The Partial Molal Volume of Hydrochloric Acid in High-temperature Water

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THE partial molal volume of the hydrogen ion is of importance in calculating the effect of pressure on ionic equilibria in natural hydrothermal solutions containing weak acid solutes. Data for this ion at high temperatures is also of interest in electrolyte solution theory.

Density measurements of salt solutions at high temperatures[1–3] were made in stainless-steel vessels.

Experimental values of ϕ^0_{HCl}, *and derived values of* ϕ^0_H *compared with* ϕ^0_{Cl}, ϕ^0_{Na}, *and* ϕ^0_{Cs}, *for temperatures to* 200°.
(Values in c.c./mole)

Temp.	25	50	75	100	125	150	175	200°
ϕ^0_{HCl}	17·8	18·0	17·4	16·0	14·1	11·2	7·0	0·5
ϕ^0_{Cl}	23·5	24·0	24·0	24·0	23·0	22·0	19·5	16
ϕ^0_H	−5·7	−6·0	−6·6	−8·0	−8·9	−10·8	−12·5	−15·5
ϕ^0_{Na}	−6·9	−5·8	−5·8	−7·2	−8·0	− 9·6	−12·0	−15·6
ϕ^0_{Cs}	15·7	16·3	16·6	15·0	14·3	12·7	9·8	7·6

A modification was made so that hydrochloric acid solutions came in contact with fused silica and mercury only. For 0·2—2 M-HCl solutions, densities reliable to $\pm$ 0·0001 were obtained up to 200°. Solutions more dilute than 0·2 M-HCl reacted slightly with mercury at 200°, producing mercuric chloride.

Values of the limiting partial molal volume ϕ^0 for hydrochloric acid were obtained by extrapolating the linear graphs of apparent molal volume ϕ^0 *versus* $m^{\frac{1}{2}}$. The Table gives the results for ϕ^0_{HCl}, and from values[3] of the partial molal volume of the chloride ion ϕ^0_{Cl}, derived values of ϕ^0_H, the partial molal volume of the hydrogen ion, are given to 200°. Comparison is made with ϕ^0 for sodium, an ion of similar volume in solution, and with ϕ^0 for the caesium ion.

The rate of decrease in ϕ^0_H with rising temperature is not as rapid as would be expected[3] for a simple ion of small radius, being less than for ϕ^0_{Li} and ϕ^0_{Na} between 100 and 200°. At temperatures over 100° the trend in ϕ^0_H with temperature is similar to that for a large alkali-metal ion.

For most ions a maximum occurs in ϕ^0_{ion} between 0° and 100°. Hydrogen, lithium, and magnesium are the only ions so far examined for which there is no maximum. All three ions have an anomalously low electrostriction effect at room temperatures, but the effect for the hydrogen ion is particularly small. At low temperatures the hydrogen ion evidently co-ordinates into the open tetrahedral water structure causing little disturbance, and the ion charge is dispersed by hydrogen bonding.

At temperatures several tens of degrees above maximum ϕ^0_{ion} values, most ions give a close to linear graph of ϕ^0_{ion} *versus* v_w, the specific volume of water.[3] The slope (Figure) at higher temperatures corresponds to a "hydration number" n, of 4. In comparison, the slopes for lithium and sodium which are also ions with an anomalously low electrostriction effect at high temperature,[3] correspond to n-values of 7 and 5—6 respectively. For caesium n is 4.

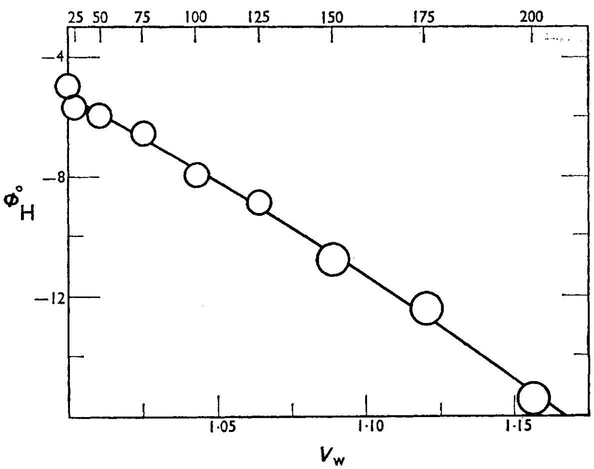

FIGURE. *Variation in the limiting partial molar volume of the hydrogen ion,* ϕ^0_H, *with the specific volume of water,* v_w *up to* 200°

Between at least 100° and 200° the hydrogen ion apparently forms a constant solution species involving four water molecules. It is suggested that there is a change in the hydrogen-ion solution between 25° and 200° from simple assimilation into the water structure at low temperatures to the formation of a specific hydrated ion at high temperatures. Corresponding graphs of ϕ^0_{ion} (t) *versus* ϕ^0_{ion} (25°) agree with this suggestion. The majority of mono- and bi-valent ions at each temperature show a simple linear relationship[3] of the type $\phi^0_{ion}(t) = a\ \phi^0_{ion}(25°) + b$. This indicates that each ion forms a rather constant ion-solution entity over the whole temperature range. The hydrogen ion is one of a small number of ions which have ϕ^0_{ion} values which deviate from average behaviour and either decrease more rapidly (Mg^{2+},SO_4^{2-}), or less rapidly (H^+,OH^-,Na^+) than average with increasing temperature.

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[1] A. J. Ellis, *J. Chem. Soc.* (*A*), 1966, 1579.
[2] A. J. Ellis, *J. Chem. Soc.* (*A*), 1967, 660.
[3] A. J. Ellis, *J. Chem. Soc.* (*A*), 1968, in the press.