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A. Distèche and S. Distèche

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

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 $\left|\begin{matrix}\text{HCl }(m_1)\\ \text{KCl }(m_2)\end{matrix}\right|$ glass $\left|\begin{matrix}\text{HR or HR + MR}\\ (m_1 + m_2)\text{ KCl}\end{matrix}\right|$ AgCl-Ag

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 $HR \leftrightharpoons R^- + H^+$ 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 $\left|\begin{matrix}(m_1)\text{ HCl}\\ (m_2)\text{ KCl}\end{matrix}\right|$ $\begin{matrix}\text{glass}\\ \text{(Corning}\\ \text{015)}\end{matrix}$ $\left|\begin{matrix}\text{HR or HR + MR}\\ (m_1 + m_2)\text{ KCl}\end{matrix}\right|$ Ag-AgCl

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 ($\Delta V_p{}^o$) induced by pressure p can be calculated at any pressure from the well-known equation

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

More recently, Hamann (4) used the cell Ag-AgCl | (m_1) HCl | Li — glass | (m_2) KCl + (m_3) KOH | AgCl-Ag to derive $\Delta V_1{}^o$ 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) KCl (0.09M)		HR or HR + MR KCl (0.1M)	Ag-AgCl
2. Ag-AgCl	HCl(0.001M) KCl (0.009M)		HR or HR + MR KCl (0.01M)	Ag-AgCl
3. Ag-AgCl	HCl (0.001M)		HR or HR + MR KCl (0.001M)	Ag-AgCl

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

$$E_{1,p}\mathbf{F}/2.3RT = \log\,(m_\text{H})^{ref.}_{1,p} - \log\,(m_\text{H})^{x}_{1,p} + 2\log\frac{(\gamma_\text{HCl})^{ref.}_{1,p}}{(\gamma_\text{HCl})^{x}_{1,p}} \qquad [2]$$

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

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

in the unbuffered half-cell, and

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

in the buffered half-cell

Here $2\log\gamma_A = \log\gamma_\text{H}\gamma_\text{R}/\gamma_\text{HR}$ 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

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

and

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