acid, o-, m-, p-nitrobenzoic, salicylic, and 3-5 di-methyl-4-nitrobenzoic acid, ammonia, mono-, di, tri-methyl amine (2-7) in water have been thoroughly studied, and some results are reported in nonaque-ous solvents (2, 6).

Log K_p/K_1 varies almost linearly with pressure between 0 and 3000 atm. In this range, at 25°C, log K_{1000}/K_1 lies between 0.1 and 0.25 for organic acids, is equal to 0.4 for carbonic acid, and amounts to ~ 0.45 for ammonia and amines.

The basic ionization constant of ammonia at 45°C is increased from $1.9\ 10^{-5}$ mole kg^{-1} at 1 atm to 1010 x 10^{-5} mole kg^{-1} at 12,000 atm (7). David and Hamann (3, 4) have measured the conductivity of water and several liquids at shock pressures between 33,000 and 127,000 atm. The ionic product of water increases by a factor as great as 10^{12} at 127,000 atm. In these spectacular experiments, the pressures are produced by Schall's method (8) of using an explo-sion to drive an intense shock wave into the water. The cell is made from polyethylene and has platinum electrodes.

Some polarographic measurements at high pres-sure have been made by Ewald and Lim (9) and by Hayashi and Kono (10); the results are consistent with the fact that pressure shifts chemical equi-libria in the direction of the more ionic species.

Galvanic Cell emf Measurements

The effect of pressure (p) on the emf (E) of a galvanic cell can be predicted from the classical re-lations

$$\left(\frac{\partial \Delta G}{\partial p}\right)_{m,T} = \Delta V \qquad [1]$$

$$\left(\frac{\partial E}{\partial p}\right)_{m,T} = \frac{-\Delta V}{n\mathbf{F}} \qquad [2]$$

where ΔG represents the free energy, ΔV the volume change when n Faraday ($\mathbf{F}$) are passed through the cell at constant molal concentration (m) and temperature (T).

If $\Delta V = 1\ cm^3$, $n = 1$, $\left(\dfrac{\Delta E}{\Delta p}\right)_{m,T} = \dfrac{1 \times 0.10133}{96.500}$

$= 1.05\ 10^{-6}$ volt/atm or $1.016\ 10^{-6}$ volt/kg cm^{-2}; 0.10133 is the factor which converts cubic centi-meter-atmospheres into joules.

Cohen and Piepenbroek (12) showed that ΔV can be considered independent of pressure for the cell Tl-amalgam-TlCNS, KCNS | KCl, TlCl-Tl-amalgam. Hainsworth, Rowley, and MacInnes (13) have given an integrated form of Eq. [2] for the cell Pt-H_2 | HCl 0.1N | HgCl-Hg up to 1000 atm. pH values for some standard buffers are given by Le Peintre (15) at 150 atm between 20° and 250°C, using a sym-metrical Pt-H_2 cell with liquid junction (quartz cell).

In a paper published in 1959, Distèche (14) showed that the symmetrical glass electrode cell: Ag-AgCl | HCl 0.1N | glass | X, KCl 0.1M | AgCl-Ag, where X stands for various electrolytes, can be used for precise pH measurements up to 1500 atm. A similar cell has been tested for industrial use in the 0-150 atm range by Le Peintre (15). The cell assem-

bly (whole glass) is reported to have been patented in 1957, and a few preliminary results up to 150°C are given (Pb-amalgam is used for the inner elec-trode), but glass corrosion very much reduces the reliability of the electrode at high temperature. Mar-burger, Anderson, and Wigle (16) described a glass cell capable of withstanding pressure, where one of the junction electrodes is made of lead, apparently directly deposited on the active glass (U tube).

A conventional glass electrode easily can be made to withstand 1500 kg cm^{-2} simply by applying the pressure to a layer of silicone oil, which acts as a liquid piston on the inner and outer solutions of the electrode (Fig. 1).

Figure 2 represents a cross section through part of a cell designed for laboratory work, which has some advantages compared with the apparatus de-scribed in 1959 (14). The use of araldite (potting resin) for making highly insulated pressure resisting seals around the electrical connections has been avoided. Crevices appear in this type of seal after prolonged use. The electrical connections shown in Fig 2. is a variant of that described by Poulter (17). Low-pressure leakage is avoided by the use of "O"
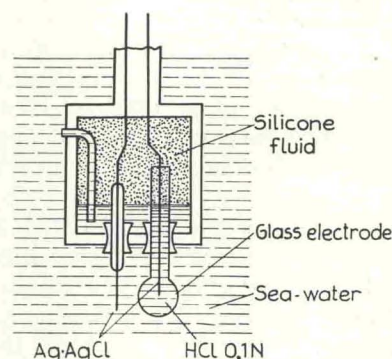

Fig. 1. Schematic drawing showing how a glass electrode can be made to withstand high pressure. From Distèche (14).
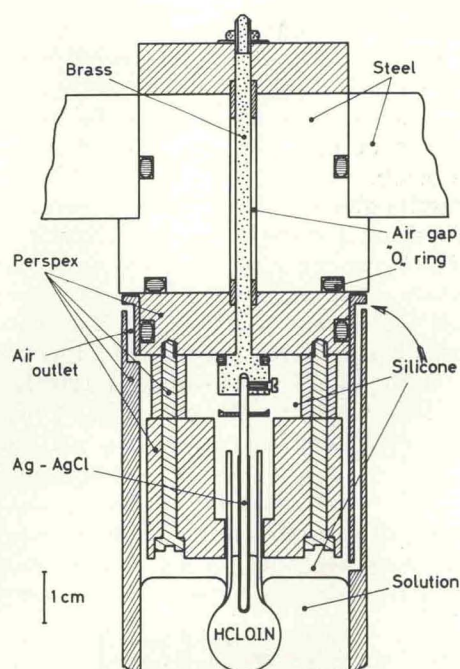

Fig. 2. Cross section through part of the glass electrode assembly

rings. The connector, which can be taken to pieces in a few minutes, is easy to build, and the insulating resistance is extremely high ($>10^4$ meg).

The glass electrode is blown from a Corning 015 glass tube and fits into a Perspex mounting block which occupies a volume as large as possible compared to the volume filled with silicone oil. This is to minimize heat transfer between the silicone and the solution.

The Ag-AgCl electrodes are made from pure silver wire, and the surface separating the two liquid phases falls on the AgCl coating. Silvered Pt wire, first sealed at the extremity of a glass tube, is to be avoided. The glass seal seldom stands repeated pressure application and short circuits appear at the junction between the AgCl coating and the glass stem. In fact, the greatest difficulty in these experiments lies in the Ag-AgCl electrodes. The slightest scratch or irregularity in the coating makes the electrodes behave erratically, and the defect is greatly emphasized at high pressure. Care also should be taken to eliminate dust deposits which generally gather at the liquid interface. Carefully made electrodes generally stand a week or more of intensive experimental work before showing some sign of aging. An emf hysteresis loop is observed when pressure is applied and suppressed. The Ag-AgCl electrodes then have to be replaced which means that the whole cell must be designed to be taken to pieces quickly and easily. Glass electrodes last indefinitely and, when carefully washed and wiped, never show any defects.

The silicone oil has a viscosity of 1 cS at 25°C. The use of a liquid of low viscosity makes filling easier and air bubbles escape quickly. One disadvantage is the rather high compressibility, which means that positive or negative heat is generated in the silicone layer. It can be shown that, with a pressure step of 1000 kg cm^{-2} applied in 40 sec, the rise of temperature is 3°C in the silicone fluid, and never exceeds 1°C in the solution.

With 250 kg cm^{-2} increments applied every 5 or 10 min, it is estimated that the total temperature rise is less than 0.25°C when the final pressure is reached. The effect can be minimized further by the use of a water-jacket at constant temperature around the pressure bomb.

The results obtained with pressure resisting glass electrodes show that the hydrogen electrode constant (2.303 RT/F) of the glass electrode is not affected by pressure. The asymmetry potential measured with 0.1M HCl or any buffer solution on both sides of the membrane varies slightly, but linearly with pressure in the investigated range (0-1000 kg cm^{-2}). The variation generally does not exceed 1 mv and is carefully determined to correct the pH measurements.

Weak Acids and Buffers

The effect of pressure on the dissociation constant (K) of a weak acid and on the activity coefficient (γ_i) of an ion species i is given by

$$\left(\frac{\partial \ln K}{\partial p}\right)_{m,T} = \frac{-\Delta V°}{RT} \quad \text{and} \quad \left(\frac{\partial \ln \gamma_i}{\partial p}\right)_{m,T} = \frac{V_i - V°_i}{RT} \quad [3]$$

where $\Delta V°$ is the algebraic difference between the partial molal volumes of the products and the reactants of the chemical equilibrium in their standard states and V_i the partial molal volume of the ion species i.

For acetic acid, acetate buffer, phosphate buffer (step 2), carbonic acid, and bicarbonate buffer, at concentrations where H$^+$ is negligible compared with the stoichiometric acid or salt concentrations, it is easy to show that log K_p/K_1 can be calculated from Eq. [4] and [5], valid respectively for acids and buffers at 22°C

$$E_1 - E_p = 0.0293 \log K_p/K_1 + 0.0293 \log \frac{\gamma_{A^-_1}\,\gamma_{H^+_P}}{\gamma_{A^-_P}\,\gamma_{H^+_1}} \quad [4]$$

$$E_1 - E_p = 0.0585 \log K_p/K_1 + 0.0585 \log \frac{\gamma_{A^-_1}}{\gamma_{A^-_P}} \quad [5]$$

where A$^-$ = acid anion, E_1 and E_p the emf of the glass electrode assembly at pressure 1 and P.

Figure 3 (14) shows a plot of $E_1 - E_p$ against pressure from which ΔV_1 corresponding to the reaction HA $\rightarrow$ H$^+$ + A$^-$ at 1 atm in 0.1M KCl (reference electrode HCl 0.1M) can be estimated. The values are given in Table I (column 1) together with $\Delta V°_1$ (columns 3 and 4) obtained from density and conductivity determinations ($E_1 - E_{1000 \text{ kg cm}^{-2}} = 1$ mv, corresponds almost exactly to $\Delta V_{1 \text{ atm}} = 1$ cm^3 (see page 1085); $E_{1000 \text{ kg cm}^{-2}}$ is obtained from the slope of $E_1 - E_p = f(P)$ at 1 atm and generally coincides with the reading at 1000 kg cm^{-2}).

Except for carbonic acid ΔV_1 is always lower than $\Delta V°_1$. Part of the difference lies in the contribution of the activity coefficient term in Eq. [4] and [5] ($\gamma_p > \gamma_1$). The data necessary to calculate log γ_1/γ_p generally are not available, but the effect of this
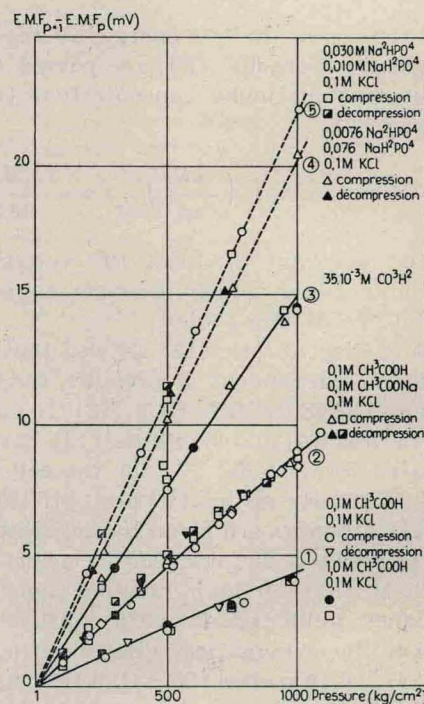

Fig. 3. Variation of the glass electrode potential with pressure for various acid and buffer solutions in 0.1M KCl (reference half-cell: 0.1M HCl). Solid lines are calculated from the data of Owen and Brinkley (11). From Distèche (14).