

Fig. 5. Glass electrode emf shifts at 22°C produced by pressure (1000 kg.cm⁻²) in bicarbonate, carbonate buffers, and sea water at $\mu = 0.75$, as a function of $pmH = -\log m_H$ measured at atm pressure. Curve 1, NaHCO₃, Na₂CO₃, CO₂ ([HCO₃⁻] + [CO₃⁼]) 0.05 - 0.09 and 0.0025 (arrow) in 0.5 NaCl. Curve 1', KHCO₃, K₂CO₃, CO₂ ([HCO₃⁻] + [CO₃⁼]) 0.05 - 0.09 in 0.5 KCl. Curve 2, NaHCO₃, Na₂CO₃, CO₂ ([HCO₃⁻] + [CO₃⁼]) 0.05 - 0.09 in 0.5 NaCl; effect of Na₂SO₄ (0.030). Curve 3, NaHCO₃, Na₂CO₃, CO₂ ([HCO₃⁻] + [CO₃⁼]) 0.05 - 0.09 in 0.5 NaCl; effect of MgSO₄ (0.030), MgCl₂ (0.026), CaCl₂ (0.01) (Precipitates are obtained at pH > 8.0). Arrows indicate results for [HCO₃⁻] + [CO₃⁼] = 0.0025 (see also curve segments 6). Curve 3', NaHCO₃, Na₂CO₃, CO₂ ([HCO₃⁻] + [CO₃⁼]) 0.05 - 0.09 in 0.5 NaCl; SO₄⁼ effect of MgSO₄ (0.030). Curve 4, NaHCO₃, Na₂CO₃, CO₂ ([HCO₃⁻] + [CO₃⁼]) 0.05 - 0.09 and 0.025 (arrows); effect of MgCl₂ (0.056). Curve 5, Natural sea water Cl⁻ % ≈ 19.5 (Atlantic), corrected at Cl⁻ % 20.0 ($\mu = 0.75$). Curve 5', Natural sea water; SO₄⁼ effect. Curve 6, Artificial sea water: [HCO₃⁻] + [CO₃⁼] = 0.0025; 0.030 MgSO₄, 0.026 MgCl₂, 0.010 CaCl₂, 0.5 NaCl (with or without boric acid in the acid range). Curve 6', Artificial sea water with boric acid (4.3 10⁻⁴) (alkaline range). Curve 7, Effect of boric acid; smoothed difference in mv between ($E_1 - E_{1000}$) in artificial sea water without boric acid (see curves 3 and 6) and ($E_1 - E_{1000}$) in the same with 4.3 10⁻⁴ boric acid (see curves 6 and 6').

Inspection of curve 1 further indicates that the results at $pmH_1 \leq 7.00$ are identical in KCl and NaCl. If one again assumes that the bicarbonate concentration corresponds to the sum of the free HCO₃⁻ ions and the undissociated sodium or potassium bicarbonate, $\log k'^{m(1)1000}/k'^{m(1)1}$ is equal to 0.359 ($\Delta E_{1000} = 21.0$ mv) at $pmH_1 7.0$, 0.376 at $pmH_1 6.0$, and 0.385 at $pmH_1 5.0$. Here the term $2 \log \gamma_{A1}/\gamma_{Ap}$ in Eq. [3] is not constant and depends on the buffer ratio.

The question that remains to be answered concerns the choice of suitable values for $pk'_{(1)1000}$ and $pk'_{(2)1000}$ in the pmH_1 range 7.0-8.5, where the emf changes induced by pressure depend on both ionization functions.

If we consider a solution containing NaCl and NaHCO₃ at atmospheric pressure, its $pmH_1 = \frac{1}{2}(pk'^{m(1)1} + pk'^{m(2)1})$; at $\mu = 0.75$, one finds $pmH_1 \approx 7.8 = \frac{1}{2}(6.0 + 9.6)$ and $[CO_2] = [CO_3^{=}]$. At $pmH_1 = 7.8$, $\Delta E_{1000} = 20.0$ mv, and simple considerations show that $[CO_2]$ will remain equal to $[CO_3^{=}]$ if $2.3 RT/F \log k'^{m(1)1000}/k'^{m(1)1}$ and $2.3 RT/F \log k'^{m(2)1000}/k'^{m(2)1}$ are taken symmetric with respect to $\Delta E_{1000} = 20.0$ mv.

For instance, 21.0 and 19.0 mv read at $pmH_1 7.0$ and 8.5 on curve 1 of Fig. 5. In that case the equilibrium $2HCO_3^- \rightleftharpoons CO_3^{=} + H_2CO_3$ is shifted. Thus, at $pmH_1 = 7.8$, if $[HCO_3^-] + [CO_3^{=}] = 0.05$, 6.10^{-5} HCO₃⁻ is formed at 1000 kg. cm⁻² at the expense of 3.10^{-5} CO₂ and 3.10^{-5} CO₃⁼, which corresponds to a 4% change of the initial CO₂ and CO₃⁼ concentrations. At $pmH_1 7.0$ and 8.5, the change of either [CO₂] and [HCO₃⁻] or [CO₃⁼] and [HCO₃⁻] is negligible when pressure is applied. If one could assume $2.3 RT/F \log k'^{m(1)1000}/k'^{m(1)1}$ and $2.3 RT/F \log k'^{m(2)1000}/k'^{m(2)1}$ to be equal to ΔE_{1000} read on curve 1 at any pmH_1 between 5.0 and 9.0, the CO₂, HCO₃⁻, CO₃⁼ concentrations would remain constant at any pressure. This is what happens at infinite dilution where $\Delta V_{(1)1}^o = \Delta V_{(2)1}^o$.

In KCl, if one neglects the slight minimum at $pmH_1 7.8$, $2.3 RT/F \log k'^{m(1)1000}/k'^{m(1)1}$ and $2.3 RT/F \log k'^{m(2)1000}/k'^{m(2)1}$ are equal within ± 0.25 mv over the range 7.0-9.0. However, this is an oversimplification since the minimum at 7.8 could be explained by the release of CO₃⁼ and HCO₃⁻ from ion pairs. HCO₃⁻ behaves as a base at $pmH_1 < 7.8$ and as an acid at $pmH_1 > 7.8$, whereas the release of CO₃⁼ always results in lowering the hydrogen ion concentration.

The choice of the values of $pk'^{m(1)1000}$ at $pmH_1 7.0$ and $pk'^{m(2)1000}$ at $pmH_1 8.5$ to be used in the pmH_1 interval 7.0-8.5 remains questionable, even in KCl, but there is no other alternative unless reliable values for $pk'^{m(1)}$ and $pk'^{m(2)}$ become available in absence of any ionic association. However, at the alkaline end of the pmH_1 interval 7.0-8.5, $pk'^{m(1)}$ needs not to be known with great precision to calculate [HCO₃⁻] or [CO₃⁼]. At $pmH_1 8.0$, an error of 0.02 ($\Delta E \approx 1.2$ mv) in $pk'^{m(1)1000}$ affects [CO₂] by 2% and [HCO₃⁻] and [CO₃⁼] by only 0.1%.

The separate salt effect of NaCl on $2.3 RT/F \log k'^{m(1)1000}/k'^{m(1)1}$ can be estimated at $pmH_1 < 5.0$ since curve 1 in Fig. 5 seems to reach a plateau in the acid range and since ΔE_{1000} is known at 0 ionic strength (25.0 mv). Thus, for the salt effect, one finds 25.0 - 22.6 = 2.4 mv. This value fits with the fact that $2 \Delta E_{1000} = 23.6$ mv at $\mu = 0.75$ in a solution containing only NaCl and saturated with CO₂. At $\mu = 0$, $2 \Delta E_{1000} = 26.2$ mv (3) and the difference 26.2 - 23.6 = 2.6 mv.

It seems reasonable to assume that the difference between ΔV_{O1} found in pure CO₂ solutions and in bicarbonate buffer at 0 ionic strength might be related to the existence of NaHCO₃ ion pairs even when the concentration of NaHCO₃ becomes very small. The same effect occurs in other buffer systems investigated with the glass electrode technique: ΔV_{O1} is always found to be smaller in buffers than in the corresponding pure acid (3), and the explanation given above might be general.

Finally, one will notice (Fig. 5, dotted part of curves 1 and 2) that Corning 015 electrodes display an alkaline error in presence of NaCl at 1000 kg. cm⁻² at $pmH_1 > 8.25$, although no such error can be detected even at 8.75 at atmospheric pressure.

Ionization of carbonic acid in presence of Mg⁺⁺, Ca⁺⁺, and SO₄⁼ in NaCl solutions, at concentrations found in sea water, at 1 atm and 1000 kg. cm⁻² and at different buffer ratios ($\mu = 0.75$).—When Ca or Mg salts are added to carbonate and bicarbonate buffers, it is well known [see Garrels, Thompson, and Siever (12)] that MgCO₃ and CaCO₃ ion pairs are formed and that the trapping of HCO₃⁻ ions is also to be considered. The dissociation of carbonic acid can still be described by the ionization functions $k'_{(1)}$ and $k'_{(2)}$ where [CO₃⁼] and [HCO₃⁻] refer to the free carbonate and bicarbonate ions (plus those bound to Na as seen in the preceding section), but it is also useful to define apparent ionization functions $k''_{(2)} = [H^+][CO_3^{=}]/[HCO_3^-]$, $k''_{(1)} = [H^+][HCO_3^-]/[CO_2]$ where [CO₃⁼]_T and [HCO₃⁻]_T correspond to the total amount of carbonate and bicarbonate. We will call $k'_{(2)}$ and $k'_{(1)}$ true ionization functions.

True and apparent ionization functions of carbonic acid in presence of Mg^{++} , Ca^{++} and $SO_4^{=}$, in NaCl solutions at 1 atm ($\mu = 0.75$).—Figure 6 gives the pmH_1 changes (in mv) produced when $MgCl_2$, curve 4; $MgCl_2 + MgSO_4$, curve 3; $MgCl_2 + MgSO_4 + CaCl_2$, curve 2; Na_2SO_4 , curve 1 are added to bicarbonate and carbonate buffers at atmospheric pressure, as a function of pmH_1 measured in the solutions containing the added salts. The reference 0.01 HCl + 0.49 NaCl solution has the same salt composition as the buffer under test it is assumed that $m_{H^+} = m_{HCl}$ and that the mean activity coefficient of HCl is the same in both compartments. The added salts are tested at concentrations normally found in sea water ($Cl\%_o = 20.0$).

Effect of $SO_4^{=}$ on the true ionization functions $k'_{(1)1}$ and $k'_{(2)1}$.—Inspection of Fig. 6 shows that the effect of $SO_4^{=}$ ions can be distinguished from the effect of Ca and Mg.

$MgCl_2$ at $pmH_1 < 6.0$ obviously does not modify $k'_{(1)1}$ which is thus the same as in pure bicarbonate solutions at the same ionic strength. The ordinate difference between curves 3 and 4 in Fig. 6 shows but little variations over the pmH_1 interval considered and allows one to calculate $pk'^{c(1)1}$ and $pk'^{c(2)1}$. Thus for the investigated buffers ($MgSO_4$ 0.030, $[HCO_3^-] + [CO_3^{=}]$ between 0.0025 and 0.09) $pk'^{c(1)1} = 5.89$ and $pk'^{c(2)1} = 9.49$ at $\mu = 0.75$ (see Fig. 2 and curve segment in Fig. 4); $pk''^{m(1)1} = 5.89 - 0.005$ and $pk''^{m(2)1} = 9.49 - 0.005$. The correction for the change of concentration scale is somewhat smaller than in pure NaCl solutions and is based on a total salt content of 36.4g and the corresponding density of sea water 1.025 at 22°C (13).

Effect of Ca and Mg and the apparent ionization functions $k''_{(1)}$ and $k''_{(2)}$.—The shape of the curves of

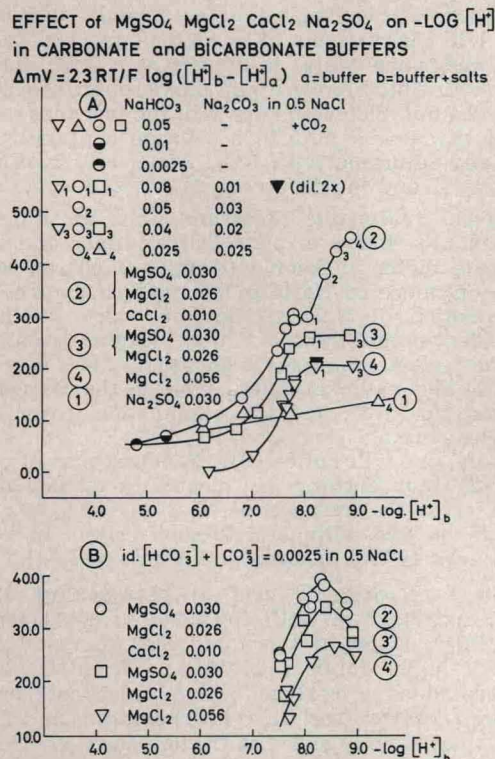


Fig. 6. Glass electrode emf shifts produced by the addition of $MgSO_4$, $MgCl_2$, $CaCl_2$, Na_2SO_4 to bicarbonate and carbonate buffers at atmospheric pressure. A. $[HCO_3^-] + [CO_3^{=}]$ 0.05 — 0.09 in 0.5 NaCl: Curve 1, effect of Na_2SO_4 (0.030); Curve 2, effect of $MgSO_4$ (0.030), $MgCl_2$ (0.026), and $CaCl_2$ (0.010). Precipitates are obtained at points 2, 3, and 4; result at pmH 4.8 corresponds to $[HCO_3^-] + [CO_3^{=}]$ 0.0025; Curve 3, effect of $MgSO_4$ (0.030) and $MgCl_2$ (0.026); Curve 4, effect of $MgCl_2$ (0.056). B. $[HCO_3^-] + [CO_3^{=}] = 0.0025$. (2'), (3'), (4') same as (2), (3), (4).

Fig. 6 which give the emf shifts resulting from the addition of Ca and Mg salts to bicarbonate and carbonate buffers can be understood if one bears in mind that removing a constant amount of $CO_3^{=}$ produces a pmH shift which is maximum at $pmH = \frac{1}{2}(pk'^{m(1)} + pk'^{m(2)})$. When the trapped $CO_3^{=}$ is a function of the initial $CO_3^{=}$ concentration, the maximum is broadened and shifted toward a more alkaline pmH . Removing HCO_3^- produces no shift at $pmH = \frac{1}{2}(pk'^{m(1)} + pk'^{m(2)})$, but results in an acidification or an alkalization at more acid or more alkaline pmH values; HCO_3^- trapping is evident in Fig. 6 in the acid range especially when $CaCl_2$ is added to the more concentrated buffers already containing $MgSO_4$ and $MgCl_2$, but the same operation produces a precipitate at $pmH > 8.1$. No precipitates are observed in the diluted buffers. The data gathered in Fig. 6 can be used to calculate the dissociation constants of $MgCO_3$, $CaCO_3$, $MgHCO_3^+$, and $CaHCO_3^+$ as Garrels *et al.* (12) have done from paH determinations on bicarbonate and carbonate buffers before and after addition of $CaCl_2$ and $MgCl_2$. This problem, which involves lengthy calculations, is quite beyond the scope of the present paper and will not be dealt with.

However, at $pmH_1 \approx 8.0$, Fig. 6 makes it possible to evaluate the apparent second ionization function of carbonic acid, $k''_{(2)}$, in presence of Ca^{++} , Mg^{++} , and $SO_4^{=}$ ions.

For buffers where $[HCO_3^-] + [CO_3^{=}] = 0.0025$, the emf shift due to the addition of 0.030 $MgSO_4$, 0.026 $MgCl_2$, and 0.010 $CaCl_2$ is equal to 38.0 mv at $pmH_1 \approx 8.3$. With $pk'^{c(2)1} = 9.67$ in the pure buffer, this leads to $pk''^{c(2)1} = 9.67 - 0.65 = 9.02$ at $\mu = 0.73$; at $\mu = 0.75$, $pk''^{c(2)1} = 9.015$.

More refined calculations taking into account the true ionization functions $k'^{c(1)}$ (5.89) and $k'^{c(2)}$ (9.49), the equilibrium $2HCO_3^- \rightleftharpoons CO_3^{=} + H_2CO_3$ which is displaced when $CO_3^{=}$ is removed, give a mean value of 9.015 ± 0.015 at $\mu = 0.75$ in the pmH_1 interval 7.9–8.5, with a minimum at 8.3 where $pk''^{c(2)1} = 9.00$. On the molal scale $pk''^{m(2)} = 9.015 - 0.005$, again at $\mu = 0.75$.

The agreement between the directly evaluated value of $pk''^{c(2)1}$ and the calculated one, implies that, in first approximation, HCO_3^- -trapping by Mg^{++} and Ca^{++} must be very small at $pmH_1 \approx 8.0$. Trapping of HCO_3^- to a greater extent than Na ions do, would lead to an apparent lowering of $pk'^{c(1)}$ and also affect $pk''^{c(2)1}$ but in a more complicated way, depending on pH. This problem will not be discussed here, and it will be assumed that between pmH_1 7.9 and 8.5 it is not necessary to introduce a first apparent ionization function, or that $pk'^{c(1)} = pk'^{c(1)}$ in buffers where $[CO_3^{=}] + [HCO_3^-] = 0.0025$.

Since $pk''^{c(2)1} - pk'^{c(2)1} = 0.48$, $[CO_3^{=}]_T \approx 3 [CO_3^{=}]$ and $[Mg - CaCO_3] \approx 2 [CO_3^{=}]$. At pmH_1 8.0 $[HCO_3^-] + [CO_3^{=}] = 0.0025$, $[CO_3^{=}] = 7.34 \cdot 10^{-5}$, $[Mg - CaCO_3] = 1.45 \cdot 10^{-4}$ or 0.22% of the total Ca and Mg concentrations, which is of the order of magnitude (0.28%) given by Garrels *et al.* (12, 15).

In buffers where $[CO_3^{=}] + [HCO_3^-] = 0.09$, $pk''^{c(2)1}$ at pmH_1 8.1 is found equal to 9.12 when directly evaluated from curve 2, Fig. 6A, and equal to 9.10 when calculated at $\mu = 0.84$, taking reaction $2HCO_3^- \rightleftharpoons CO_3^{=} + H_2CO_3$ into consideration and neglecting the possibility of HCO_3^- trapping in the alkaline range. The apparent ionization function $pk''^{c(2)1}$ is thus not only dependent on pH but also on the concentration of the buffering species. This remark is important and needs to be taken into consideration when dealing with data to be valid in natural sea water.

True and apparent ionization functions of carbonic acid, in presence of Mg^{++} , Ca^{++} , and $SO_4^{=}$, in NaCl solutions at 1000 kg. cm^{-2} ($\mu = 0.75$).—Comparison of curves 1 and 2 in Fig. 5 shows that ΔE_{1000} observed in pure buffer solutions is reduced by a constant amount in the presence of 0.030 Na_2SO_4 , between pmH_1 6 and 9.5 (the reference 0.01 HCl + 0.49 NaCl solution has