Hückel–Onsager relationship is opposed by the lower structural temperature of water at increased salt concentrations. The pressure effect on conductance in water is greatest at low temperatures.

For "carbonic acid," ΔV^1 becomes more positive with increasing temperature. A similar behaviour was calculated by Owen and Brinkley[18] for ΔV^1 for the ionisation of water. They considered that ΔV^1 would continue to increase with temperature until at very high temperatures the ionisation of weak acids was decreased by pressure. It is thought more likely that ΔV^1 increases with temperature, passes through a maximum, and becomes increasingly negative at high temperatures. The present results for "carbonic acid" show that the increase in ΔV^1 for a given temperature rise becomes less at higher temperatures. It is known that at temperatures approaching, and exceeding the critical temperature of water, increased pressure greatly increases the ionisation of all electrolytes.[19]

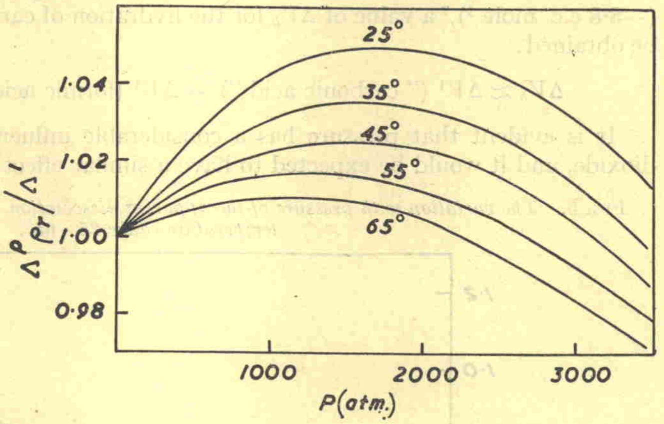


FIG. 3. 0·01m-*Potassium hydrogen carbonate.*

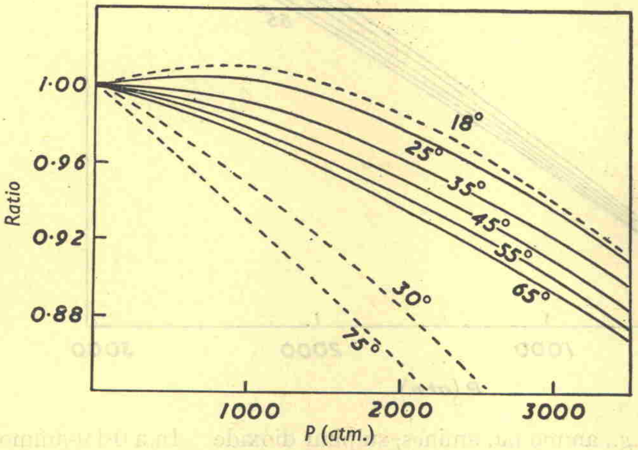


FIG. 4.

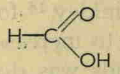
—— *Values of* Λ_0^P/Λ_0^1 *for* $KHCO_3$ *solutions at* 25°, 35°, 45°, 55°, *and* 65°.

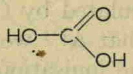
– – – – *Bridgman's values for ratio* η^1/η^P *at* 18°, 30°, *and* 75°

The effect of pressure on the ionisation of "carbonic acid" has not been studied before in detail, although Brander[20] found that pressure had an abnormally large influence on the conductance of carbon dioxide solutions. Owen and Brinkley[18] calculated ΔV^1 at infinite dilution by use of experimental values for the partial molal volumes of the hydrogen and bicarbonate ions, and of carbon dioxide in solution.

Owen and Brinkley's estimated value of ΔV^1 for "carbonic acid" at 25° was -29 c.c. mole^{-1}, but it was based on an early experimental value of the partial molar volume of carbon dioxide in solution. They assumed that $-\Delta K$ for ionisation was greater than $1{\cdot}0 \times 10^{-3}$; the present results show it to be equal to $1{\cdot}9 \times 10^{-3}$ at 25°.

True carbonic acid, H_2CO_3, has a dissociation constant at 25° and 1 atm. of $1{\cdot}72 \times 10^{-4}$, which is very close to the value of K_a given by Harned and Owen[21] for formic acid ($1{\cdot}772 \times 10^{-4}$ at 25°). As the two molecules are very similar they would be expected to differ only slightly in properties:



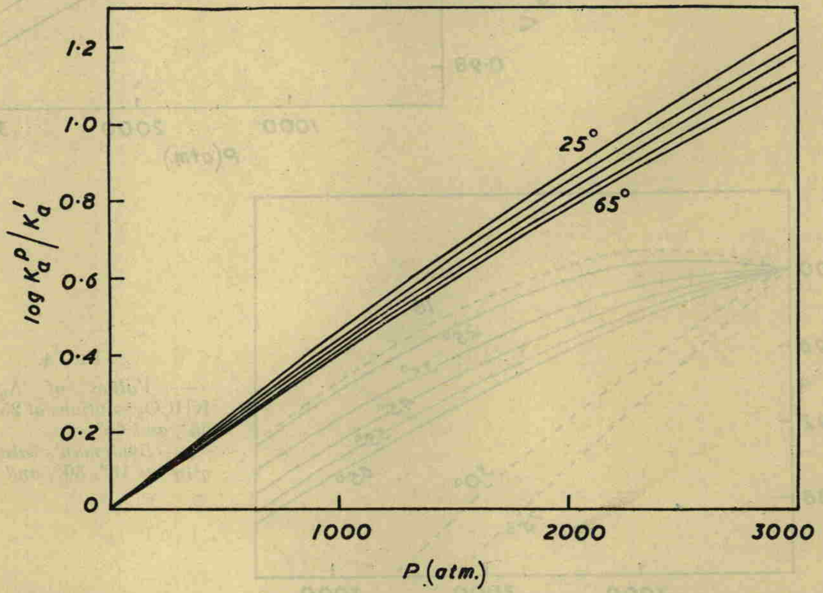


If it is assumed that ΔV^1 at 25° for the ionisation of H_2CO_3 is equal to that for formic acid ($-8{\cdot}8$ c.c. mole^{-1}),[7] a value of ΔV_h for the hydration of carbon dioxide to carbonic acid can be obtained:

$$\Delta V_h \approx \Delta V^1 \text{ (`` carbonic acid '')} - \Delta V^1 \text{ (formic acid)} = -17{\cdot}7 \text{ c.c. mole}^{-1}.$$

It is evident that pressure has a considerable influence on the hydration of carbon dioxide, and it would be expected to have a similar effect on the hydration of other gases which form ionised solutions, *e.g.*, ammonia, amines, sulphur dioxide. In a $0{\cdot}1$M-ammonia solution, Moore and Winmill[22] found that NH_3 was present to the extent of 46·2% and $NH_4{\cdot}OH$ 52·4%. The true dissociation constant of $NH_4{\cdot}OH$ is about 4×10^{-5}.

FIG. 5. *The variation with pressure of the apparent dissociation constant of " carbonic acid " in the temperature range 25—65°.*



Hamann[3] considered that the increased ionisation of weak electrolytes at high pressure was due essentially to the enhanced solvation of the ions with respect to the un-ionised molecules. He calculated the change in free energy of hydration of singly charged ions at high pressures using Born's formula:

$$\Delta G^\circ \text{ (solvation)} = -\frac{\boldsymbol{N}\boldsymbol{e}^2}{2r}\left(1 - \frac{1}{D}\right)$$

where $\boldsymbol{N}$ is Avogadro's number, $\boldsymbol{e}$ the electronic charge, D the dielectric constant, and r the mean radius of the two ions. As r decreases and D increases with pressure, ΔG° (solvation) increases.

That this is an oversimplification for weak acids and bases of the hydrated gas type is shown by the present series of results. A calculation for the effect of pressure on ammonia ionisation was given by Hamann,[3] using the compressibility of cæsium fluoride as a model