(2)}$, γ_{HCl} and γ_{H^+} . This " SO_4^{2-} effect",

¹ Added on proof.

observed in presence of NaCl + $MgCl_2$ and $CaCl_2$, is uncommonly large and of the same order of magnitude in each case as shown by the data obtained at $\mu = 0.75$:

	in NaCl	in sol. + $MgSO_4$	Δ
$pk'_{(1)}$	6.00	5.89	0.11
$pk'_{(2)}$	9.60	9.49	0.11
$2 \log \gamma_{HCl}$	1.734	1.617	0.117
$\log \gamma_{H^+}$	0.017	1.887	0.13

Further, at 1000 kg cm^{-2} , SO_4^{2-} ions apparently increase $pk'_{(1)}$ and $pk'_{(2)}$ by a constant amount which corresponds to an emf shift between 2.0 and 2.7 mv, depending on the buffer concentration (Fig. 5), whereas the effect of the same pressure on the reference half-cell containing SO_4^{2-} is equal to 3.3 mv (Fig. 8). It actually appears that the greatest part of the SO_4^{2-} effect must find its explanation in the formation of SO_4H^- ions in the reference half-cell, which invalidates the assumption $m_{H^+} = m_{HCl}$ [see Jones and Monk (17)]. Taking $K_{HSO_4^-} = 1.13 \cdot 10^{-2}$, $\gamma_{SO_4^{2-}} = 0.12$, $\gamma_{HSO_4^-} = 0.68$, assuming 54% of the sulfate to be free ions [see the data of Garrels and Thompson for sea water (15)] and $a_{H^+} = 7.7 \cdot 10^{-3}$ ($paH = 2.113$, see Fig. 9), one finds $pmH_1 = 2.088$ instead of 2.00, which accounts for 80% of the apparent SO_4^{2-} effect on $pk'_{(1)}$ and $pk'_{(2)}$ at 1 atm. One will notice that $2 \log \gamma_{HCl} = 1.698$ in 0.01 HCl + 0.49 NaCl + 0.056 $MgCl_2$ (see p. 336) and that at the same ionic strength, $2 \log \gamma_{HCl}$ in 0.01 HCl + NaCl is equal to 1.730. Although the salt effects of individual ions are not necessarily additive, the difference 0.032 indicates that the SO_4^{2-} effect is probably not larger than the calculated value 0.088, since the total effect of SO_4^{2-} and Mg^{++} is equal to 0.117. In other words, pmH_1 in the SO_4^{2-} containing reference solutions is found equal to 2.085 if one assumes that γ_{HCl} in 0.01 HCl + 0.49 NaCl + 0.030 $MgSO_4$ + 0.026 $MgCl_2$ has the same value as that derived from measurements in 0.01 HCl + 0.49 NaCl + 0.056 $MgCl_2$. At 1000 kg cm^{-2} , with $K_{HSO_4^-} = 2.26 \cdot 10^{-2}$, $pmH_{1000} = 2.043$; the difference $pmH_1 - pmH_{1000} = 0.045$ represents equally 80% of the effect of pressure observed in Fig. 8. Further studies on the equilibrium of sulfuric acid will be necessary to verify these estimates, especially since $-\Delta V_1^\circ$ for SO_4H^- is only known from density measurements, with values between 12.0 and 20.6 $cm^3 \text{ mole}^{-1}$ (Hamann, private communication).

If the above corrections were valid, then the values of pk' , pk'' , pmH given in this paper would have to be increased by 0.09 at 1 atm; the calculated values of paH_1 in Table I and the values of $pK''_{(1)1}$, $pK''_{(2)1}$ remain unchanged whatever the correction; $\Delta pk'$, $\Delta pk''$ at 1000 kg cm^{-2} and the corresponding ΔpH would have to be increased by 0.045.

These corrections would lead to another coherent set of dissociation functions to calculate the equilibrium of H_2CO_3 in sea water from the corresponding corrected pmH measurements giving exactly the same results as the set of functions of Table II.

Although a precise knowledge of the salt effect of SO_4^{2-} ions is needed for an approach toward the absolute values of $k_{(1)}$, $k_{(2)}$, and pmH in sea water, this search is only of academic interest for most of the oceanographic calculations. Finally, it appears that these could best be made from straight forward $pwH = -\log m_{H^+} \gamma_{H^+} \gamma_{Cl^-}$ determinations at any pressure (using half-cells without SO_4^{2-}) and apparent constants defined as $K'' \gamma_{Cl^-} = k' \gamma_{H^+} \gamma_{Cl^-}$, thus keeping the advantages of junctionless cells and eliminating the apparent arbitrariness of the different systems of ionization functions. Sufficient data are given in this paper to make this conversion, since the effect of pressure on γ_{HCl} can easily be calculated in pure HCl [see Harned and Owen (10), p. 507].

Acknowledgment

The authors wish to express their gratitude to Dr. R. G. Bates, Chief of Electrochemical Analysis Section, National Bureau of Standards, to Professor B. B. Owen, of the Scripps Institute of Oceanography, to Professor R. Pytkowicz and Dr. Culberson, Oceanography Department, Oregon University, for their help in preparing and discussing the manuscript.

Manuscript received July 5, 1966; revised manuscript received Dec. 14, 1966.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1967 JOURNAL.

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