

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.

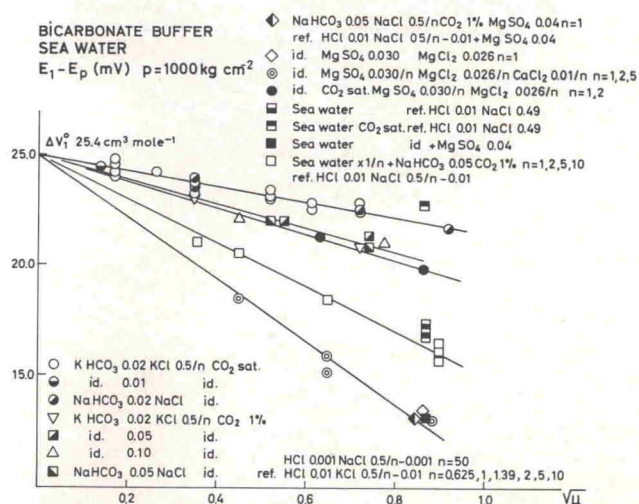


Fig. 1. Glass electrode emf shifts at 22°C produced by pressure (1000 kg. cm^{-2}) in bicarbonate buffers, at different buffer ratios, as a function of $\sqrt{\mu}$, in NaCl, KCl, in presence of Mg^{++} , Ca^{++} , SO_4^- ions, and in sea water.

