The Effect of Pressure on pH and Dissociation
Constants from Measurements with
Buffered and Unbuffered Glass
Electrode Cells

h. Pistêche and S. Pistêche

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Acetic, Formic, Phosphoric, Carbonic Acids Adenosinetriphosphate and Phosphorylcreatine
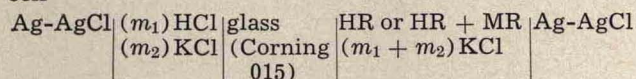
A. Distèche and S. Distèche

Laboratory of General Biology, Zoology Institute, University of Liege, Liege, Belgium

ABSTRACT

The cell Ag-Ag Cl | HCl (m_1) | glass | HR or HR + MR | AgCl-Ag
         | KCl (m_2) | | $(m_1 + m_2)$ KCl |

is used to measure the effect of pressure on the ionization constant K of weak acids (HR) in the presence or not of the corresponding Na or K salt (MR). Double extrapolation, to zero weak electrolyte concentration and zero KCl concentration, yields log K_p/K_1 values at $p = 1000$ kg cm^{-2} and the molal volume change on ionization for the reaction HR $\rightleftharpoons$ R$^-$ + H$^+$ is computed at 1 atm for acetic acid, formic acid, carbonic acid (buffered and unbuffered solutions), phosphoric acid (2^d step), adenosinetriphosphate and phosphorylcreatine.

It has been shown in previous papers (1-3) that the cell

Ag-AgCl | (m_1) HCl | glass | HR or HR + MR | Ag-AgCl
        | (m_2) KCl | (Corning | $(m_1 + m_2)$ KCl |
        | | 015) |

can be used to measure the effect of pressure on the ionization of a weak acid HR in the presence or absence of its Na or K salt (MR). Dissociation constants K can be computed from the emf measurements by extrapolation to zero ionic strength and zero weak electrolyte concentration, and the volume change (ΔV_p^o) induced by pressure p can be calculated at any pressure from the well-known equation

$$\left(\frac{\partial \ln K}{\partial p} \right)_{m,T} = \frac{-\Delta V^o}{RT} \quad [1]$$

More recently, Hamann (4) used the cell Ag-AgCl | (m_1) HCl | Li — glass | (m_2) KCl + (m_3) KOH | AgCl-Ag to derive ΔV_1^o for water.

In the present paper, we shall investigate in more detail the pressure dependence of the ionization constants of acetic, formic, phosphoric (2nd step), and carbonic acids, either in buffer solutions or in pure acid solutions. Data for organophosphorus compounds such as adenosinetriphosphate and phosphorylcreatine are also described.

Experimental

The equipment described in 1962 (2) is used. It was found that slight hysteresis effects, which sometimes appear when new Ag-AgCl or glass electrodes are tried, are minimized by applying several pressure cycles before making the final experiment.

Methods.—The methods used to derive ionization constants from emf measurements are classic and can be used, in principle, to calculate K and ΔV^o at any pressure with the aid of Eq. [1].

In practice, the choice of a particular method is limited by the fact that the glass electrode cell under pressure exhibits two types of asymmetry potentials: one, normal, which can be taken into account by measuring the emf of the cell with the reference solution on both sides of the glass membrane, and another which arises (2) when the KCl concentration is different in the two compartments. To eliminate this last cause of error, it was found convenient to use the following three cells

1. Ag-AgCl | HCl (0.01M) || HR or HR + MR | Ag-AgCl
            | KCl (0.09M) || KCl (0.1M) |

2. Ag-AgCl | HCl (0.001M) | HR or HR + MR | Ag-AgCl
            | KCl (0.009M) | KCl (0.01M) |

3. Ag-AgCl | HCl (0.001M) | HR or HR + MR | Ag-AgCl
            | | KCl (0.001M) |

The asymmetry due to KCl in cell 3 can be neglected.

The emf (E) of the cells at 1 atm or at pressure p is expressed by the relation

$$E_{1,p} \mathbf{F}/2.3RT = \log (m_H)^{ref.}_{1,p} - \log (m_H)^x_{1,p}$$
$$+ 2 \log \frac{(\gamma_{HCl})^{ref.}_{1,p}}{(\gamma_{HCl})^x_{1,p}} \quad [2]$$

where m_H is the hydrogen ion concentration (molal scale), γ_{HCl} the mean activity coefficient for HCl, and where *ref.* and x, respectively, refer to the reference half-cell and the cell compartment containing the weak acid HR or its buffer HR + MR (M = Na or K) at concentrations m_{HR} and m_{MR}.

The dissociation constant K of the weak acid is given by the relations

$$\log K = \log \frac{m_H^2}{m_{HR} - m_H} + 2 \log \gamma_A$$
$$= \log k - (A\sqrt{\mu} \pm B\mu) \quad [3]$$

in the unbuffered half-cell, and

$$\log K = \log \frac{m_H(m_{MR} + m_H)}{m_{MR} - m_H} + 2 \log \gamma_A$$
$$= \log k - (A\sqrt{\mu} \pm B\mu) \quad [4]$$

in the buffered half-cell

Here $2 \log \gamma_A = \log \gamma_H \gamma_R/\gamma_{HR}$ and $(A\sqrt{\mu} \pm B\mu)$ is the usual function of the ionic strength μ used to estimate $2 \log \gamma_A$.

The combination of [2], [3], and [4] leads to the expressions

$$2(E_1 - E_p)\mathbf{F}/2.3RT = \log \frac{K_p}{K_1} + \log \frac{(m_{HR} - m_H)_p}{(m_{HR} - m_H)_1}$$
$$+ 2 \log \frac{(\gamma_A)_1}{(\gamma_A)_p} + 4 \log \frac{(\gamma_{HCl})^{ref.}_1}{(\gamma_{HCl})^{ref.}_p} - 4 \log \frac{(\gamma_{HCl})^x_1}{(\gamma_{HCl})^x_p} \quad [5]$$

and

$$(E_1 - E_p)\mathbf{F}/2.3RT = \log \frac{K_p}{K_1} + \log \frac{(m_{HR} - m_H)_p}{(m_{HR} - m_H)_1}$$
$$\cdot \frac{(m_{MR} + m_H)_1}{(m_{MR} + m_H)_p} + 2 \log \frac{(\gamma_A)_1}{(\gamma_A)_p}$$

$$+ 2 \log \frac{(\gamma_{HCl})_1^{ref.}}{(\gamma_{HCl})_p^{ref.}} - 2 \log \frac{(\gamma_{HCl})_1^{x}}{(\gamma_{HCl})_p^{x}} \quad [6]$$

for the unbuffered and buffered half-cells, respectively.

When m_H is negligible compared to m_{HR} and m_{MR}, the ionic strength remains constant in the x compartment. The effect of pressure on γ_{HCl} is small

$$\left[\log \frac{(\gamma_{HCl})_{1000}}{(\gamma_{HCl})_1} = 0.003 \text{ in HCl } 0.1M \text{ (5)} \right]$$

and as a first approximation one can neglect the terms containing γ_{HCl} which cancel each other at infinite dilution of the weak electrolyte because of the symmetry of the cells.

Equations [5] and [6] then simplify to

$$2(E_1 - E_p)\mathbf{F}/2.3RT = \log \frac{K_p}{K_1} + 2\log \frac{(\gamma_A)_1}{(\gamma_A)_p} = \log \frac{k_p'}{k_1'} \quad [7]$$

and

$$(E_1 - E_p)\mathbf{F}/2.3RT = \log \frac{K_p}{K_1} + 2\log \frac{(\gamma_A)_1}{(\gamma_A)_p} = \log \frac{k_p'}{k_1'} \quad [8]$$

for the unbuffered and buffered half-cells, respectively.

The primes indicate that $\log k'$ is only known with approximation. The choice of the best suited concentration scales to eliminate $\log (\gamma_{A1}/\gamma_{Ap})$ by extrapolation to zero concentration of both weak electrolyte and KCl, is based on the following considerations.

Activity coefficients and pressure are related by the well-known equation

$$\left(\frac{\partial \ln \gamma}{\partial p} \right)_{m,T} = \frac{\overline{V}_2 - \overline{V}_2^{\circ}}{RT} \quad [9]$$

where $\overline{V}_2$ and $\overline{V}_2^{\circ}$ are the partial molal volumes of the solute (subscript 2), respectively, at any concentration m, and in the standard state (unit activity, or at infinite dilution in the pure solvent). Integration of [9] yields the simplified relation (5)

$$\log \gamma_p = \log \gamma_1 + C(p-1)\sqrt{md_o} \quad [10]$$

in which C is a constant and d_o the density of water.

Infinite dilution in 0.1M KCl (cell 1), 0.01M KCl (cell 2), and 0.001M KCl (cell 3) can be used to define three other reference states and for each medium the partial molal volumes in the standard state will be shifted in first approximation, according to Eq. [11] (6).

$$^{KCl}\overline{V}_2^{\circ} = \overline{V}_2^{\circ} + A_V \sqrt{2d_o} \sqrt{\mu} \quad [11]$$

where A_V is a constant.

It follows that extrapolation of $E_1 - E_p$ (Eq. [7] and [8]) on the $\sqrt{m}$ scale will yield values of $\log K_p/K_1$ corresponding to each auxiliary reference state. Equations [1], [9], and [11] show that subsequent extrapolation on the $\sqrt{\mu}$ scale to zero KCl concentration will give $\log K_p/K_1$ in pure water. Further, it is to be expected, if p is not too great, that the two extrapolations will be linear.

When m_H is not negligible, it is practical to calculate m_H' from Eq. [2] using γ_{HCl} values corresponding to the ionic strength at pressure 1 and p. The prime indicates the approximation introduced by the fact that the effect of pressure on the activity coefficient is neglected and that it is assumed that γ_{HCl} in KCl or NaCl is not affected by the weak electrolyte. The values used for γ_{HCl} are taken from Harned and Owen (7). $(m_H')_{1,p}$ is used to calculate $(\log k' - A\sqrt{\mu'})_{1,p}$ from Eq. [3] and [4], again neglecting the effect of pressure on the constant A, which is close to unity.

$$(- \log k' + \sqrt{\mu'})_p - (- \log k' + \sqrt{\mu'})_1 = \Delta pK', \text{ or } \log$$

k_1'/k_p' is then calculated and can be used for the double extrapolation on the $\sqrt{m}$ and $\sqrt{\mu}$ scales as above.

An alternative consists in twice extrapolating, either $(- \log k' + \sqrt{\mu'})$ or $- \log k' + A\sqrt{\mu'} \pm B\mu'$ or simply, $\log k'$, at pressures 1 and p, on the best suited concentrations scale ($\sqrt{\mu}$ or μ) depending on the nature of the electrolyte.

Since the effect of pressure on the activity coefficients is neglected in the calculations, it can be deduced from the difference between the slopes of the extrapolated functions. If needed, the corrected activity coefficients can be used to calculate the ionization functions k (Eq. [3] and [4]) with more accuracy, which in turn will lead to a more precise knowledge of K after a second double extrapolation.

The volumes change on ionization at infinite dilution, (ΔV_1°), is calculated from the slope of a graph of $\log K_p/K_1$ vs. pressure at 1 atm (Eq. [1]).

When simplified Eq. [7] and [8] are valid, ΔV_1 values can be read from the slope of $E_1 - E_p = f(p)$ at 1 atm and yield ΔV_1° by double extrapolation.

It is easy to show (2) that $\Delta V_1 = 1.016 \times (E_1 - {}^*E_{1000})$ if V is expressed in cm^3 $mole^{-1}$, E in millivolts, p in kg cm^{-2}.

${}^*E_{1000}$ is measured on the tangent of $(E_1 - E_p) = f(p)$ drawn through $p = 1$. In most cases $(E_1 - E_p)$ is a linear function of p up to 1000 kg cm^{-2} and therefore the values for $\log K'_{1000}/K_1' = \Delta pK'$ or simply the direct experimental emf shift $(E_1 - E_{1000})$ can be used to extrapolate. In practice, for the media investigated, it was found that whenever $(E_1 - E_p) = f(p)$ graphs displayed some slight curvature, the tangent through $p = 1$ safely could be drawn through E_p at $p = 500$ kg cm^{-2}, with $\Delta V_1 = 2 \times 2.1016 \times (E_1 - E_{500})$ if the effect of dissociation of the weak electrolyte can be neglected.

Corning 015 glass membranes give the correct hydrogen electrode constant, 2.3 $RT/\mathbf{F} \pm 1$ mv or 2%, independently of pressure, the uncertainty being within the limits of the experimental errors.

Results

Acetic acid and acetate buffer.—Figure 1 gives $2\mathbf{F}/2.3RT$ $(E_1 - E_p) = \Delta pk' = \log k_p'/k_1'$ $(p = 500$ kg $cm^{-2})$
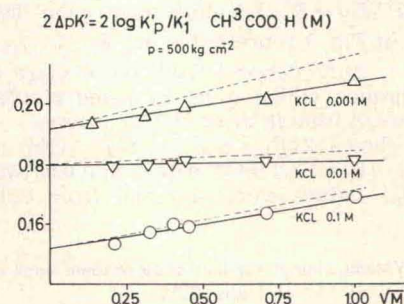

Fig. 1. Acetic acid in KCl 0.1, 0.01 and 0.001M KCl. Extrapolation of $\log k_p'/k_1'$ and $\log K_p'/K_1'$ to zero acetic acid concentration. Solid lines, $\log k_p'/k_1'$ (eq. [7]); dotted lines, $- \log k_p' + \sqrt{\mu_p'} + \log k_1' - \sqrt{\mu_1'} = \Delta pK'$ (eq. [2] and [3]).
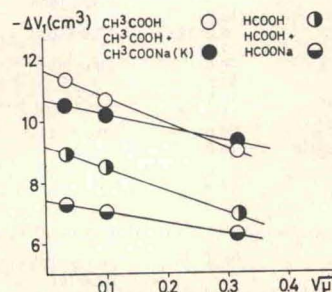

Fig. 2. Extrapolation of $- \Delta V_1$ (cm^3 $mole^{-1}$) to zero KCl concentration for acetic acid, acetate buffer, formic acid, and formate buffer.
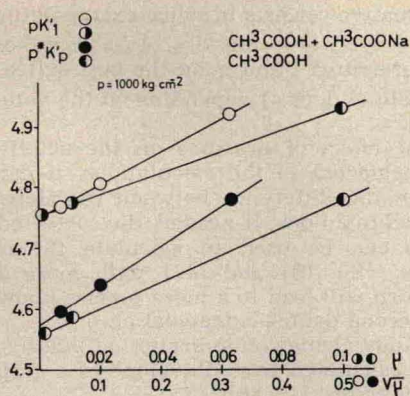
Fig. 3. Extrapolation of pK_1' and pK_p' values obtained at zero acetic acid and acetate buffer concentration, to zero KCl concentration; μ scale, acetic acid; $\sqrt{\mu}$ scale, acetate buffer. $p*K_p'$ at 1000 kg cm^{-2} is calculated from the slope of $(E_1 - E_p)$ $= f (p)$ at 1 atm for acetic acid; $p*K_p' = pK'_{1000}$ for acetate buffer where $(E_1 - E_p) = f (p)$ is linear.
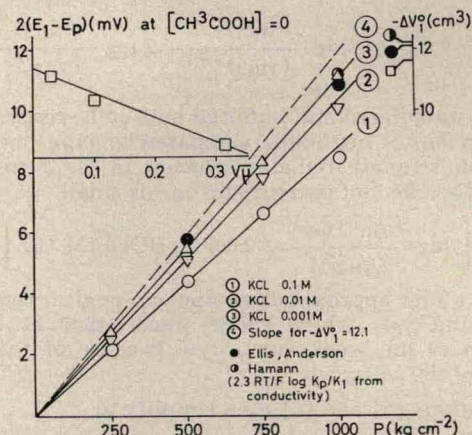

Fig. 4. 2 $(E_1 - E_p) = 2.3 \, RT/F \log k_p'/k_1' = f (p)$ at zero acetic acid concentration, in 0.1, 0.01, and 0.001M KCl. Inserts: extrapolation of 2 $(E_1 - E_p)$ to zero KCl concentration and corresponding $- \Delta V_1^\circ$ value (11.6 cm^3 mole^{-1}). 2.3 $RT/F \log$ K_p/K_1 and ΔV_1° from conductivity data [Ellis and Anderson (8); Hamann (9, 10)] are indicated together with the limiting slope of 2 $(E_1 - E_p) = f (p)$ for $- \Delta V_1^\circ = 12.1$.

for acetic acid solutions as a function of $\sqrt{m}$ (Eq. [7]; $2 \times \Delta pK'$ is taken as ordinate to facilitate comparison with Fig. 5 for acetate buffer and for simplicity the symbol K' is used instead of k'). Corresponding values of ΔV_1 at $[CH_3COOH] = 0$ are extrapolated to $[KCl] = 0$ in Fig. 2, which gives $-\Delta V_1^\circ = 11.6$ cm^3.

The slope of the extrapolated function depends both on the ionic strength and the undissociated acid concentration. This explains the difference between the slope for 0.01M KCl and that observed for 0.1M and 0.001M KCl.

A more elaborate treatment (Eq. [2] and [3]) where $pK' = - \log k' + \sqrt{\mu'}$ is first extrapolated on the μ scale to $\mu = 0.1$, 0.01, and 0.001, and then (Fig. 3) to $[KCl] = 0$ on the $\sqrt{\mu}$ scale, yields $-\Delta V_1^\circ = 11.5$ cm^3 mole^{-1}. The * sign of $p*K_p$ in Fig. 3 denotes that the dissociation constant at $p = 1000$ kg cm^{-2} is calculated from 2×2 $(E_1 - E_{500})$ values (see page 351). The dotted lines in Fig. 1 represent $- \log k_p' + \sqrt{\mu_p'} + \log k_1' - \sqrt{\mu_1'} = \Delta pK'$ derived from these more complicated calculations which give the same result as the simple treatment used to draw the solid lines.

Figure 4 shows $2(E_1 - E_p) = f(p)$ (Eq. [7]) at $[CH_3COOH] = 0$ in KCl 0.1M, 0.01M, and 0.001M, where the $(E_1 - E_p)$ values were obtained from extrapola-

tions of the emf readings on the $\sqrt{m}$ scale at $p = 250$, 500, 750, and 1000 kg cm^{-2}.

The curvature in $2(E_1 - E_p) = f(p)$ is apparent at $p = 1000$ kg cm^{-2} but only in 0.1 and 0.01M KCl. The extrapolation at $[KCl] = 0$ is also given on Fig. 4 and the corresponding $-\Delta V_1^\circ$ value is 11.6 cm^3 mole^{-1}.

This figure is in agreement with our previous preliminary determinations (2) and in reasonable agreement with density and conductivity data (Table I).

The $-\Delta V_1^\circ$ values, published by Ellis and Anderson (8) for $p = 1$, $p = 500$, $p = 1000$ kg cm^{-2} and by Hamann and Strauss (9) for $p = 1$ and $p = 1000$ kg cm^{-2} are indicated on Fig. 4 either in cm^3 mole^{-1} or converted into emf values, together with the limiting slope corresponding to $-\Delta V_1^\circ = 12.1$ cm^3 mole^{-1} (8).

It is clearly seen that the main difference between the conductivity data and our determinations lies in the estimation of the curvature of $2(E_1 - E_p) = f(p)$ $= 2.3RT/F \log k_p'/k_1'$.

In a buffer containing equal molalities of acetic acid and sodium acetate, $E_1 - E_p$ is a linear function of p up to 1000 kg cm^{-2} at all the KCl concentrations investigated. $(E_1 - E_{1000})$ together with $\Delta pK' = \log K_{1000}'/K_1'$ is given in Fig. 5 as a function of the square root of the total salt and acid concentrations.

The drop of $(E_1 - E_{1000})$ at high dilutions shows that Eq. [7] is no longer valid, and that it is necessary to take the dissociation of acetic acid into account (Eq. [4]) to get the correct values for $\Delta pK' = - \log k_1'$ $+ \sqrt{\mu_1'} + \log k_p' - \sqrt{\mu_p'}$.

Extrapolation on the $\sqrt{\mu}$ scale is given in Fig. 2 and shows that $-\Delta V_1^\circ = 10.7$ cm^3 mole^{-1} which agrees with our previous determinations (2) but is 0.9 cm^3 smaller than $-\Delta V_1^\circ$ in acetic acid solutions.

Extrapolation of $- \log k' + \sqrt{\mu'}$ at $p = 1$ and $p = 1000$ kg cm^{-2} first on the μ scale to zero buffer concentration and then to $[KCl] = 0$ on the $\sqrt{\mu}$ scale (Fig. 3), gives identical results. No difference was found with potassium acetate or when the buffer ratio MR/HR is reduced to ⅛.

The value of pK_1 in the unbuffered cell is 4.76, and 4.75 when the buffer is used, in agreement with the results obtained by Hamann (9, 10) (4.77), and by Ellis and Anderson (8) (4.75) from their conductivity determinations. (The extrapolation line for acetate buffer in Fig. 3 has been shifted 0.01 pK unit to coincide with the data for acetic acid, to better show the difference of the effect of pressure).

Formic acid and formate.—Formic acid has been extensively studied in a previous paper (2) from which

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

	Glass electrode $-\Delta V_1^\circ$	Density $-\Delta V_1^\circ$	Conductivity $-\Delta V_1^\circ$
Acids and buffers	cm^3 mole^{-1}	cm^3 mole^{-1}	cm^3 mole^{-1}
Acetic acid	11.6	12.5 (10)	12.2 (9)
		9.2 (6)	12.1 (8)
		11.5 (14)	
Acetate buffer	10.7		
Formic acid	9.2[1] (2)	8.0 (10)	8.8 (10)
Formate buffer	7.4		
Carbonic acid $K_{(1)}$	26.6	29.0 (6)	26.5 (13)
Bicarbonate buffer	25.5		
Phosphoric acid $K_{(1)}$	17.7[1] (2)		15.5 (8)
Phosphate buffer $K_{(1)}$	15.7[1] (2)		
Phosphate buffer $K_{(2)}$	24.0	28.1[2] (15)	
Adenosine triphosphate (pH 7.0)	24.0		
Phosphorylcreatine (pH 7.0)	21.2		

Volume change for ionization of water at 1 atm, 25°C, Hamann (4).

	20.4 (4)	20.55 (16)	
		23.4 (6)	

[1] Average values taken from Distèche (2) multiplied by the factor 1.016 (see page 35) which was neglected in the 1962 paper.
[2] $\Delta V_1 = -24.1$ cm^3 mole^{-1} is reported from dilatometric experiments by Linderstrom-Lang and Jacobsen (11).
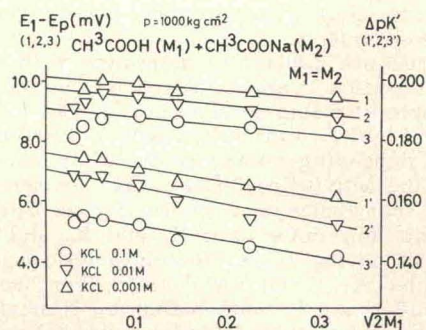
Fig. 5. Acetate buffer in 0.1, 0.01, and 0.001M KCl. 1, 2, 3: $(E_1 - E_p) = 2.3\ RT/F \log k_p'/k_1'$ as a function of the total acetate and acetic acid concentration. 1', 2', 3': extrapolation of $\Delta_p K' = -\log k_1' + \sqrt{\mu_1'} \log k_p' - \sqrt{\mu_p'}$ (Eq. [2] and [4]) to zero buffer concentration.
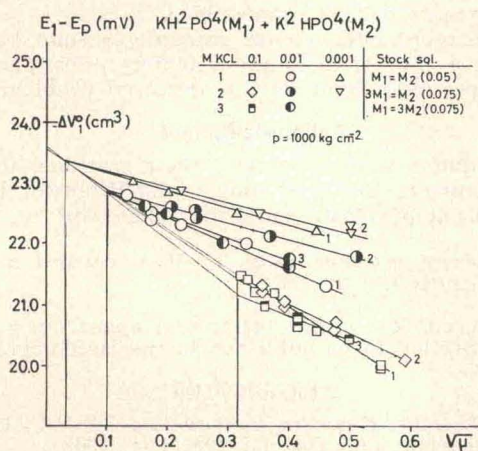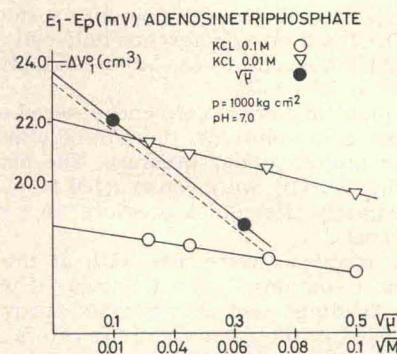

Fig. 7. Adenosinetriphosphate in 0.1 and 0.01M KCl. Extrapolation of $(E_1 - E_p) = 2.3\ RT/F \log k_p'/k_1'$ to zero ATP concentration ($\sqrt{m}$ scale) and to zero KCl concentration ($\sqrt{\mu}$ scale); $-\Delta V_1° = 24.0\ cm^3\ mole^{-1}$. Dotted lines, both extrapolations are made on the $\sqrt{\mu}$ scale.

Fig. 6. Phosphate buffer $K_{(2)}$ in 0.1, 0.01, and 0.001M KCl. Extrapolation of $(E_1 - E_p) = 2.3\ RT/F \log k_p'/k_1'$ to zero KCl and buffer concentration at three different buffer ratios; $-\Delta V_1° = 24.0\ cm^3\ mole^{-1}$.
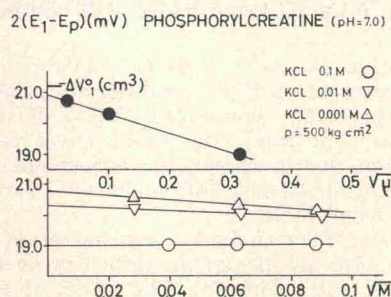

Fig. 8. Phosphorylcreatine in 0.1, 0.01, and 0.001M KCl. Extrapolation of $2\ (E_1 - E_p) = 2 \times 2.3\ RT/F \log k_p'/k_1'$ to zero phosphorylcreatine concentration (lower curves) and to zero KCl concentration (upper curve); $-\Delta V_1° = 21.2\ cm^3\ mole^{-1}$.
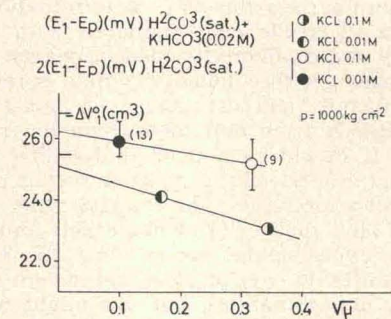

Fig. 9. Extrapolation of $2\ (E_1 - E_p) = 2.3\ RT/F = \log k_p'/k_1'$ for carbonic acid (saturated solution) and $(E_1 - E_p) = 2.3\ RT/F \log k_p'/k_1'$ for bicarbonate buffer (H_2CO_3 sat. $+$ 0.02M $KHCO_3$) to zero ionic strength; $-\Delta V_1° = 26.6\ cm^3\ mole^{-1}$ and 25.5 $cm^3\ mole^{-1}$. The circles on the upper curve represent average values derived from 13 and 9 determinations in 0.01M KCl and 0.1M KCl respectively; the horizontal lines indicate the highest and lowest values.

we take the necessary data to extrapolate $-\Delta V_1$ to [KCl] $= 0$ on the $\sqrt{\mu}$ scale as shown in Fig. 2. $-\Delta V_1° = 9.2\ cm^3\ mole^{-1}$ in fairly good agreement with the conductivity determinations (Table I) [8.8 cm^3 $mole^{-1}$, Hamann (10)]. Data for formate buffer, treated in the same way as the acetate buffer, yield $-\Delta V_1 = 7.4$ $cm^3\ mole^{-1}$ (Fig. 2).

It is seen on this same figure that the curves for acetic acid and formic acid, for acetate buffer and for formate buffer, run nearly parallel with each other.

Phosphate buffer (2nd step).—In Fig. 6, the results obtained for three different buffer ratios are plotted on the $\sqrt{\mu}$ scale and the double extrapolation leads without any difficulty to $-\Delta V_1° = 24.0\ cm^3\ mole^{-1}$, which is to be preferred to a preliminary estimate, 23.4 cm^3 $mole^{-1}$, published in 1962.

Density measurements predict $-\Delta V_1° = 28.1\ cm^3$ $mole^{-1}$ (14) but dilatometric experiments by Linderstrom-Lang and Jacobsen [see ref. (11)] give 24.1 cm^3 $mole^{-1}$.

Adenosine triphosphate and phosphorylcreatine.— Figure 7 indicates that $-\Delta V_1°$ (24.0 $cm^3\ mole^{-1}$) is the same in phosphate buffer and in ATP solutions at $pH = 7.0$, the double extrapolation being done on the $\sqrt{m}$ and $\sqrt{\mu}$ scales. A slightly smaller value is obtained if both extrapolations are made on the $\sqrt{\mu}$ scale (dotted line).

Figure 8 shows the corresponding results for phosphorylcreatine. $-\Delta V_1° = 21.2\ cm^3\ mole^{-1}$ and is considerably smaller than the volume change observed for phosphate buffer ($K_{(2)}$) and ATP.

The ΔV values are calculated from readings at 500 kg cm^{-2} because of the rather marked curvature of the $(E_1 - E_p) = f(p)$ curve.

Control analysis before and after a pressure run failed to indicate any hydrolysis.

It is well known (12) that the $pK_{(2)}$ of phosphoric acid in phosphorylcreatine is strongly affected by the methylguanidinium group, its value being 4.6 instead of 7.2. The difference observed for $\Delta V_1°$ is related to this phenomenon insofar as it is related to the ionic solvation energy difference between H_3PO_4 and its ester.

Carbonic acid and bicarbonate buffer.—Our previous determinations of ΔV_1 for carbonic acid in 0.1M KCl (1) gave values as high as 31.0 and 32.3 $cm^3\ mole^{-1}$, but only 22.8–23.9 $cm^3\ mole^{-1}$ for the bicarbonate buf-

fer (values corrected for the asymmetry due to KCl when 0.1M HCl is used as reference half-cell). Density data (6) predict 29.0 cm^3 $mole^{-1}$ and conductivity data give 26.5 cm^3 $mole^{-1}$ (13).

Experimental difficulties were encountered especially with carbonic acid solutions, the pH of which shows long-term instability under pressure. The curves giving $(E_1 - E_p) = f(p)$ were constructed from readings taken immediately after quick pressure steps separated by long intervals.

The same problems were met with at the start of the new determinations. Later, however, it was found that stable readings can be obtained provided the silicone oil used in the glass electrode cell is saturated with CO_2 as well as the aqueous solutions and the cell filled from pipettes where the gas phase is pure CO_2. These precautions limit the possibility of CO_2 exchanges between both liquid phases and the escape of CO_2 in the pressure bomb or elsewhere.

The circles on the upper curve of Fig. 9 correspond to the average value of, respectively, 9 and 13 determinations in 0.1M KCl and 0.01M KCl saturated with CO_2.

Extrapolation at $\sqrt{\mu} = 0$ gives $-\Delta V_1° = 26.6$ cm^3 cm^{-3} in agreement with the conductivity experiments.

Bicarbonate buffer containing 0.02M $KHCO_3$ was tested in the same way. The results show very much less dispersion, are in reasonable agreement with our previous determinations, and yield on extrapolation $-\Delta V_1° = 25.5$ cm^3 $mole^{-1}$.

Extrapolation at zero buffer concentration was not tried in this case because of the difficulty of maintaining the buffer ratio constant. The effect of H_2CO_3 on log K_p'/K_1', however, is small (5) compared to the effect of the ionic strength, so that it seems safe to extrapolate.

Discussion

Table I summarizes the $\Delta V_1°$ determinations made with a glass electrode cell compared with the data from density and conductivity measurements.

The agreement with conductivity data is fairly good for acetic, formic, and carbonic acid, but the value found for H_3PO_4 from emf measurements is about 2 cm^3 higher. It should be noticed that H_3PO_4 is highly dissociated in diluted solutions which means relatively small pH shifts for large $\Delta pK'$ changes when pressure is applied. This makes ΔV calculations much more sensitive to experimental errors. The ΔV found for phosphate buffer $K_{(1)}$ is in close agreement with the conductivity determinations, but this might be fortuitous since we notice that systematically ΔV values for buffers, from pH measurements, are smaller than the values obtained for pure acid solutions.

The difference is much larger than possible experimental errors: 0.9, 1.8, 2.0, 1.1 cm^3 for acetate, formate, phosphate $K_{(1)}$, and bicarbonate buffer, respectively.

The difference is identical with Na or K salts. This practically eliminates the possibility of an error due to asymmetry in cation composition between the cell compartments since the reference half-cell always contains KCl except for the experiments in 0.001M KCl where the effect of KCl is negligible. However, the cell cannot be made symmetrical with respect to anions. Though it seems rather unlikely, these could be ad-

sorbed on the glass membrane and cause errors in the buffer measurements.

pK values are difficult to determine with precision when dissociation is appreciable and it is known that, for example, the data for phosphoric acid $K_{(1)}$ buffer at different buffer ratios extrapolate to different values of log K depending on the choice of the function to estimate the activity coefficients (17). It can however be shown that a change of the activity coefficients used to calculate m_H shifts both K_p and K_1 and has but little effect on log K_p/K_1 for phosphoric acid, phosphate buffer $K_{(1)}$, and formic acid. For acetic acid, acetate buffer and formate buffer m_H is small except at very high dilutions and can be completely neglected for carbonic acid and bicarbonate buffer.

The fact that the observed differences exist even at infinite dilution eliminates as explanation all the effects which affect the activity coefficients: ionic associations, uncomplete dissociations, salting in and out effects, etc., unless one admits that some of these effects only disappear at extreme dilutions where emf measurements become impossible.

More experiments on, for example, acetate buffer, covering a very wide range of buffer ratios, perhaps will throw more light on this unsolved problem.

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