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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