

$$+ 2 \log \frac{(\gamma_{\text{HCl}})_{1}^{\text{ref.}}}{(\gamma_{\text{HCl}})_{p}^{\text{ref.}}} - 2 \log \frac{(\gamma_{\text{HCl}})_{1}^{x}}{(\gamma_{\text{HCl}})_{p}^{x}} \quad [6]$$

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

$$\left[\log \frac{(\gamma_{\text{HCl}})_{1000}}{(\gamma_{\text{HCl}})_{1}} = 0.003 \text{ in HCl } 0.1\text{M} \quad (5) \right]$$

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

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

and

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

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

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

where \bar{V}_2 and \bar{V}_2° 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)

$$\log \gamma_p = \log \gamma_1 + C(p-1)\sqrt{m d_0} \quad [10]$$

in which C is a constant and d_0 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).

$$\text{KCl} \bar{V}_2^\circ = \bar{V}_2^\circ + A_V \sqrt{2d_0} \sqrt{\mu} \quad [11]$$

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). $(m_{\text{H}})_{1,p}$ 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 $\text{cm}^3 \text{ mole}^{-1}$, 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 $p = 500 \text{ kg cm}^{-2}$, 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, $2.3 RT/F \pm 1 \text{ mv}$ or 2%, independently of pressure, the uncertainty being within the limits of the experimental errors.

Results

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

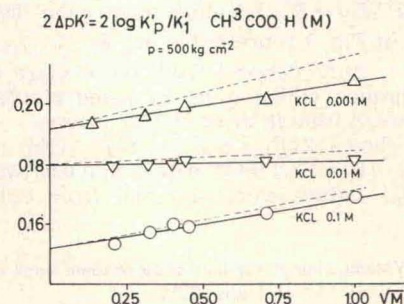


Fig. 1. Acetic acid in KCl 0.1, 0.01 and 0.001M KCl. Extrapolation of $\log k_p'/k_1'$ and $\log K_p/K_1'$ to zero acetic acid concentration. Solid lines, $\log k_p'/k_1'$ (eq. [7]); dotted lines, $-\log k_p' + \sqrt{\mu_p'} + \log k_1' - \sqrt{\mu_1'} = \Delta pK'$ (eq. [2] and [3]).

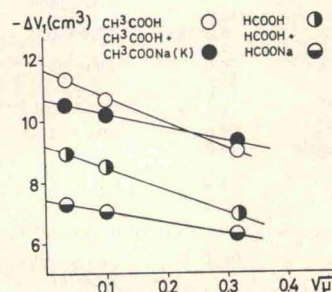


Fig. 2. Extrapolation of $-\Delta V_1$ ($\text{cm}^3 \text{ mole}^{-1}$) to zero KCl concentration for acetic acid, acetate buffer, formic acid, and formate buffer.

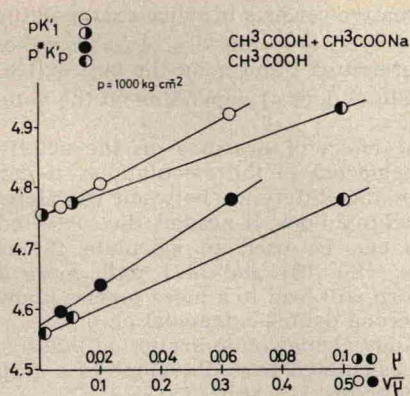


Fig. 3. Extrapolation of pK_1' and pK_p' values obtained at zero acetic acid and acetate buffer concentration, to zero KCl concentration; μ scale, acetic acid; $\sqrt{\mu}$ scale, acetate buffer. p^*K_p' at 1000 kg cm^{-2} is calculated from the slope of $(E_1 - E_p) = f(p)$ at 1 atm for acetic acid;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

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 $[\text{CH}_3\text{COOH}] = 0$ are extrapolated to $[\text{KCl}] = 0$ in Fig. 2, which gives $-\Delta V_1^\circ = 11.6 \text{ cm}^3$.

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 $\mu = 0.1, 0.01, \text{ and } 0.001$, and then (Fig. 3) to $[\text{KCl}] = 0$ on the $\sqrt{\mu}$ scale, yields $-\Delta V_1^\circ = 11.5 \text{ cm}^3 \text{ mole}^{-1}$. The * sign of p^*K_p' in Fig. 3 denotes that the dissociation constant at $p = 1000 \text{ kg cm}^{-2}$ is calculated from $2 \times 2 (E_1 - E_{500})$ 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 $[\text{CH}_3\text{COOH}] = 0$ in KCl 0.1M, 0.01M, and 0.001M, where the $(E_1 - E_p)$ values were obtained from extrapola-

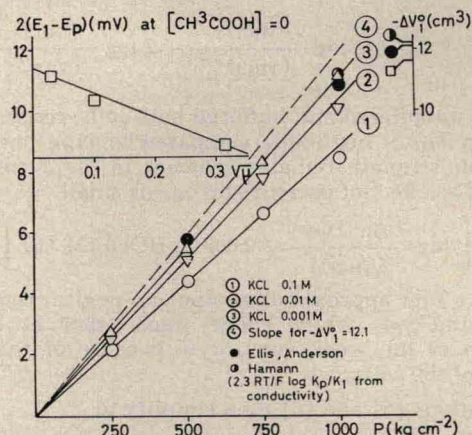


Fig. 4. $2(E_1 - E_p) = 2.3 RT/F \log k_p'/k_1' = f(p)$ at zero acetic acid concentration, in 0.1, 0.01, and 0.001M KCl. Inserts: extrapolation of $2(E_1 - E_p)$ to zero KCl concentration and corresponding $-\Delta V_1^\circ$ value ($11.6 \text{ cm}^3 \text{ mole}^{-1}$). $2.3 RT/F \log K_p/K_1$ and 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 $-\Delta V_1^\circ = 12.1$.

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

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

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 $p = 1, p = 500, p = 1000 \text{ kg cm}^{-2}$ and by Hamann and Strauss (9) for $p = 1$ and $p = 1000 \text{ kg cm}^{-2}$ are indicated on Fig. 4 either in $\text{cm}^3 \text{ mole}^{-1}$ or converted into emf values, together with the limiting slope corresponding to $-\Delta V_1^\circ = 12.1 \text{ cm}^3 \text{ mole}^{-1}$ (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 $-\Delta V_1^\circ = 10.7 \text{ cm}^3 \text{ mole}^{-1}$ 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 $p = 1000 \text{ kg cm}^{-2}$ first on the μ scale to zero buffer concentration and then to $[\text{KCl}] = 0$ 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 $1/2$.

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	$\text{cm}^3 \text{ mole}^{-1}$	$\text{cm}^3 \text{ mole}^{-1}$	$\text{cm}^3 \text{ mole}^{-1}$
Acetic acid	11.6	12.5 (10) 9.2 (6) 11.5 (14)	12.2 (9) 12.1 (8)
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 $\Delta V_1 = -24.1 \text{ cm}^3 \text{ mole}^{-1}$ is reported from dilatometric experiments by Linderstrom-Lang and Jacobsen (11).