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 $pmH_1 = 7.90$ in 0.05 $NaHCO_3$ + 0.5 NaCl solutions containing 0.030 $MgSO_4$, 0.026 $MgCl_2$, and 0.010 $CaCl_2$ at various concentrations of CO_2.

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 $MgSO_4$ or 0.030 $MgSO_4$ + 0.026 $MgCl_2$ with or without 0.010 $CaCl_2$ (also see Fig. 1 and 3). Lowering of the total CO_2 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 $-\Delta V^o_1 = 25.4$ cm^3 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 $MgCl_2$ alone to 0.5 NaCl + 0.05 $NaHCO_3$, saturated with CO_2, 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 $MgSO_4$ + 0.026 $MgCl_2$ 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 $SO_4^=$ when 0.030 Na_2SO_4 is added to pure bicarbonate buffers (curves 1 and 2 in Fig. 5). The fact that $MgSO_4$ is less dissociated than Na_2SO_4 probably explains the difference in magnitude between the effects of 0.030 Na_2SO_4 and 0.030 $MgSO_4$. Since the ordinate difference between curve 4 and 3 is nearly constant, the $SO_4^=$ effect of $MgSO_4$ 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 $SO_4^=$ 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 $MgCO_3$ and $CaCO_3$ ion pairs, formed at atmospheric pressure, further dissociate at higher pressures, liberating $CO_3^=$ ions which alter the $[CO_2]/[CO_3^=]$ ratio of the buffer, eventually shift reaction $2HCO_3^- \leftrightharpoons CO_3^= + H_2CO_3$, 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 $MgCl_2$ 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 $MgSO_4$ is substituted for part of the $MgCl_2$, log k'^m_{1000}/k'^m_1 is lowered by an amount corresponding to the $SO_4^=$ 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 $k''^m_{(2)1000}/k''_{(2)1} = 0.178$ ($\Delta E_{1000} = 10.4$ mv). A more elaborate treatment using $pk'^m_{(1)1000}$ and $pk'^m_{(2)1000}$, taking into account the equilibrium $2HCO_3^- \leftrightharpoons CO_3^= + H_2CO_3$, the amount of $MgCO_3$ 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 ± 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, $pk'_{(1)} \doteq pk''_{(1)}$. At $pmH_1 \leqq 7.0$, comparison of the curves of Fig. 5 and 6 for the more concentrated buffers, where HCO_3^- trapping by Ca^{++} seems obvious, shows that pressure must have only a very small effect on the dissociation of any trapped HCO_3^- 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 $MgSO_4$, 0.026 $MgCl_2$ and 0.010 $CaCl_2$.

The sea water samples come from the Atlantic Ocean (north of Spain, Cl ‰ = 19.5) and have been equilibrated with $CO_2 + N_2$ mixtures, or small amounts of Na_2CO_3 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 $SO_4^=$. 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} H_3BO_3 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 cm^3 mole^{-1} at zero borate buffer (H_3BO_3 + borax) concentration, to -30.7 cm^3 mole^{-1} in NaCl 0.01 and to -31.4 cm^3 mole^{-1} in NaCl 0.001; $\Delta V_1^o = -32.1$ cm^3 mole^{-1}. In 0.5 NaCl + 0.030 $MgSO_4$ + 0.026 $MgCl_2$ and 0.010 $CaCl_2$, at pH 7.9, $\Delta V_1'$ is equal to -23.1 cm^3 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], $pk'^m_{(1)1000} = 8.605\text{-}0.39 = 8.215$. 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 HCO_3^- 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 H_3BO_3 concentration, estimated from $pk'^m_{(1)1}$ and

$pk'^{m}_{(1)1000}$ found for boric acid in sea water ($\Delta[HCO_3^-]_T = 0.39\ 10^{-4}$; $\Delta[H_3BO_3] = 0.38\ 10^{-4}$).

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 $H_3BO_3 + CO_3^= \leftrightharpoons HCO_3^- + H_2BO_3^-$ must be considered.

Without going into the details of a quantitative analysis, it is immediately clear that the emf shifts observed at $pmH_1 > 8.0$ 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 $[CO_3^=]_T$ and $[HCO_3^-]_T$ 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 pmH_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 pmH_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 $pk''^{m}_{(2)}$ 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 pmH_1 7.8; the difference of 3.3 mv is due to the effect of pressure on γ_{HCl} in the presence of $MgSO_4 + MgCl_2 + CaCl_2$ 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 $\Delta V_1^o = -25.4$ cm^3 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^{++}, $SO_4^=$; *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, $MgSO_4$, $MgSO_4 + MgCl_2$, $MgSO_4 + MgCl_2 + CaCl_2$ is given in Fig. 7 for several values of n assuming $m_{H^+} = m_{HCl}$. 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 y can be calculated from log γ: in NaCl solutions at $\mu = 0.5$ log γ = log y — 0.004; the correction factor is —0.0047, —0.0055, —0.063, —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 γ_{HCl} drop from $\bar{1}.864$ to $\bar{1}.849$.

The pressure dependency of γ_{HCl} in 0.01 HCl + 0.49 NaCl containing $MgSO_4$, $MgSO_4 + MgCl_2$ 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 $[CO_3^=] + [HCO_3^-] = 0.09 - 0.0025$. That the specific salt effect of CO_2, $CO_3^=$, 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 $[CO_3^=] + [HCO_3^-]$ concentration from 0.09 to 0.0025 has only a very small effect on ΔE_{1000} at a given ionic strength (0.75).

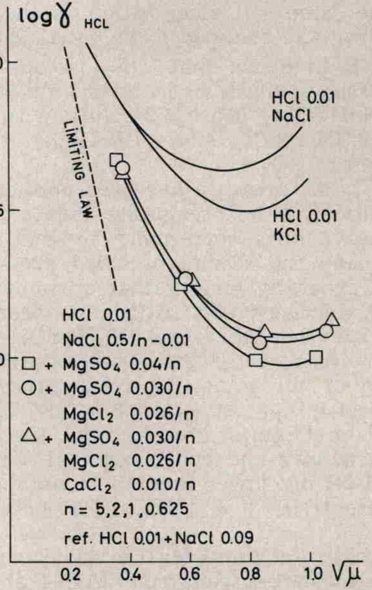

Fig. 7. Mean activity coefficient (γ_{HCl}) of HCl in NaCl, KCl; apparent values in presence of $MgSO_4$, $MgCl_2$, $CaCl_2$ as a function of $\sqrt{\mu}$.

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 $[H^+]$, assuming γ_{HCl} to be equal in both solutions. Ordinary paH 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 paH electrodes display a much more sluggish response and great errors can be introduced

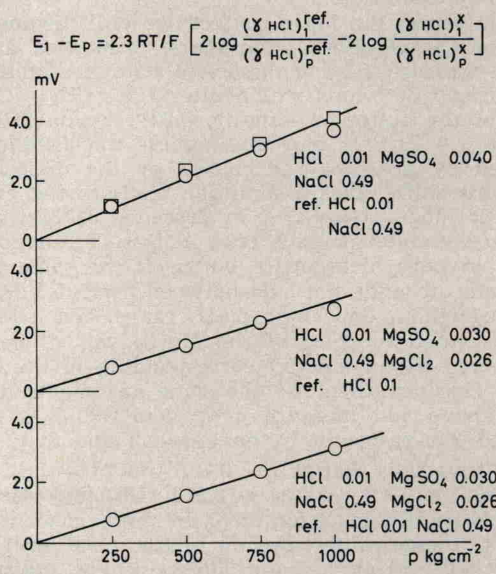

Fig. 8. Effect of pressure on 2 log $(\gamma_{HCl})^{ref}{}_1/(\gamma_{HCl})^{ref}{}_p$ — 2 log $(\gamma_{HCl})^{x}{}_1/(\gamma_{HCl})^{x}{}_p$ 2.3 $RT/F = E_1 - E_p$, where ^{ref} and ^{x} correspond to the inner and outer compartment of the glass electrode cell; effect of $MgSO_4$ and $MgCl_2$.