Preprinted from the Journal of the Chemical Society,
December, 1959, (750), pages 3689—3699.

750. *The Effect of Pressure on the First Dissociation Constant of " Carbonic Acid."*

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The apparent first dissociation constant of " carbonic acid " has been determined for pressures up to 3000 atm. in the temperature range 25—65° c. An increase of 2500 atm. increases this constant approximately ten-fold owing largely to the increased hydration of carbon dioxide to H_2CO_3 at high pressure.

The effects of pressure on the molar conductances of potassium chloride, hydrochloric acid and potassium hydrogen carbonate in water at these temperatures are compared with previous results. There is little change in the effects of pressure in the concentration range 0·0001—0·1M.

As only 0·259% of the equilibrium mixture, $CO_2 + H_2O$, or " carbonic acid," is hydrated to H_2CO_3 in water at 25°,[1] increased pressure influences two equilibria

$$H_2O + CO_2 \rightleftharpoons H_2CO_3; \quad H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

For comparison, the effects of pressure on the dissociation of simple weak acids such as formic, acetic, propionic acid, are available from the reviews of Cohen and Schut,[2] and Hamann.[3]

Davies's method [4] was used to obtain the acid dissociation constants for " carbonic acid " between 25° and 65°, and at various pressures. The degree of dissociation, α, of the mixture $CO_2 + H_2O$ into H^+ and HCO_3^- ions was assumed to equal the ratio Λ/Λ', where Λ is the molar conductance of the mixture and Λ' the sum of the molar conductances of the ions H^+ and HCO_3^- at the ionic strength of the solution examined. Λ' was obtained by interpolation of conductance values for hydrochloric acid, potassium chloride, and potassium hydrogen carbonate solutions at various concentrations, temperatures, and pressures. As indicated by Hamann [3] it is safe to assume that Kohlrausch's law of independent ionic mobilities is obeyed under the conditions used.

The thermodynamic apparent dissociation constant K_a is given on the molal scale by the expression

$$K_a = [\alpha^2 m/(1 - \alpha)]\gamma_{\pm}{}^2/\gamma_{\text{HA}}$$

where m is the molal concentration of total carbon dioxide, and $\gamma_{\pm}$ the mean activity coefficient of the H^+ and the HCO_3^- ion. γ_{HA}, the activity coefficient of the undissociated acid, was taken as unity at all pressures and temperatures. Values for $\gamma_{\pm}$ were obtained from the Debye–Hückel equation in the form

$$-\log f_{\pm} = \{1{\cdot}8123 \times 10^6 (DT)^{-3/2} c^{\frac{1}{2}}\}/\{1 + 50{\cdot}29 \times 10^8 (DT)^{-\frac{1}{2}} a c^{\frac{1}{2}}\}$$

a was taken as 5×10^{-8} cm., and changes of the molar concentration c and the dielectric constant D with pressure were taken into consideration. At the low ionic strengths used, the molar activity coefficient $f_{\pm}$ can be taken as equal to the molal activity coefficient $\gamma_{\pm}$. As the term DT changes little with temperature in the range 25—65°, it was sufficient for the accuracy of the experiments to apply the 25° values of $\gamma_{\pm}$ for various pressures and concentrations at all the temperatures.

A comparison of Hamann's results [3] with earlier data [2,5] for the conductance of strong electrolytes in water at high pressures showed that there were appreciable deviations and these are discussed below in relation to the values obtained for solutions of potassium chloride and hydrochloric acid in the process of obtaining dissociation constants.

EXPERIMENTAL

Apparatus.—The stainless-steel pressure vessel (25 c.c.; 3 in. diam.) had two manganin wire electrical leads through its walls; these were insulated in a packing gland of compressed polystyrene. Into the vessel was placed the conductivity cell containing the solution, and the appropriate electrical leads were soldered together inside the vessel.

The conductivity cell (constant 0·365 cm.$^{-1}$) was a Teflon cylinder, open at one end, of 7 c.c. capacity. A tight-fitting Teflon piston supporting the electrodes separated the solution in the cell from medicinal paraffin used to transmit pressure within the pressure vessel. The electrode assembly in the cell consisted of platinum foil electrodes tightly bound by fine platinum wire to the arms of a U-shaped Pyrex glass piece. A thick platinum lead from one electrode supported the assembly from the Teflon piston, and a lead of fine wire from the other electrode to the piston allowed for the slight play caused by the contraction of Teflon under pressure. The cell therefore incorporated the advantages of the sliding piston design of Jamieson,[6] and almost constant spacing of the electrodes by glass. The platinum in the cell was lightly coated with platinum black.

Sealed platinum-in-glass electrodes are usually broken by the application of a few thousand atm. pressure. In cells with electrodes spaced by plastic, corrections are needed for the high and often irreproducible compressibility of these substances. For example, a marked discontinuity is apparent in the conductivity results of Hamann and Strauss [7] at 5000 atm. where Weir [8] reported a phase change in Teflon with a 2% decrease in volume. Disadvantages of other cells used previously include direct contact of the solution with kerosene [5] and with mercury.[9]

Pressures were developed by hand hydraulic pumps and a pressure intensifier. Bourdon gauges were calibrated against a Harwood manganin-coil resistance gauge supplied calibrated to $\pm 0{\cdot}1\%$. With allowance for small variations in the Bourdon gauges, the pressures reported should be accurate to within $\pm 0{\cdot}5\%$.

The pressure vessel and a paraffin reservoir were heated in an oil-bath controlled to $\pm 0{\cdot}05°$. The mass of the vessel damped out temperature variations in the bath. About 2 hr. were required for the apparatus to reach initial thermal equilibrium, and a further 30 min. were required after a change of pressure for equilibrium to be regained.

The resistances were measured with a capacity-compensated non-inductive Wheatstone bridge using a 1000 c.p.s. valve oscillator as an A.C. source. Corrections to the conductances were made for the resistance of lead wires and the change in cell constant with pressure. The latter was 0·1% change per 1000 atm.

Measurements of the cell resistance were taken again at 1 atm. pressure at the end of each run. In no case were hysteresis effects important.

Materials and Method.—Solutions of potassium chloride, hydrochloric acid and potassium hydrogen carbonate were prepared from "AnalaR" reagents. A large volume of "carbonic acid" solution was prepared in a closed flask, and the liquid and the gas phase were allowed to equilibrate. A portion of this solution was run into the conductance cell, and another portion analysed.

Throughout the experiments with "carbonic acid" the pressure on the cell was kept above 50 atm. to prevent bubbles forming in the cell. A short extrapolation was made to get conductances at 1 atm. No significant amount of carbon dioxide was lost from the cell during the measurements.

The distilled water in the cell was assumed to have two types of impurity, *viz.*, carbon dioxide and stray strong electrolyte ions. The conductance blank due to the latter, κ_i changes very little with pressure, while that of ionised carbonic acid, κ_c, increases considerably. From the conductance of the solvent at various pressures it was possible to obtain the values of κ_i and κ_c. As an example, for the water used in the experiment at 25° and 1 atm., κ_i was approximately $1{\cdot}0 \times 10^{-6}$ and κ_c $0{\cdot}5 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$.

When corrections for the solvent were made to the conductances of potassium chloride solutions $(\kappa_i + \kappa_c)$ was subtracted, but for hydrochloric acid and potassium hydrogen carbonate only the blank κ_i, for pressure and temperature, was applied.

The correction for solvent conduction was of the order of a few units % for solutions with an ion concentration of 10^{-3}m, but reached a maximum of 20% of the total conduction for 10^{-4}m potassium chloride at 25° and 3000 atm. The blank correction to the "carbonic acid" conductivities was greatest at 65° and 1 atm. where it amounted to about 10%.

Buchanan and Hamann [9] defined the molal conductance of an electrolyte as Λ (molal) $= 1000L'/m$, where m is the molality of the electrolyte, which is independent of pressure, and L' the specific conductance of the solution corrected for the solvent blank.