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ABSTRACT

The effect of pressure on the dissociation of carbonic acid has been investigated over a wide range of *p*H (*pa*H 5.1-9.6) and ionic strength (0-1.0) in NaCl and KCl, using junctionless glass electrode cell measurements. At 22°C, $\Delta V_1° = -25.4$ cm^3 mole^{-1} and -25.6 cm^3 mole^{-1} for the first and second ionization steps, respectively. The directly measured *pm*H or *pc*H shifts induced by pressure in sea water between paH_1 5.1 and 9.1 are explained by the enhanced dissociation of H_2CO_3, HCO_3^-, $CaCO_3$, and $MgCO_3$, the effect of $SO_4^=$ and the interference of boric acid ($\Delta V_1° = -32.1$ cm^3 mole^{-1}). Values of the ionization functions $k'_{(1)} = [H^+][HR^-]/[H_2R]$ and $k'_{(2)} = [H^+][R^=]/[HR^-]$ 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 $[CO_3^=]_{total}$, $[HCO_3^-]_{total}$ from *in situ pa*H 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 $HR \rightleftharpoons H^+ + R^-$ by the equation

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

Data are available for $\Delta V_1°$ at atmospheric pressure, zero salt concentration, and zero weak electrolyte concentration for carbonic acid calculated from density measurements, conductivity, and glass electrode determinations:

Reaction	Density, 25°C $-\Delta V_p°$ ($p = 1$ atm) cm^3 mole^{-1}	Conductivity, 25°C $-\Delta V_p°$ ($p = 1$ atm) cm^3 mole^{-1}	Glass electrode, 22°C $-\Delta V_p°$ ($p = 1$ atm) cm^3 mole^{-1}
$H_2CO_3 \rightarrow HCO_3^- + H^+$	29.0 (1)	26.5 (2)	26.6 (3) (unbuffered cell) 25.5 (3) (buffered cell) 25.4 (this paper; buffered cell)
$HCO_3^- \rightarrow CO_3^= + H^+$	27.8 (1)	—	25.6 (this paper; buffered cell)

The $\Delta V_1°$ 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 $k_{(1)}$, $k_{(2)}$ ($k_{(1)} = [H^+][HCO_3^-]/[CO_2]$, $k_{(2)} = [H^+][CO_3^=]/[HCO_3^-]$) in presence of NaCl or KCl, over a wide ionic strength range (0-0.8), at various buffer ratios (*pa*H 5.1-9.6). The effect of Ca^{++}, Mg^{++}, and $SO_4^=$ 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:

$$\text{Ag} - \text{AgCl} \;\left|\; \begin{array}{c}\text{Ref. compartment}\\ \text{HCl }(0.01)\\ \text{MCl }(m_3 - 0.01)\end{array} \;\right|\; \text{glass} \;\left|\; \begin{array}{c}\text{x compartment}\\ \text{HR}(m_1) + \text{MR}(m_2)\\ \text{MCl }(m_3)\end{array} \;\right|\; \text{AgCl} - \text{Ag}$$

where M represents Na or K.

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

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

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

$$(E_1 - E_p)\mathbf{F}/2.3\,RT = \log\frac{K^m{}_p}{K^m{}_1} + 2\log\frac{\gamma_{A1}}{\gamma_{Ap}} + 2\log\frac{(\gamma_{HCl})^{ref}{}_1}{(\gamma_{HCl})^{ref}{}_p} - 2\log\frac{(\gamma_{HCl})^{x}{}_1}{(\gamma_{HCl})^{x}{}_p} \qquad [3]$$

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

$$(E_1 - E_p)\,\mathbf{F}/2.3\,RT = \log\frac{K^m{}_p}{K^m{}_1} + 2\log\frac{\gamma_{A1}}{\gamma_{Ap}} = \log\frac{k'^m{}_p}{k'^m{}_1} \qquad [4]$$