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  $\mu$ , and then to zero KCl or NaCl concentration, is not required.

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

Concentrations (m) and activity coefficients  $(\gamma)$  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  $\gamma$ , 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  $K^c$ ,  $k^c$ ,  $K^m$ ,  $k^m$ 

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

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

$$\gamma = \eta [(d - \Sigma c_i M_i / 1000) / d_2]$$
 [6]

$$m_{\gamma}d_{o} = cy$$
 [7]

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

 $\log K^{m}_{p}/K^{m}_{1} = \log K^{c}_{p}/K^{c}_{1} - \log d_{op}/d_{o1}$ [9]

$$\log k^{m}_{p}/k^{m}_{1} = \log k^{c}_{p}/k^{c}_{1} - \log d_{p}/d_{1}$$
 [9']

Combining [7] and [2] gives

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

If the activity coefficients can be made to cancel in both ref and x compartments of the glass electrode,  $(E_1 - E_p)\mathbf{F}/2.3 \text{ RT}$  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  $\mu$  (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,  $c \simeq m$  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  $m_{\rm H}$  + needs be computed in the reference solution, since  $m_{\rm Cl}$ - $^{\rm x} = m_{\rm Cl}$ - $^{\rm ref}$ .

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<sup>+</sup>] 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<sup>-2</sup> (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.<sup>1</sup>  $n^{\circ}$  18331 unsensitive toward Na<sup>+</sup> 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  $\Delta E_{1000}$ is generally between 0 and  $\pm 1.0$  mv. Higher values indicate defective Ag-AgCl electrodes.

Highest grade reagents (Merck) and air-free bidistilled 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 atm and p = 1000 kg.  $cm^{-2}$ .—Figure 1 shows  $\Delta E_{1000}$  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  $-\Delta V_{1^0} = 25.4$  cm<sup>3</sup> mole<sup>-1</sup>, 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  $\mu$  at p = 1 atm and  $pK^{c}_{(1)p} + \log d_p/d_1$  at p = 1000 kg. cm<sup>-2</sup> (log  $d_p/d_1 = 0.017$ ). The absolute values of  $pK^{c}_{(1)}$  (6.38) and  $pk'^{c}_{(1)}$  are

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  $(y_{\text{HCI}})^{\text{ref}}/(y_{\text{HCI}})^{\text{x}}$  term in Eq. [1] (c scale) is calculated from the values of  $\gamma_{\text{HCI}}$ in NaCl and KCl taken from Harned and Owen (10). It is assumed that  $\gamma_{\text{HCI}}$  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  $\mu \ge 0.5$ ,  $\gamma_{\text{HCI}}$  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,

<sup>1</sup> Electronic Instruments Limited, Richmond, Surrey, England.



Fig. 1. Glass electrode emf shifts at 22°C produced by pressure (1000 kg.cm<sup>-2</sup>), in bicarbonate buffers, at different buffer ratios, as a function of  $\sqrt{\mu}$ , in NaCl, KCl, in presence of Mg<sup>++</sup>, Ca<sup>++</sup>, SO<sub>4</sub><sup>=</sup> ions, and in sea water.

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Fig. 2. First ionization function  $(k'c_{(1)})$  of carbonic acid and as a function of  $\mu$  at atm pressure and 1000 kg.cm<sup>-2</sup> in NaCl and KCl at 22°C. Effect of MgSO<sub>4</sub> + MgCl<sub>2</sub>.

-0.0081, -0.009 at  $\mu$ 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 = 1000kg. cm<sup>-2</sup>.—Figure 3 gives  $\Delta E_{1000}$  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  $-\Delta V_1^{\circ} = 25.6$  cm<sup>3</sup> mole<sup>-1</sup>, which is practically the same result obtained in bicarbonate buffers. The value calculated by Owen and Brinkley (1) from density determinations is 27.8 cm<sup>3</sup> mole<sup>-1</sup>.

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<sup>-2</sup>; the results in 0.5 and 0.8 NaCl do not depend on the buffer ratio and are identical either with NaHCO<sub>3</sub> 0.08 + Na<sub>2</sub>CO<sub>3</sub> 0.01 or with NaHCO<sub>3</sub> 0.025 + Na<sub>2</sub>CO<sub>3</sub> 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,  $\Delta E_{1000}$  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<sup>-2</sup>) in carbonate buffers, at different buffer ratios, as a function of  $\sqrt{\mu_{\nu}}$  in NaCl or KCl, in presence of Mg<sup>++</sup>, Ca<sup>++</sup>, SO<sub>4</sub><sup>=</sup>, and in sea water.



Fig. 4. Second ionization function  $(k'^{c}_{(2)})$  of carbonic acid as a function of  $\sqrt{\mu}$  at atm pressure and 1000 kg.cm<sup>-2</sup> in NaCl and KCl at 22°C. Sulfate effect of 0.030 MgSO<sub>4</sub> (+0.026 MgCl<sub>2</sub>).

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

Curves 1 and 1' from Fig. 5 give  $\Delta E_{1000}$  at  $\mu = 0.75$  (ionic strength of sea water at  $Cl\%_0 = 20.0$ ) as a function of  $pmH_1$ , in NaCl and KCl. The emf shifts depend only slightly on the total CO<sub>2</sub> concentration in the range investigated ([HCO<sub>3</sub>-] + [CO<sub>3</sub>-] 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  $pmH_1 \ge 8.5$  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  $Na^+ - CO_3^=$  or  $Na^+$ NaCO3<sup>-</sup> will dissociate under pressure, and free  $CO_3$  = 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  $CO_3^{=}$  than sodium ions also have a much larger lowering effect on the emf changes produced by pressure in carbonate buffers.

Since  $K^+$  or Na<sup>+</sup> may also form ions pairs with  $HCO_3^-$ , 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  $NaCO_3^-$  and  $NaHCO_3$  would have to be taken into account and also the equilibrium  $2HCO_3^- \rightleftharpoons CO_3^- + H_2CO_3$ , which is displaced when  $CO_3^-$  or  $HCO_3^-$  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<sup>-2</sup>, [CO<sub>3</sub>=] and [HCO<sub>3</sub>-] refer to the total concentration of CO<sub>3</sub>= of HCO<sub>3</sub>-, 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  $\Delta E_{1000}$  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 ( $\Delta E_{1000} = 19.0 \text{ mv}$ ) and 0.350 ( $\Delta E_{1000} = 20.8 \text{ mv}$ ) in NaCl and KCl, respectively.