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Electrochemical Measurements at High Pressures

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ABSTRACT

pH measurements with a glass electrode at 1000 kg cm⁻² give direct evidence of the pressure induced ionization constant shift and permit calculation of the corresponding volume change for the reaction $HA \rightarrow A^- + H^+$. Extrapolation at zero ionic strength and zero acid concentration is used to determine log K_{1000}/K_1 for formic acid, phosphoric acid, and phosphate buffer (step 1). Data concerning phosphate buffer (step 2), acetic acid, acetate buffer, carbonic acid, bicarbonate buffer, sodium bicarbonate, sodium acetate, and ammonia are given together with the results of direct pH measurements at great ocean depth (2350m). Work done in the same field but based on conductivity determinations is briefly reviewed.

The field of application of electrochemical technique in high-pressure chemistry is almost completely restricted to electrolytic conductance and galvanic cell emf measurements, the former receiving much more attention.

Conductance Measurements

New cell design [Teflon-Pt (1)] has made it possible to obtain more accurate results over a wide pressure range (1-12,000 atm) in the last 10 years. The subject has been fully reviewed by Hamann (2) and co-workers (3, 4), Ellis (5), Clark and Ellis (6), and is briefly dealt with here.

The results show that the limiting conductance of strongly dissociated salts first increases slightly up to 1000-2000 atm, but decreases at higher pressures. The effect is related to viscosity and dielectric constant changes in the solvent. HCl and KOH behave differently, their conductance being reduced much less by high pressures.

In contrast, the molal conductance of weak acids and bases increases steadily with pressure. This is due to enhanced ionization and is best demonstrated by the shift of the ionization constants (K) computed from conductivity measurements. Formic acid, acetic acid, propionic acid, carbonic acid, benzoic acid, o-, m-, p-nitrobenzoic, salicylic, and 3-5 dimethyl-4-nitrobenzoic acid, ammonia, mono-, di, trimethyl amine (2-7) in water have been thoroughly studied, and some results are reported in nonaqueous 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 explosion to drive an intense shock wave into the water. The cell is made from polyethylene and has platinum electrodes.

Some polarographic measurements at high pressure 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 equilibria 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 relations

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

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

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

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

= $1.05 \ 10^{-6}$ volt/atm or $1.016 \ 10^{-6}$ volt/kg cm⁻²; 0.10133 is the factor which converts cubic centimeter-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-H₂ | 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 symmetrical Pt-H₂ 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 assembly (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 electrode), but glass corrosion very much reduces the reliability of the electrode at high temperature. Marburger, 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 described 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. 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 (>10⁴ 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 carefuly 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 0.1*M* 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 *p*H measurements.

Weak Acids and Buffers

The effect of pressure on the dissociation constant (K) of a weak acid and on the activity coefficient (γ_1) of an ion species i is given by

$$\left(\frac{\partial \ln K}{\partial p}\right)_{m,T} = \frac{-\Delta V^{\circ}}{RT} \text{ and } \left(\frac{\partial \ln \gamma_{i}}{\partial p}\right)_{m,T} = \frac{V_{i} - V^{\circ}_{i}}{RT}$$
[3]

where ΔV° 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

$$E_{1} - E_{p} = 0.0293 \log K_{p}/K_{1} + 0.0293 \log \frac{\gamma_{A^{-}p} \gamma^{H^{+}p}}{\gamma_{A^{-}p} \gamma^{H^{+}1}} [4]$$
$$E_{1} - E_{p} = 0.0585 \log K_{p}/K_{1} + 0.0585 \log \frac{\gamma_{A^{-}p}}{\gamma_{A^{-}p}} [5]$$

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 0.1*M* KC1 (reference electrode HCl 0.1*M*) can be estimated. The values are given in Table I (column 1) together with ΔV°_1 (columns 3 and 4) obtained from density and conductivity determinations ($E_1 - E_{1000 \text{ kg cm}^{-2}} = 1 \text{ mv}$, corresponds almost exactly to $\Delta V_{1 \text{ atm}} = 1 \text{ cm}^3$ (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 ΔV°_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 0.1*M* KCI (reference halfcell: 0.1*M* HCI). Solid lines are calculated from the data of Owen and Brinkley (11). From Distèche (14).

ELECTROCHEMICAL MEASUREMENTS

 $-\Delta V_1$ (0.1*M* KCl), cm³ mole⁻¹ $-\Delta V^{\circ}_{1},$ cm³ mole⁻¹ $-\Delta V^{\circ}_{1}$, cm³ mole⁻¹ $-\Delta V^{\circ_1}$, cm³ mole⁻¹ Glass electrode ref. 0.1M HCl¹⁴ (() = molarities) Glass Density Conductivity Acids electrode 12.5(2)-11.5(19) 8.2-9.3* 10.8-11.5* 12.2(7) Acetic 9.2(11) (0.1 - 1.0)8.8-9.1 8.0(2) Formic 8.8(2) 16.2(21) Phosphoric (K_1) 17.5 29.0(11) 29.0-30.0 24.9(5) Carbonic (K_1) $(3.5.10^{-2})$ Buffers 8.7-9.7* 10.3-10.8* Acetate (HA 0.1-NaA 0.1) 14.6-15.2 Phosphate (K_1) 22.0 28.1 (21) ** Phosphate (K_2) 23.0 (NaH₂ 0.03-Na₂H 0.01) 20.3 (NaH₂ 0.0076-Na₂H 0.076) Bicarbonate 22.7-20.7 (NaH 2.10⁻³-3.5.10⁻² HA 2.10⁻⁴-3.5.10⁻²)

Table I. Volume change for ionization of some weak acids at 1 atm and 22°C

* The lower values are read from the curves of Fig. 3 and similar ones at 1000 kg cm-2; the higher values are obtained from the slope of the curves at 1 atm.

** $\Delta V^1 = -24.1$ cm³ is reported from dilatometric experiments by Linderstrom-Lang and Jacobsen (22).

factor is expected to be small (18). It also should be noticed that we have assumed so far that the *p*H of the reference half-cell (0.1*M* HCl) is not affected by pressure and that the effects of pressure on the specific electrode reactions cancel out. ΔV_1 corresponds in fact to the total volume change in the observed cell at 1000 kg cm⁻².

We will now describe how the ΔV_1° values listed in column 2 of Table I have been obtained.

When $[H^+]$ is no longer negligible compared to the stoichiometric concentrations, K_p and K_1 must be calculated using the classical methods to determine dissociation constants from electromotive force data.

For acids (formic acid, phosphoric acid (step 1), $E_1 - E_p$ is then given by

$$E_{1} - E_{p} = 0.0293 \log \frac{K_{p}}{K_{1}} + 0.0293 \log \frac{(m_{\text{HA}} - m_{\text{H}^{+}})_{p}}{\log \frac{(m_{\text{HA}} - m_{\text{H}^{+}})_{p}}{(m_{\text{HA}} - m_{\text{H}^{+}})_{1}}} + f(\sqrt{\mu}) \quad [6]$$

where $f(\sqrt{\mu})$ stands for the activity coefficient term and m for the stoichiometric acid and H⁺ concentrations on the molal scale $[m_1 = m_p = (M_1/\rho_1)_1 = (M_1/\rho_1)_p$ in diluted solutions; M_1 is the corresponding concentration on the molar scale, ρ_1 the density of water at 1 atm; the approximation $m_1 = m_p \simeq M_1$ has been used throughout this paper].

Figure 4 shows how $E_1 - E_p$ varies with the concentration M_1 of formic acid in 0.1*M*, 0.01*M*, and 0.001*M* KCl, the corresponding reference half-cells containing 0.1*M*, 0.01*M*, and 0.001*M* HCl.

Figure 4 also gives $\Delta pK' = -\log k'_1 + \sqrt{\mu_1} + \log k'_p - \sqrt{\mu_p}$ where $k' = m'^{*}_{\text{H}+}/(m_{\text{HA}} - m'_{\text{H}+})$ and $\sqrt{\mu}$ is the usual estimate for the activity coefficient term. The primes indicate the uncertainty introduced by the values of $\gamma_{\text{H}+}$ used to calculate $m'_{\text{H}+}$. They correspond to the mean activity coefficient for HCl in KCl

solutions, used by Harned and Owen (20) in their determinations of the dissociation constant of formic acid. As a first approximation it has been assumed that the activity coefficients do not change with pressure.

Values for $\Delta p K'$ in 0.001*M* KCl agree fairly well with the expected one which lies between 0.137 $[\Delta V_{1}^{\circ} = -8.0 \text{ cm}^{3}$ (2,7)] and 0.150 $[\Delta V_{1}^{\circ} = -8.8 \text{ cm}^{3}$ (7)].

In 0.1*M* KCl, $\Delta pK'$ drops unexpectedly at low acid concentrations, with 0.1*M* HCl as reference. It is easy to show that the anomaly disappears when a small constant is added to the observed emf shifts, and there exists experimental evidence to give a meaning



Fig. 4. Formic acid in KCI solutions. Top: $\Delta pK' = -\log k'_1 + \sqrt{\mu_1} + \log k'_p - \sqrt{\mu_p} \ (p = 1000 \text{ kg cm}^{-2})$ as a function of the acid concentration. Bottom: observed emf shifts (Δmv). (HCI + KCI 0.1 and 0.001 is simplified for HCI 0.01M + KCI 0.09M and HCI 0.001M + KCI 0.009M).

to this constant increment. If 0.01M KCl + 0.09MKCl is used as reference, the observed Δ mv values for formic acid in 0.1M KCl are about 0.8-0.9 mv greater than with 0.1M HCl. Similarly a 0.6 mv shift is obtained when 0.001M HCl + 0.009M KCl is used instead of 0.01M HCl. A further tenfold dilution of the reference solution indicates that the differences with 0.001M HCl are within the experimental errors (± 0.1 mv), but the emf of the reference electrode shows then a slow linear drift which makes the determination of the absolute pK values impossible, although pressure induced emf changes are still measurable.

It is to be expected that with HCl + KCl as reference solution, the effect of pressure on the activity coefficient γ_{H^+} almost or completely cancels on both sides of the glass membrane. This might not be the case with HCl alone, except at high dilutions, but there remains the difficulty that the activity coefficient in pure HCl solutions than appears to be more affected by pressure then when KCl is present. The pH of 0.1M HCl would have to decrease from 1.09 to 1.075 to explain the observed shift, if γ_{H^+} in presence of KCl is supposed to remain constant. Such a large change is rather unexpected (18). Another explanation is that the asymmetry potential of the glass electrode changes with pressure when KCl is absent in one of the half-cells which might imply that the glass membrane under pressure would become slightly sensitive to K ions also. The phenomenon might also take place at the Ag-AgCl electrodes or more likely, represent the net effect of pressure on the protode reaction $(H_3O^+ \rightarrow H_2O + p)$ on both sides of the glass membrane. A complete analysis of this problem needs more experiments and is beyond the scope of this paper.

Figure 5 is a plot of $-\log k'$ as a function of $\sqrt{\mu}$ to attempt to extrapolate the results both at $\mu = 0$ and zero acid concentration. The general aspect of this diagram is in reasonable agreement with the results of Harned and Owen (20) regarding the ionic strength and medium (undissociated acid) effects.

Great accuracy is not claimed for the absolute value of the dissociation constant ($pK_1 = 3.71$ instead of 3.75); it can be seen that a better value (3.74) is obtained when the results in 0.1M KCl







Fig. 6. Phosphoric acid (step 1) in KCl solutions. Top: $\Delta p K' = -\log k'_1 + \sqrt{\mu_1} + \log k'_p - \sqrt{\mu_p} (p = 1000 \text{ kg cm}^{-2})$ as a function of the acid concentration (\sqrt{M}) . Bottom: observed emf shifts (Δ mv).

and 0.01*M* KCl alone are considered. More data are needed in 0.01*M* and 0.001*M* KCl, but those available are sufficient to determine ΔpK with some accuracy. The linear extrapolation of $-\log k'_p$ from $\mu = 0.1$ to $\mu = 0.001$ through $-\log k'_p$ at $\mu = 0.01$ is seen to be possible only when HCl + KCl is used in the reference half-cell instead of 0.1 and 0.01*M* HCl. The diagram shows that the activity coefficient term $(\sqrt{\mu})$ used to calculate $\Delta pK'$ in Fig. 4 is an overestimate. The corrected values are: $-0.66 \sqrt{\mu_1}$ and $-0.52 \sqrt{\mu_p}$ at $\mu = 0.1$, in agreement with the value at 1 atm given by Harned and Owen (20) and derived from the equation

$$-\sqrt{\mu_1}/(1+1.175\sqrt{\mu_1})+0.19\mu_1=\log\gamma_{\rm H^+}\gamma_{\rm A^-}/\gamma_{\rm HA}$$

Pressure mainly affects the coefficient of the term in μ_{1} .

The most probable value for ΔV_{1}° , 8.8-9.1 cm³, corresponding to $\Delta pK = 0.150 - 0.155$ is in good agreement with the density and conductivity data (2, 7). The contribution of the activity coefficient change is about 1.5 cm³ at $\mu = 0.1$.

The effect of pressure on the ionization constant of phosphoric acid (step 1) has also been studied.

Figure 6 shows $E_1 - E_p$ as a function of $\sqrt{M_1}$ in 0.1*M* and 0.001*M* KCl, using 0.1*M* and 0.001*M* HCl as reference. As for formic acid, a shift of about 0.9 mv is observed when 0.01*M* HCl + 0.09*M* KCl is used. The corresponding $\Delta pK'$ values calculated in the same way as for formic acid are shown in the upper part of Fig. 6. Again $\Delta pK'$ drops too much at high dilution in 0.1*M* KCl and the same explanation holds.

The contribution of the second term on the right side of Eq. [6] is very important in the case of H₈PO₄ and makes the $\Delta pK'$ values much more sensitive to experimental errors. $\Delta pK'$ extrapolates around 0.300 ($\Delta V_{*1}^{\circ} = -17.5 \text{ cm}^{\circ}$) in 0.001*M* KCl, which is rather



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

too high compared to the -16.2 cm³ 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 cm³ 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 $0.1M \text{ KH}_2\text{PO}_4$, $0.011M \text{ H}_3\text{PO}_4$, 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 ($\Delta V_1^{\circ} = -15.2$



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^s) on both Fig. 7 and 8. The contribution of the activity coefficient term is $\simeq 0.7$ cm³ at $\mu = 0.1$. Figure 9 indicates that the results are better repre-

sented on the
$$\mu$$
 scale. $pK' = pk' + \frac{\sqrt{\mu}}{1 + 1.96\sqrt{\mu}}$ 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 $(\Delta V_{1}^{\circ} = -14.6 \text{ cm}^{\circ})$, 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 ΔV_{1}° for phosphate buffer is about 2 or 3 cm³ smaller than ΔV_{1}° for H₃PO₄ 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 cm³) in much better agreement with the density data of Smith (21).

Preliminary results for acetic acid in 0.001 KCl lead to $\Delta p K = 0.180$ ($\Delta V_{1}^{\circ} = -10.8 \text{ cm}^{\circ}$); for acetate buffer, $\Delta p K = 0.175$ ($\Delta V_{1}^{\circ} = -10.3 \text{ cm}^{\circ}$). 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 $\Delta V_{1}^{\circ} - 11.5$ and -10.8 cm° 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 0.001*M* KCl point toward $\Delta pK = 0.390$ or $\Delta V_{1}^{\circ} = -23.0$ cm³, a value which is still about 5 cm³ too small compared to the one obtained from density measurements (21).

We have not reinvestigated (14) the effect of pressure on H_sCO_a and bicarbonate buffer in dilute KCl solutions. Taking into account the apparent reference cell shift (0.8-0.9 mv) for 0.1*M* HCl and a reasonable estimate of 0.5 mv for the activity coefficient contribution, would lead to ΔV_1° values for bicarbonate buffer between -22.0 and -24.0 cm³, not too far from the value (-24.9 cm³) 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 cm³) and are in disagreement with the pH shift observed in H₂CO₃ solutions, which lies between 14.5 and 15.0 mv in 0.1*M* KCl (reference 0.1*M* HCl) ($\Delta V_1 = -30.6$ and -31.8 cm³, 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 pH > 9. The shift can be computed however from the emf change observed in NaHCO₈ solutions, the pH of which is known to be given by

$pH = \frac{1}{2} pK_1 + \frac{1}{2} pK_2$

The observed value, with 0.1*M* HCl as reference, is 22.6 mv at 1000 kg cm⁻² for a 0.1*M* solution in 0.1*M* 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 cm³. The expected ΔV_1° is -27.8 cm³ (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 *p*H of a sodium acetate solution is known to be given by

$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_{HA} + \frac{1}{2} \log M$

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 CO₂-free NaOH, and very carefully adjusted at the neutralization

point (pH = 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

$pH = pK_w - \frac{1}{2} pK_{NH_4OH} + \frac{1}{2} \log M$

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 10⁻⁴M 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 NH₄OH. The agreement is thus to be accepted with caution, although no change in the asymmetry potential shift could be detected before and after 20min treatment in 10⁻⁴M NH₄OH.

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).



Fig. 11. pH changes recorded from the Bathyscaphe FNRS III between 0 and 2350m in the Mediterranean Sea. Curves 1, 2, 3 give $E_1 - E_p = f(P)$, E_1 corresponding to the pH values at the surface (S_1, S_2, S_3) . Curve 4 gives $E_1 - E_p = f(P)$ for sea water of constant composition. Curve 0 represents the simultaneous temperature record. From Distèche and Dubuisson (25).

the lower end of a pressure resisting steel cylinder containing a d-c amplifier with cathode follower output, driving a pen recorder, on which the pHshifts are observed as the distance between two traces, one of which represents the zero drift of the apparatus. The error on ΔpH is certainly less than 0.01 pH unit and very close to 0.005 pH unit.

The curves on Fig. 11 were obtained during two dives. They represent direct manual measurements (large dots) with a precision potentiometer circuit and the data taken from the recorded curves (small dots). After a small increase near the surface, the pH is seen to decrease exponentially (~0.15 pH unit) from 0 to 400m. From 400m to 2350m, the bicarbonate/CO₂ ratio remains constant since the observed pH change corresponds to the effect of pressure on water of constant composition. A slight acid gradient is found near the bottom. The results obtained from the surface to the sea bottom agree with those recorded during the return to the surface, and there is a distinct correlation between the temperature curve and the pH curve.

Conclusion

The author is fully aware that his investigations on the behavior of a glass electrode at high pressure in various electrolytes cover only an extremely small portion of a very wide field. The important fact is that the reproducibility and the precision of the pH measurements with a glass electrode are affected by pressure but little or not at all. This statement is not a proof that the electrode gives, under all circumstances, the value of the hydrogen ion activity, but considering as a whole the results which have been obtained so far, makes one feel confident, since many results agree well with what is known from conductance and density data.

Further instrumental development is possible. A bright gold electrode can be added to the glass electrode cell for rH measurements¹ and it is planned to try glass electrodes sensitive to Na⁺ and K⁺ (26, 27).

The use of multielectrode cells, including a conductivity cell, would certainly broaden the field of electrochemical investigation at high pressures (properties of electrolytes, protein chemistry, kinetics, oceanography, and industrial technology).

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¹The potential of the cell Au-FeSO₄ 0.05M, Fe₂(SO₄)₅ 0.025M, HCl 0.1*M*, AgCl-Ag changes very little with pressure in the range 0-1000 atm, and it might be interesting to replace the internal Ag-AgCl electrode of the glass electrode by a redox half cell; for the use of a glass electrode and an external redox half cell for rH determinations in oceanographic research, see ref. (28) and (29).

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