

greater the lower the temperature. Activity coefficients also increase with pressure.

If  $E_1$  is the emf at pressure 1 of the glass-electrode cell filled with a weak acid or a buffer solution as outside fluid, and  $E_p$  the emf at pressure  $p$ , then using (1) and (2) provided  $\frac{1}{2} \log [\text{HA}]$  and  $\log [\text{A}^-]/[\text{HA}]$  remain constant and neglecting the potential differences arising from the Ag—AgCl electrodes, one has, after correction for the asymmetry potential, at 22°C

$$E_1 - E_p = 0.0293 \log \frac{K_p}{K_1} + 0.0293 \log \frac{f_{\text{A}_1^-} f_{\text{H}_p^+}}{f_{\text{A}_p^-} f_{\text{H}_1^+}} \quad (4)$$

$$E_1 - E_p = 0.0585 \log \frac{K_p}{K_1} + 0.0585 \log \frac{f_{\text{A}_1^-}}{f_{\text{A}_p^-}} \quad (5)$$

The contribution of the activity coefficient term in (4) and (5) is probably small as estimated from the few available data calculated from Eq. (3). A 10% increase at 1000 atmos of the activity coefficient appears to be exceptional for a 1–1 electrolyte (e.g. NaOH). This would correspond to an emf change of about 2 mv.

The values for  $Kp/K_1$  calculated from Eq. (3) by Owen and Brinkley<sup>3</sup> for acetic acid and for carbonic acid (first and second dissociation steps) have been used to draw the full lines of curves 1, 2, and 3 of Fig. 5, and curve 4 of Fig. 6, taking into account Eq. (4) and (5).

The experimental data, corrected for asymmetry potential but not for the activity coefficient variation, are in good agreement with the calculated values for acetic acid, carbonic acid (first dissociation step), and acetate buffer (Fig. 5). The results shown in Fig. 6 (curves 2 and 3) for the bicarbonate buffer do not fit. The observed emf difference at any pressure is only 75% of the expected calculated value which corresponds to twice the ordinate read from curve 3 of Fig. 5. It is doubtful that this is due to the experimental difficulties outlined above, since the results for carbonic acid do agree with theory. When the CO<sub>2</sub> con-

centration is high enough the losses caused by CO<sub>2</sub> escape are very small, as shown by the fact that the zero shift following compression and decompression is zero or a few tenths of a millivolt. A possible effect of carbonic acid and its salts on the potential of the outside Ag—AgCl electrode is also excluded. Exactly the same results are obtained when the outside electrode is placed in a U tube containing 0.1 M KCl and closed at one end with a filter paper stopper in contact with the buffer solution. One possible explanation would be that the dissociation of NaHCO<sub>3</sub> is affected by pressure, or that hydrolysis complicates the equilibrium.

There is a slight shift of the curves when the ratio [salt]/[acid] is varied. The greatest emf variation seems to be obtained when this ratio is unity.

The results with phosphate buffers indicate a similar effect. In both cases, it is clear that the emf variation is almost independent of the ratio [salt]/[acid].

The initial pH of the sea water has no effect or an extremely small effect, on the variation of the emf with pressure (Fig. 6, curve 1). The curve indicates the magnitude of the variation which should normally be found if measurements were carried out at different depths in sea water of constant composition. Any departure from the expected change will mean that other factors than pressure are involved. It is clear that the analysis of corresponding sea-water samples will be necessary for the full interpretation of the pH results at different levels. Temperature recording is also a necessary complement.

The equipment needed for all these experiments to be carried out with the French bathyscaphe F.N.R.S. III will be described in another paper.

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<sup>3</sup> B. B. Owen and S. R. Brinkley, *Chem Revs.* **29**, 461 (1941); see also H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions* (Reinhold Publishing Corporation, New York, 1943).