

DISCUSSION

Figs. 1—3 summarise the results for hydrochloric acid, potassium chloride, and potassium hydrogen carbonate, and also show some values of Λ^P/Λ^1 obtained by previous workers. The agreement is not good, and the results of Hamann and Strauss⁷ are anomalous. The effect of pressure on conductance was found to decrease with temperature in the manner reported by Korber¹⁴ and Zisman.⁵

Zisman⁵ and Hamann and Strauss⁷ examined the effects of pressure on conductance up to pressures of 10,000 atm. The latter workers suggested that Zisman's results were in error by several units %, but the present observations do not support this suggestion.

FIG. 1. 0.01M-Hydrochloric acid. — Our values. ---- Literature values: A, Hamann and Strauss, ref. 7; B, Korber, ref. 14; C, Buchanan and Hamann, ref. 9; D, Zisman, ref. 5.

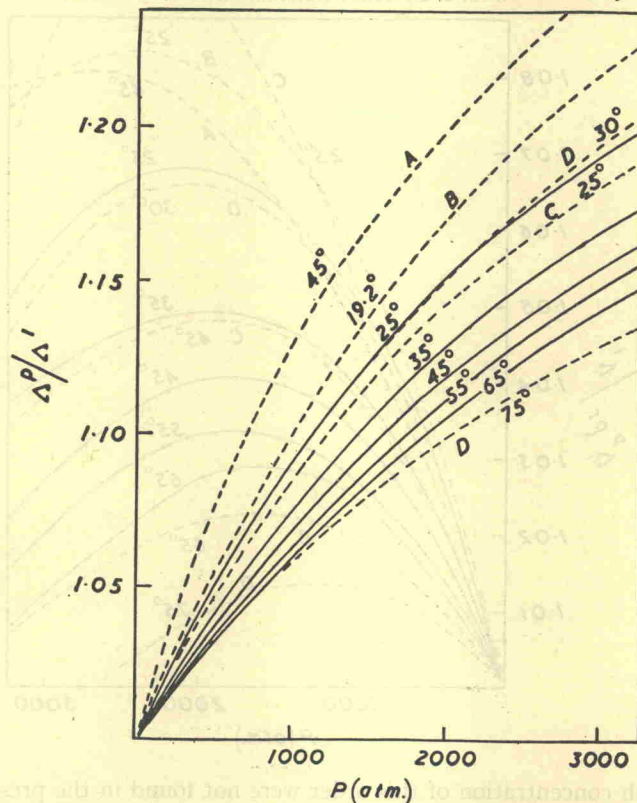


Fig. 4 shows the ratios Λ_0^P/Λ_0^1 for potassium hydrogen carbonate solutions, together with Bridgman's ratios¹⁵ of the viscosity η^1/η^P for 18°, 30°, and 75°. The variation of Λ_0^P/Λ_0^1 with pressure is similar for most salts in that the values pass through an initial maximum or a curvature in the same sense before decreasing steadily with increasing pressure.

For 16 salts Zisman⁵ showed that at 30° and 75° the ratio Λ^P/Λ^1 decreased almost linearly with pressure in the range 3000—8000 atm., and always with the same slope. The increase in the viscosity of water at these temperatures and pressures is also approximately linear with pressure, but the increase in viscosity is more rapid than the decrease in conductance for the same temperature.

The compressibility of ions, derived from measurements on crystals of the alkali halide type, is only about one tenth of the compressibility of water at moderate pressures.¹⁵ The effect of pressure on conductance should therefore be related mainly to changes in solvent structure and in ion-solvent interaction.

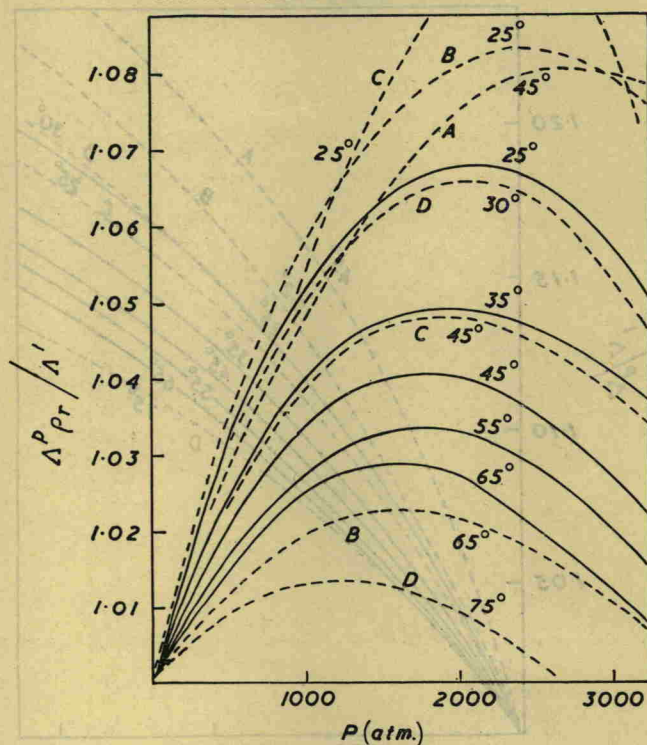
For a 1:1 electrolyte the Debye-Hückel-Onsager equation can be written¹⁶ in the form

$$\Lambda_0 - \Lambda = \left[\frac{A\Lambda_0}{(DT)^{3/2}} + \frac{B}{\eta(DT)^{1/2}} \right] c^{1/2}$$

A and B are positive constants and D is the dielectric constant.

Both D and η for pure water increase at high pressures and Λ_0 decreases. As discussed by Hamann,³ the effect of pressure on conductance could be expected to decrease with increasing concentration. For example, for potassium chloride it would be expected that at 3000 atm. Λ_0^P/Λ_0^1 would be about 3.5% greater than Λ^P/Λ^1 for a 0.1M-solution.

FIG. 2. 0.01M-Potassium chloride.



Variations with concentration of this order were not found in the present experiments with solutions up to 0.1M. However, Korber's results¹⁴ provide a good example of the decreasing pressure effect at higher concentrations.

The apparent disagreement with the Debye-Hückel-Onsager equation below 0.1M must result from the assumption that the values of D and η for the salt solutions at high pressures correspond to those for water at the same temperature. Zisman⁵ showed that the initial maximum in the graph of Λ^P/Λ^1 for neutral salts was greatest and occurred at highest pressures for small ions of high valency. These are order-producing ions which, in the terminology of Frank and Evans,¹⁷ lower the structural temperature of water. In Fig. 4 the variation of η^1/η^P with pressure corresponds to the ratio Λ_0^P/Λ_0^1 for a rather higher temperature. It is not sufficient to relate the changes in conduction at high pressure with the changes in physical properties of pure water at the same temperature.

For aqueous solutions there appear to be two opposing factors in operation which tend to counterbalance each other with changing concentrations below about 0.1M. The decreased pressure effect on conductance predicted at higher concentrations by the Debye-