

FIG. 5. Variation of the glass-electrode potential with pressure for various acid and buffer solutions. Solid lines 1, 2, and 3 are calculated from the data of Owen and Brinkley using Eqs. (4) and (5).

both directly and indirectly (through the corresponding pressure change), the following procedure was adopted to obtain the data of Figs. 4 and 5. The pressure is slowly increased to the desired value, with a final increment never exceeding 250 kg/cm<sup>2</sup>. After 30 min rest, the emf is measured and the pressure read; a second reading is taken after 5 min more, and it generally agrees with the first reading; if not, further readings are taken until equilibration is attained.

All these operations are carried out in a constant temperature room at 22°C and it is estimated that the total temperature rise when a final pressure of 1000 kg/cm<sup>2</sup> is reached is probably less than 0.25°C.

The temperature coefficients of the cell for phosphate, acetate buffer, and 0.1N HCl are, respectively, 0.97, 0.60, and 0.045 mv per degree. The error introduced in this way by the estimated temperature rise is thus small. The effect

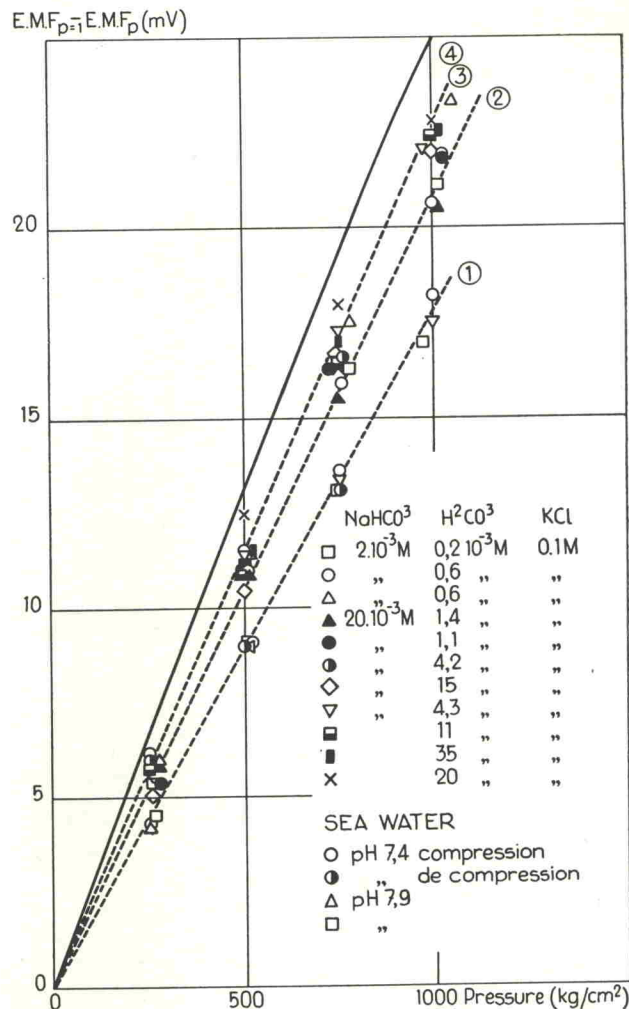


FIG. 6. Variation of the glass-electrode potential with pressure for bicarbonate buffer (2 and 3) and sea water (1). Solid line 4 is calculated from the data of Owen and Brinkley for the second dissociation step of carbonic acid [Eq. (5)].

of a temperature shift of this magnitude on the chemical equilibria in the electrolyte solutions can be neglected.

However, if more precision is required, a constant temperature (oil or water) jacket around the main pressure chamber and eventual continuous recording of the temperature inside the electrode container must be provided for.

With bicarbonate buffer (Fig. 6), especially when the concentrations are very low, additional difficulties are met with, probably caused by CO<sub>2</sub> diffusion causing long-range instability and also related to the fact that it is almost impossible to preserve the homogeneity of the gas solution when filling the apparatus. In this case, advantage can be taken from the observed time lag between a sudden pressure increment and the temperature rise at the electrode. Most of the emf plots of Fig. 6 for NaHCO<sub>3</sub> correspond to the differences between readings taken just before and



immediately after each quick pressure step. Large time intervals (30 to 60 min) separate each set of readings. When the concentration of  $\text{H}_2\text{CO}_3$  is relatively important, the stability is sufficient to use the procedure first described.

The two methods give reproducible data and the curves can be constructed either by increasing or decreasing the pressure.

The results obtained with 0.1*N* HCl in and outside the electrode (Fig. 4) correspond to the asymmetry potential of the glass electrode including the eventual difference between the potentials of the two Ag-AgCl electrodes. Freshly prepared glass electrodes have a small asymmetry potential of about 1 mv or less but aged ones may show a greater value. About the same results are obtained with either acetate or phosphate buffer instead of HCl inside and outside the electrodes.

The asymmetry potential of freshly prepared Ag-AgCl electrodes is negligible and its variation with pressure is unmeasurable with our equipment. Aged Ag-AgCl electrodes, especially when scratched show a small asymmetry which varies with pressure.

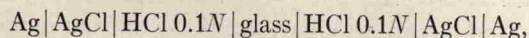
For all the glass electrodes so far investigated, the asymmetry potential was found to become more and more positive with increasing pressure (i.e., a more and more positive potential is needed to compensate the electrode potential), whereas for the buffers and weak acids investigated as outside fluid the emf of the cell always decreases. The emf values of Figs. 5 and 6 thus have been corrected at each pressure *p* by adding the corresponding asymmetry potential to the difference in mv between the emf measured at atmospheric pressure and the emf at pressure *p*.

A calomel electrode, either of the saturated type or filled with 0.1*N* HCl, has been tried as outside reference electrode. The emf changes with pressure fall on an exponential curve and long-range instability with zero shifts make such electrodes unsuitable in this case.

We were not able to detect any static electricity effects caused by friction even when the silicone fluid is rapidly compressed or decompressed.

#### INTERPRETATION

The results plotted in Fig. 4 show that the effect of pressure on the symmetrical cell,



is to modify slightly the asymmetry potential of the glass electrode. The effects on both Ag/AgCl electrodes may be assumed to cancel provided that the electrodes are freshly prepared. The asymmetry potential is often thought to arise from strains in the membrane, which may vary under the influence of pressure.<sup>2</sup>

<sup>2</sup> M. M. Dole, *The Glass Electrode* (John Wiley & Sons, Inc., New York, 1941).

The data obtained with 0.01*N* HCl, 0.09*M* KCl (Fig. 4) as outside solution are of special interest, since the hydrogen ion activity on both sides of the membrane varies so slightly with pressure in the range investigated, that it may be regarded as constant within the precision of the emf measurements. It seems clear that the glass-electrode constant (equal or nearly equal to  $2.3026 RT/F$ , the hydrogen electrode constant) is not modified by pressure, provided that one takes into account the asymmetry potential variations.

Let us now consider the results obtained with buffers, acetic acid, carbonic acid, and sea water.

It seems reasonable to assume that the effects of pressure on both Ag-AgCl electrodes still compensate almost completely. In most of the experiments, the  $\text{Cl}^-$  concentration is equal inside and outside the electrode and the ionic strength is kept at 0.1, except for sea water. We will further notice (Fig. 4) that the shape of the emf variation with pressure measured with 0.1*N* HCl outside the glass electrode is the same when 0.1*N* HCl is replaced by 0.1*N* HCl + 0.5*M* NaCl (approximate concentration of sea water).

The pH of an aqueous solution of a weak acid HA is given by the following equation:

$$pH = -\log[H^+]f_{H^+} = \frac{1}{2}pK_{HA} - \frac{1}{2}\log[HA] + \log\frac{f_{A^-}}{f_{HA}f_{H^+}} \quad (1)$$

When the dissociation constant  $K_{HA}$  is small, the real concentration  $[HA]$  may be made equal to the stoichiometric concentration of the acid with a fair degree of accuracy.

The pH of an aqueous solution of a weak acid HA and its sodium salt NaA is represented by

$$pH = pK_{HA} + \log\frac{[A^-]}{[HA]} + \log\frac{f_{A^-}}{f_{HA}} \quad (2)$$

At pH between  $pK_{HA}-1$  and  $pK_{HA}+1$ , the stoichiometric concentrations  $[\text{salt}]$  and  $[\text{acid}]$  may be substituted for  $[A^-]$  and  $[HA]$ , respectively.

For dilute solutions, the activity coefficient  $f_{HA}$  of the undissociated acid is generally assumed to be unity in both equations.

Pressure is known to affect the dissociation constant and the activity coefficients according to

$$\left(\frac{\partial \ln K}{\partial p}\right)_{T,m} = \frac{-\Delta\bar{V}^0}{RT} \quad \text{and} \quad \left(\frac{\partial \ln f_i}{\partial p}\right)_{T,m} = \frac{\bar{V}_i - \bar{V}_i^0}{RT} \quad (3)$$

where  $\Delta\bar{V}^0$  is the algebraic difference between the partial molal volumes of the products and the reactants of the chemical equilibrium in their standard states and  $\bar{V}_i$  the partial molal volume of the ion species *i*.

For weak electrolytes calculations show that  $K_{HA}$  increases with pressure and that the relative increase is the