

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

Acids	$-\Delta V_1$ (0.1M KCl), cm <sup>3</sup> mole <sup>-1</sup>	$-\Delta V_1^\circ$ , cm <sup>3</sup> mole <sup>-1</sup>	$-\Delta V_1^\circ$ , cm <sup>3</sup> mole <sup>-1</sup>	$-\Delta V_1^\circ$ , cm <sup>3</sup> mole <sup>-1</sup>
	Glass electrode ref. 0.1M HCl <sup>14</sup> ( ) = molarities	Glass electrode	Density	Conductivity
Acetic	8.2-9.3* (0.1-1.0)	10.8-11.5*	12.5 <sup>(2)</sup> -11.5 <sup>(19)</sup> 9.2 <sup>(11)</sup>	12.2 <sup>(7)</sup>
Formic		8.8-9.1	8.0 <sup>(2)</sup>	8.8 <sup>(2)</sup>
Phosphoric (K <sub>1</sub> )		17.5	16.2 <sup>(21)</sup>	
Carbonic (K <sub>1</sub> )	29.0-30.0 (3.5.10 <sup>-2</sup> )		29.0 <sup>(11)</sup>	24.9 <sup>(5)</sup>
Buffers				
Acetate	8.7-9.7* (HA 0.1-NaA 0.1)	10.3-10.8*		
Phosphate (K <sub>1</sub> )		14.6-15.2		
Phosphate (K <sub>2</sub> )	22.0 (NaH <sub>2</sub> 0.03-Na <sub>2</sub> H 0.01) 20.3 (NaH <sub>2</sub> 0.0076-Na <sub>2</sub> H 0.076)	23.0	28.1 <sup>(21)</sup> **	
Bicarbonate	22.7-20.7 (NaH 2.10 <sup>-3</sup> -3.5.10 <sup>-2</sup> ) HA 2.10 <sup>-4</sup> -3.5.10 <sup>-2</sup> )			

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

\*\*  $\Delta V_1^\circ = -24.1$  cm<sup>3</sup> 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 pH of the reference half-cell (0.1M HCl) is not affected by pressure and that the effects of pressure on the specific electrode reactions cancel out.  $\Delta V_1$  corresponds in fact to the total volume change in the observed cell at 1000 kg cm<sup>-2</sup>.

We will now describe how the  $\Delta V_1^\circ$  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

$$E_1 - E_p = 0.0293 \log \frac{K_p}{K_1} + 0.0293 \log \frac{(m_{HA} - m_{H^+})_p}{(m_{HA} - m_{H^+})_1} + f(\sqrt{\mu}) \quad [6]$$

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,  $\rho_1$  the density of water at 1 atm; the approximation  $m_1 = m_p \approx M_1$  has been used throughout this paper].

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

Figure 4 also gives  $\Delta pK' = -\log k'_1 + \sqrt{\mu_1} + \log k'_p - \sqrt{\mu_p}$  where  $k' = m_{H^+}^2 / (m_{HA} - m_{H^+})$  and  $\sqrt{\mu}$  is the usual estimate for the activity coefficient term. The primes indicate the uncertainty introduced by the values of  $\gamma_{H^+}$  used to calculate  $m_{H^+}$ . 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  $\Delta pK'$  in 0.001M KCl agree fairly well with the expected one which lies between 0.137 [ $\Delta V_1^\circ = -8.0$  cm<sup>3</sup> (2, 7)] and 0.150 [ $\Delta V_1^\circ = -8.8$  cm<sup>3</sup> (7)].

In 0.1M KCl,  $\Delta pK'$  drops unexpectedly at low acid concentrations, with 0.1M 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

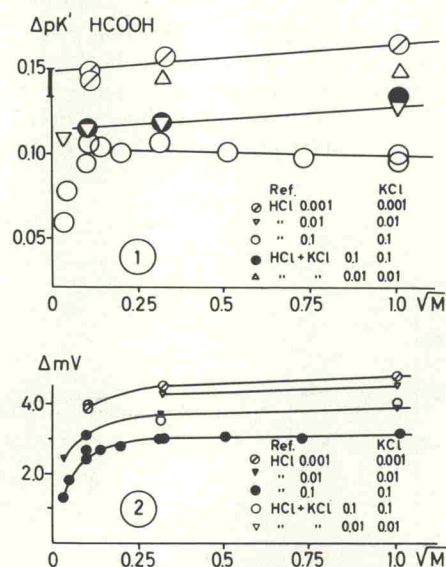


Fig. 4. Formic acid in KCl solutions. Top:  $\Delta pK' = -\log k'_1 + \sqrt{\mu_1} + \log k'_p - \sqrt{\mu_p}$  ( $p = 1000$  kg cm<sup>-2</sup>) as a function of the acid concentration. Bottom: observed emf shifts ( $\Delta mv$ ): (HCl + KCl 0.1 and 0.001 is simplified for HCl 0.01M + KCl 0.09M and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

to this constant increment. If 0.01M KCl + 0.09M KCl is used as reference, the observed  $\Delta$  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 of the reference solution indicates that the differences 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  $\gamma_{H^+}$  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 than 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  $\gamma_{H^+}$  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

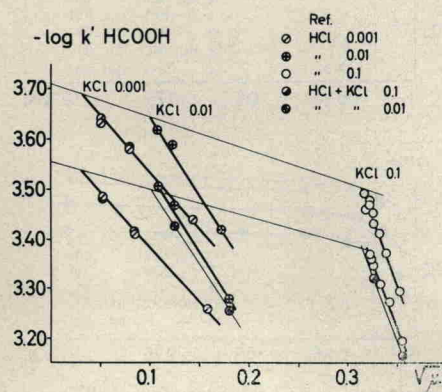


Fig. 5. Formic acid in KCl solutions. Extrapolation of  $-\log k'_1$  and  $-\log k'_p$  at  $\mu = 0$  and zero acid concentration (HCl + KCl 0.1 and 0.01 is simplified for HCl 0.01M + KCl 0.09M and HCl 0.001M + KCl 0.009M;  $-\log k'_1 > -\log k'_p$ ).

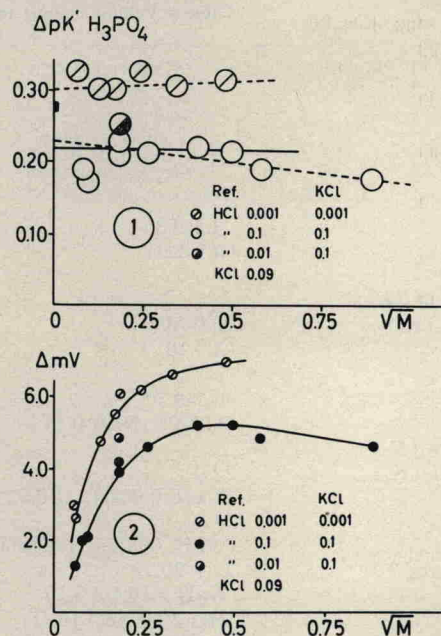


Fig. 6. Phosphoric acid (step 1) in KCl solutions. Top:  $\Delta pK' = -\log k'_1 + \sqrt{\mu_1} + \log k'_p - \sqrt{\mu_p}$  ( $p = 1000 \text{ kg cm}^{-2}$ ) as a function of the acid concentration ( $\sqrt{M}$ ). Bottom: observed emf shifts ( $\Delta$  mv).

and 0.01M KCl alone are considered. More data are needed in 0.01M and 0.001M KCl, but those available are sufficient to determine  $\Delta pK'$  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 0.01M 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

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

Pressure mainly affects the coefficient of the term in  $\mu_1$ .

The most probable value for  $\Delta V^{\circ}_1$ , 8.8-9.1  $\text{cm}^3$ , 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  $\text{cm}^3$  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 0.1M and 0.001M KCl, using 0.1M and 0.001M HCl as reference. As for formic acid, a shift of about 0.9 mv is observed when 0.01M HCl + 0.09M 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 0.1M 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  $H_3PO_4$ , and makes the  $\Delta pK'$  values much more sensitive to experimental errors.  $\Delta pK'$  extrapolates around 0.300 ( $\Delta V^{\circ}_1 = -17.5 \text{ cm}^3$ ) in 0.001M KCl, which is rather