

I have attempted to determine whether this mechanism is, in fact, involved by measurement of the conductances of rapidly frozen aqueous solutions of electrolytes—solutions in which the contribution of the mass transport mechanism is presumably greatly depressed. Solutions of hydrochloric acid, nitric acid, hydrofluoric acid, potassium hydroxide, lithium hydroxide, potassium chloride, and lithium fluoride were cooled rapidly to liquid-air temperature, then heated to the temperature at which the conductance was to be determined. The conductances were determined in the temperature range -120°C . to -40°C . Each system was studied at temperatures lower than its lowest reported eutectic temperature; at these temperatures the frozen masses appeared solid and felt hard. At liquid-air temperature in all cases the specific conductances were less than the limit of detection (2×10^{-10} mho cm^{-1}) of the apparatus. As the frozen solutions of the acids and bases were warmed to the temperature of measurement, the conductance rose quickly to a maximum, then decreased over a period of hours (presumably the decrease arises from a slow phase separation). The frozen solutions of salts showed no conductance at temperatures below their eutectics; this observation supports the assumption that the mass transport mechanism is insignificant. The maximum conductance was taken as characteristic of the acid and base solutions at each temperature. The measurements were made with a direct-current instrument at fields of 1–10 volts cm^{-1} and current densities at 10^{-8} – 10^{-6} amp. cm^{-2} .

The value of the conductance for a given solution and temperature could be reproduced only to within a factor of two or three, probably because of the cracking of the solid and variations in the amounts of solute 'frozen in'. Following are some typical results:

Substance	Temperature	Specific conductance
0.06 N HCl	-115°C .	6×10^{-9} mho cm^{-1}
0.06 N HCl	-106	3×10^{-8}
0.06 N HCl	-94	9×10^{-8}
0.08 N LiOH	-69	2×10^{-8}
0.08 N LiOH	-51	1.5×10^{-8}
0.08 N LiOH	-42	2×10^{-8}
0.056 N NHO_2	-84	3×10^{-9}
0.056 N HNO_2	-70	1×10^{-9}

The observation that the frozen solutions conduct strengthens the suggestion that the proton transmission mechanism contributes to the mobility of hydrogen and hydroxyl ions in aqueous solutions. It may be worthy of mention that estimates of activation energies for the conduction process, made either from ratios of conductances at various temperatures or by application of the absolute rate theory of Stearn and Eyring to the equivalent conductances at each temperature, yield values between 6 and 10 kcal. mole $^{-1}$. These values are, of course, very uncertain; nevertheless, they may suggest that rotation in the lattice is rate-determining, since the activation energy for rotation of a water molecule in ice has been estimated from the temperature dependence of relaxation time of polarization to be about 8 kcal. mole $^{-1}$.

In any event, it seems that the pure proton tunnelling mechanism of Bernal and Fowler cannot be the only one involved. Both the strong temperature-dependence of conductance in ice and the fact that deuterium ion in heavy water has an abnormally high conductance lead to this conclusion. Whether the tunnelling effect contributes significantly cannot

be decided easily because of the control over the rate by rotation or some other comparatively slow process.

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² Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

³ Wannier, *Ann. d. Phys.*, **24**, 545 (1935).

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Volumetric Estimation of Thallium

A NUMBER of processes have been described for the volumetric estimation of thallium. All these methods are based on the oxidation of thallium from the thallose to the thallic state by potassium permanganate¹, bromate², iodate³ or ceric sulphate⁴ solutions; but no attempt has been made to use a precipitation reaction for this determination.

Bromophenolblue (tetrabromo-phenolsulpho-naphthalein), which has been used previously as an acid-alkali indicator and as an adsorption indicator⁵ in the determination of mercurous ions, has been found by me to be a very suitable indicator for the determination of thallose ions also. 10 c.c. of $N/10$ potassium iodide is mixed with four drops of 0.1 per cent solution of bromophenolblue in alcohol, and thallose nitrate solution (about $M/10$) is run in from the burette. When the exact equivalent amount of the solution has been added, half a drop in excess of the solution turns the yellow-coloured precipitate to a beautiful green colour, the end-point being reversible.

Further work is in progress. The details of the process will be published in detail elsewhere.

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Band Spectrum of ClO in Flames

BAND systems attributed to the monoxides of bromine and iodine have been obtained by Vaidya^{1,2} in flames of ethyl bromide and methyl iodide. Recently, Coleman and Gaydon³ have made a further study of the BrO bands using various flames, including one of hydrogen burning in a mixture of oxygen and bromine vapour; the occurrence of the bands in this flame supports the assignment to BrO. There does not appear to be any detailed record of the corresponding band system of ClO, although Urey and Bates⁴ reported the existence of a band system, which they thought to be due to ClO, when chlorine was introduced into an oxy-hydrogen flame. As part of a series of investigations on the inhibitory action of halogen compounds on flames, we have examined the spectrum of a flame of hydrogen burning in an atmosphere of oxygen mixed with a little chlorine. A system of bands has been obtained in the blue to near ultra-violet, which appear to be analogous to the known systems of BrO and IO and