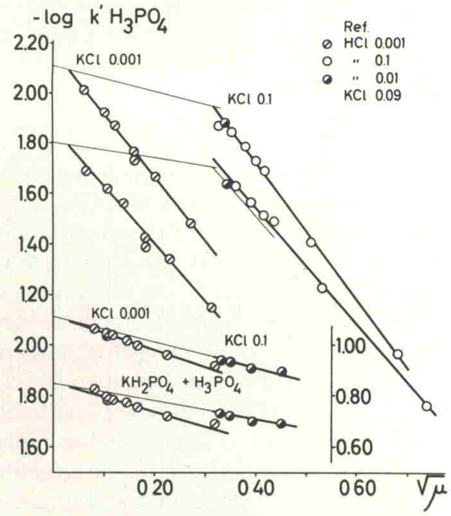

Fig. 7. Phosphoric acid (step 1) and phosphate buffer (buffer ratio $[A^-]/[HA] \simeq 10/1$) in KCl solutions. Extrapolation of $-\log k'_1$ and $-\log k'_p$ at $\mu = 0$ and zero acid and buffer concentration ($-\log k'_1 > -\log k'_p$; the upper left hand scale is continued on the right below).

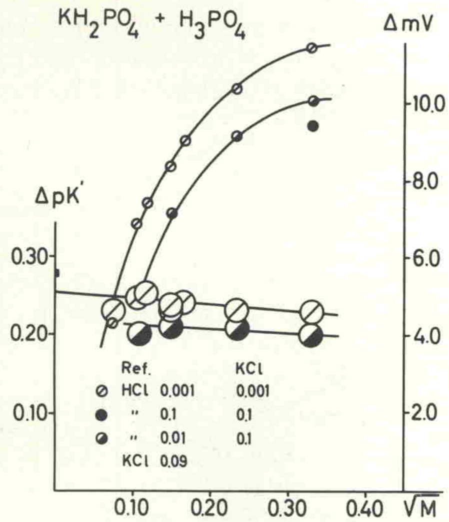

Fig. 8. Phosphate buffer (step 1) in KCl solutions. $\Delta pK' = -\log k'_1 + \sqrt{\mu_1} + \log k'_p - \sqrt{\mu_p}$ ($p = 1000$ kg cm^{-2}) and Δ mv observed (emf shifts) as a function of the buffer concentration ($[HA] + [A^-] = M$).

too high compared to the -16.2 cm^3 obtained by Smith (21) from density measurements.

Figure 7 gives $-\log k'_1$ and $-\log k'_p = f(\sqrt{\mu})$ and may be extrapolated to $\mu = 0$ and zero acid concentration. The absolute value of pK_1 (2, 11) is in agreement with the value 2.13 given by Bates (23); the most probable value for ΔpK is again 0.300, and the contribution of the activity term at $\mu = 0.1$ is equal to 1.03 cm^3 which is somewhat less than for formic acid.

The results gathered for phosphate buffer (step 1) are given in Fig. 7, 8, and 9. The stock buffer solutions contained $0.1M$ KH_2PO_4, $0.011M$ H_3PO_4, and KCl, and were diluted with corresponding KCl solutions. This buffer ratio explains why the medium effect of undissociated H_3PO_4 is very much reduced, compared with pure H_3PO_4 solutions. The extrapolated value of ΔpK lies around 0.260 ($\Delta V°_1 = -15.2$

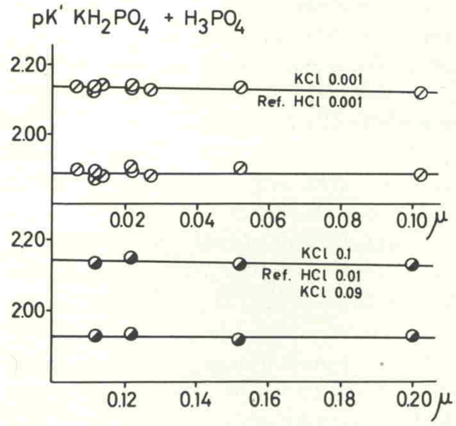

Fig. 9. Phosphate buffer (step 1) in KCl solutions. Extrapolation of $pK' = pk' + \sqrt{\mu}/(1 + 1.96\sqrt{\mu})$ at 1 and 1000 kg cm^{-2} on the μ scale ($pK'_1 > pK'_p$).

cm^3) on both Fig. 7 and 8. The contribution of the activity coefficient term is $\simeq 0.7$ cm^3 at $\mu = 0.1$. Figure 9 indicates that the results are better represented on the μ scale. $pK' = pk' + \dfrac{\sqrt{\mu}}{1 + 1.96\sqrt{\mu}}$ is then used to extrapolate at $\mu = 0$ (23), again assuming that pressure has no effect on the activity coefficients. ΔpK seems now to be closer to 0.250 ($\Delta V°_1 = -14.6$ cm^3), whereas the absolute value of pK_1 is in excellent agreement with the data of Bates.

We have so far no explanation for the fact that $\Delta V°_1$ for phosphate buffer is about 2 or 3 cm^3 smaller than $\Delta V°_1$ for H_3PO_4 alone. It should be noticed however that extrapolation at nearly equal buffer ratios on the $\sqrt{\mu}$ scale (Fig. 8) yields values for ΔpK between 0.280 and 0.270 (-16.4 and -15.8 cm^3) in much better agreement with the density data of Smith (21).

Preliminary results for acetic acid in 0.001 KCl lead to $\Delta pK = 0.180$ ($\Delta V°_1 = -10.8$ cm^3); for acetate buffer, $\Delta pK = 0.175$ ($\Delta V°_1 = -10.3$ cm^3). Some uncertainty arises from the slight curvature of $E_1 - E_p = f(P)$ which is generally absent in the other investigated media. The emf values at 500 kg cm^{-2} give for $\Delta V°_1$ -11.5 and -10.8 cm^3 for the acid and the buffer, respectively. The agreement with the results obtained from conductivity and density measurements is satisfactory (see Table I).

The effect of the ionic strength on ΔpK in phosphate buffer (step 2) seems to be quite small. The importance of the buffer ratio will have to be investigated carefully, but the observed shifts in $0.001M$ KCl point toward $\Delta pK = 0.390$ or $\Delta V°_1 = -23.0$ cm^3, a value which is still about 5 cm^3 too small compared to the one obtained from density measurements (21).

We have not reinvestigated (14) the effect of pressure on H_2CO_3 and bicarbonate buffer in dilute KCl solutions. Taking into account the apparent reference cell shift (0.8-0.9 mv) for $0.1M$ HCl and a reasonable estimate of 0.5 mv for the activity coefficient contribution, would lead to $\Delta V°_1$ values for bicarbonate buffer between -22.0 and -24.0 cm^3, not too far from the value (-24.9 cm^3) proposed recently by Ellis (5) from conductivity measurements. These ΔV°_1 values are however much lower than the figure given by Owen and Brinkley (11) (29.0 cm^3) and are in disagreement with the pH shift observed in H_2CO_3 solutions, which lies between 14.5 and 15.0 mv in 0.1M KCl (reference 0.1M HCl) ($\Delta V_1 = -$ 30.6 and $-$31.8 cm^3, after correction for the reference shift).

The increase of the second dissociation constant of carbonic acid is not measurable with a glass electrode without careful investigation of the effect of pressure on the alkaline error at $p\text{H} > 9$. The shift can be computed however from the emf change observed in $NaHCO_3$ solutions, the pH of which is known to be given by

$$p\text{H} = \tfrac{1}{2}\, pK_1 + \tfrac{1}{2}\, pK_2$$

The observed value, with 0.1M HCl as reference, is 22.6 mv at 1000 kg cm^{-2} for a 0.1M solution in 0.1M KCl. It is close to the 22.7 mv change obtained for bicarbonate buffer. This gives, after correction for the reference half-cell shift, a corresponding value of ΔV_1 equal to $-$23.6 cm^3. The expected ΔV°_1 is $-$27.8 cm^3 (11).

It appears from Table I, which summarizes our findings, that the observed pH shifts induced by pressure in acetic acid, formic acid, phosphoric acid (step 1), and perhaps carbonic acid are in reasonable agreement with the pK decrease or ΔV°_1 values calculated from density and conductivity data. However, the recorded emf changes in buffer solutions appear to be systematically too small and the difference is too great to be accounted for in terms of activity coefficient contributions or reference cell shifts. On the other hand, the experiments described in the next section tend to show that the behavior of the glass electrode under pressure is normal in the alkaline region, so that the cause of the observed discrepancy will have to be sought elsewhere (ionic association, hydration, incompletely dissociated salts, etc.).

Sodium Acetate, Ammonia (Ionic Product of Water)

The ionic product of water K_w increases by a factor of 2.36 at 1000 atm according to the calculation of Owen and Brinkley (11). Several experiments can be carried out with a glass electrode to obtain experimental data about this shift. The pH of a sodium acetate solution is known to be given by

$$p\text{H} = \tfrac{1}{2}\, pK_w + \tfrac{1}{2}\, pK_{\text{HA}} + \tfrac{1}{2} \log M$$

The pK decrease observed from pH measurements for acetic acid lies between 0.180 and 0.195 at 1000 atm, the pK_w shift is expected to be 0.373. The observed pH change for Na-acetate should thus be equal to 0.277-0.284 pH, or 16.2-16.6 mv at 21°C. The experimental values in four successive experiments with 0.1M HCl as reference are: 16.0, 16.5, 16.7, 17.2 mv. The mean value corrected for the reference shift is 17.4 mv. The agreement is acceptable despite the fact that the pH of Na-acetate solutions is somewhat unstable. The solution should be prepared from acetic acid and CO_2-free NaOH, and very carefully adjusted at the neutralization point ($p\text{H} = 8.4$). At lower pH values, the observed shifts fall between that for acetate buffer and Na-acetate.

The pH of ammonia solutions is given by

$$p\text{H} = pK_w - \tfrac{1}{2}\, pK_{\text{NH}_4\text{OH}} + \tfrac{1}{2} \log M$$

The expected pH shift estimated from the data of Hamann and co-workers (24, 7) ($\log Kp/K_1 = 0.465$) can be shown to be 0.140 pH or 8.2 mv. The observed values for a $10^{-4}M$ solution in 0.1M KCl, with 0.1M HCl as reference, are 9.2 and 8.4 mv at pH 9.64. However, the glass electrode is known to present an alkaline error above pH 9, and the effect of pressure in this region has not been investigated. Further, Ag-AgI electrodes should be substituted to the Ag-AgCl electrodes, AgCl being soluble in NH_4OH. The agreement is thus to be accepted with caution, although no change in the asymmetry potential shift could be detected before and after 20-min treatment in $10^{-4}M$ NH_4OH.

Sea Water

The effect of pressure on the pH of sea water reveals a linear pH decrease which amounts to 0.3 pH at 1000 kg cm^{-2} (14).

The pressure resisting glass electrode has been adapted for deep sea investigations, and Distèche and Dubuisson (25) have been able to record the pH of the water of the Mediterranean Sea from the French Bathyscaphe to 2.350m depth.

The electrode cell is shown on Fig. 10 which is self-explanatory. The cell assembly is attached to

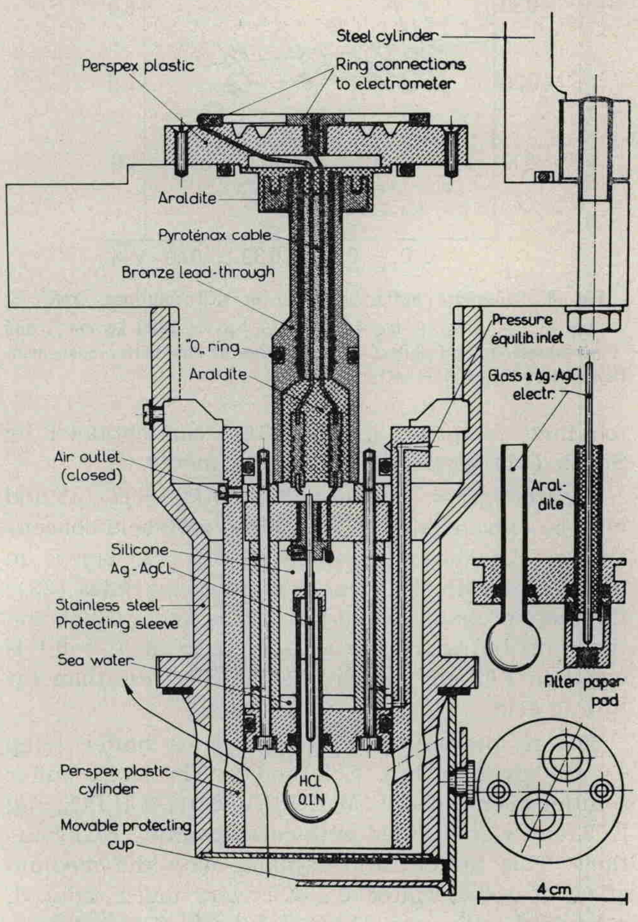

Fig. 10. Glass electrode assembly for deep sea investigations. From Distèche and Dubuisson (25).