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 cm^3 mole^{-1} instead of -25.6 cm^3 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 $CO_3^=$ 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 $\Delta V_1°$ 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 cm^3 mole^{-1} in H_2CO_3, -25.4 cm^3 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.

ADDENDUM[1]

Interpretation of the $SO_4^=$-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 $SO_4^=$ 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^= - $ 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
$pk'_{\sigma(1)}$	6.00	5.89	0.11
$pk'_{\sigma(2)}$	9.60	9.49	0.11
$2 \log \gamma_{HCl}$	$\bar{1}.734$	$\bar{1}.617$	0.117
$\log \gamma_{H^+}$	0.017	1.887	0.13

Further, at 1000 kg cm^{-2}, $SO_4^=$ 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 $SO_4^=$ is equal to 3.3 mv (Fig. 8). It actually appears that the greatest part of the $SO_4^=$ $-$ 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 $K_{HSO_4^-} = 1.13 \ 10^{-2}$, $\gamma_{SO_4^=} = 0.12 \ \gamma_{HSO_4^-} = 0.68$, assuming 54% of the sulfate to be free ions [see the data of Garrels and Thompson for sea water (15)] and $a_{H^+} = 7.7 \ 10^{-3}$ ($paH = 2,113$, see Fig. 9), one finds $pmH_1 = 2.088$ instead of 2.00, which accounts for 80% of the apparent $SO_4^= -$ effect on $pk'_{(1)}$ and $pk'_{(2)}$ at 1 atm. One will notice that 2 $\log \gamma_{HCl} = \bar{1}.698$ 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 $\bar{1}.730$. Although the salt effects of individual ions are not necessarily additive, the difference 0.032 indicates that the $SO_4^= -$ effect is probably not larger than the calculated value 0.088, since the total effect of $SO_4^=$ and Mg^{++} is equal to 0.117. In other words, pmH_1 in the $SO_4^=$ 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 $K_{HSO_4^-} = 2.26 \ 10^{-2}$, $pmH_{1000} = 2.043$; 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 $- \Delta V_1°$ for SO_4H^- is only known from density measurements, with values between 12.0 and 20.6 cm^3 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 $SO_4^=$ 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 $SO_4^=$) 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

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

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