# Partial Molal Volume of Boric Acid in Water at High Temperature

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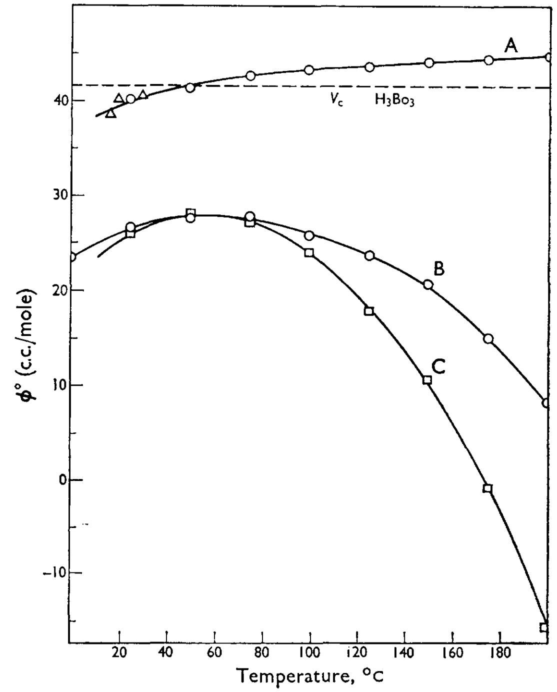
To calculate the effect of pressure on weak acid ionisation at high temperatures, of interest in studying natural hydrothermal solutions, values of partial molal volumes, $\phi°$, for a range of ions and molecular species are required.

Precise density measurements on aqueous salt solutions at temperatures up to 200° have already given values of $\phi°$ for electrolytes of varying ionic charge and radius, *cf.* ref. 1 and later work.

Boric acid, $H_3BO_3$, is essentially a non-electrolyte down to the lowest concentrations used in the density measurements (0·1m) and it is a convenient molecular solute, being non-corrosive, of suitable solubility, and not requiring the control of a gas pressure (as for $H_2SO_3$, $NH_4OH$, $H_2S$) to maintain constant concentration.

This note outlines the contrasting temperature dependence of the partial molal volume of boric acid, and of salts of simple univalent and divalent ions. It is the first report of the variations in $\phi°$ for a non-electrolyte in water over a wide temperature range.

The methods used were as outlined earlier,[1] with solution densities based on the 17° to 30° values for boric acid solutions of von Endredy.[2] At each temperature the value of the apparent partial molal volume, $\phi$, of boric acid calculated from the measured density of solutions ranging from 0·1m to 0·5m had no significant variation with concentration within the possible errors of the determinations (values of $\phi$ for 0·1m solution $\pm$ 0·2 c.c./mole at 50°, to $\pm$ 0·7 c.c./mole at 200°). The limiting partial molal volume $\phi°$ was therefore taken as the mean of the $\phi$ values. Trends in $\phi°$ for boric acid with temperature are shown in the Figure in



*Variation with temperature of the partial molal volumes,* $\phi°$*, of* (A) *boric acid,* (B) *potassium chloride, and* (C) *barium chloride,* Δ*-von Endredy's results.*

comparison with our $\phi^\circ$ values for potassium chloride and barium chloride. The molecular volume of crystalline boric acid, $V_c$, is also shown, the small thermal expansion effect being ignored.

The behaviour of the ionic and molecular solutes are seen to contrast strongly. Firstly, considerable electrostriction volume loss occurs on solution of the salts (over 100 c.c./mole for $BaCl_2$ at 200°), but for boric acid the volume changes on solution amount to only a few c.c./mole at all temperatures investigated. At temperatures below 50° the predominant trend with both ionic and molecular solutes is to collapse the partially ordered open structure of water through the breaking of water hydrogen bonding by electrical and by mechanical effects, respectively. At high temperatures boric acid causes a minor expansion of water through added disorder in the packing of water molecules, but the salts create a denser average water structure through the transfer of water molecules from the increasingly lower density bulk solvent to a rather constant and higher density solvation shell about the ions.[1] The temperature at which the partial molal volume of boric acid equals the crystalline molecular volume, $V_c$, occurs about 55°, the same temperature at which a flat maximum in $\phi^\circ$ values occurs for many salts.[1] In comparison, it is interesting that for the model of water[3] involving a mixture of two solid-like species resembling Ice I and Ice III the contribution of the open Ice I like species becomes negligible at rather similar temperatures (40° to 50°).

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[1] A. J. Ellis, *J. Chem. Soc.* (*A*), 1966, 1579

[2] A. von Endredy, *Z. anorg. Chem.*, 1935, **222**, 285.

[3] M. S. Jhon, J. Grosh, T. Ree, and H. Eyring, *J. Chem. Phys.*, 1966, **44**, 1465.