

## Polywater: is it Silica Sol?

By BARBARA F. HOWELL\* and JEAN LANCASTER

(Graduate Center for Cloud Physics Research, University of Missouri-Rolla, Rolla, Missouri 65401)

**Summary** All the reported properties of poly- or anomalous water are shown by mixtures of silica, water, and sodium oxide and all attempts to prepare it by condensation of ordinary water were unsuccessful.

We have made exhaustive attempts to prepare poly- or anomalous water using an accurately thermostatted, sealed chamber which held liquid water and a rack to hold capillaries in the water vapour. The water vapour temperature was controlled so as to produce 97% water vapour saturation. Water does not condense in 50–100  $\mu\text{m}$  fused-silica capillaries under these conditions.

Extreme care was taken to ensure the cleanliness of the apparatus, attempts to grow anomalous water in fused silica capillaries, on 100 mesh fused-silica powder, and on Cabosil (a colloidal form of silica) were all unsuccessful.

Electron microprobe analyses of residues from water which had condensed on fused silica powder at 100% water vapour saturation showed silicon and oxygen to be the principle constituents with *ca.* 3% nickel, 1% magnesium, and less than 1% each of manganese and iron. The solid separating from the liquid which had condensed in the fused-silica capillaries at 100% water vapour saturation showed

nearly equal amounts of silicon and sodium, *ca.* 6% chlorine, and <2% each of magnesium, sulphur, potassium, chlorine, phosphorus, and calcium. No boron or carbon was found in either of these samples.

Properties of the liquid obtained after condensation of water on silica are for the most part those of water, but with increased values for electrical conductivity and surface tension; i.r. and n.m.r. spectra are those of ordinary water.

Attempts to produce polydeuterium oxide in the thermostatted apparatus did not give shifts in the i.r. peaks at 1400 and 1100  $\text{cm}^{-1}$  analogous to those for anomalous water. However, peaks at 1400 and 1100  $\text{cm}^{-1}$  were obtained using water squirted from freshly-drawn, Pyrex capillaries which had been placed in a beaker of water and allowed to fill. Since condensation from the vapour state into the capillaries is considered a requirement for anomalous water formation, this result confirms conclusions reached by Davis<sup>1</sup> and Rousseau<sup>2</sup> that these absorption peaks are due to impurities rather than to anomalous water.

Most of the reported properties of anomalous water are properties possessed by silica sols. However, the presence of at least one other substance is necessary to give the elevated density, refractive index, and freezing point

behaviour reported for anomalous water if these properties are to be observed in a transparent liquid material. In common with anomalous water, silica sols have been known to undergo distillation,<sup>3</sup> they have lower electrical conductivity and higher surface tensions and viscosity than ordinary water, and they evaporate leaving a residue. Mixtures of sodium oxide and silica show densities as high as 1.673, refractive indices of 1.4473,<sup>4</sup> and hysteresis curves upon freezing, all of which are characteristic of anomalous water. We measured the vapour pressure of a silica-water mixture, (53% silica), between 25 and 90 °C, using a closed system containing the silica mixture. The system was evacuated and pressure measurements were made with a Wianko pressure transducer which had been calibrated against a high-precision bourdon-tube pressure gauge.

When the logarithm of the vapour pressure obtained from these measurements is plotted against the reciprocal of the absolute temperature a nearly linear relationship is found with a slope of 6.2 kcal mol<sup>-1</sup>. This is the "heat of vapourization," and extrapolation of the plot gives the b.p. of the mixture as 300 to 400 °C. Deryaguin<sup>5</sup> reports 6.1 and *ca.* 250 °C respectively for these properties of anomalous water.

We conclude that anomalous water is not a one-component allotropic form of ordinary water, and that all of its reported properties are exhibited by mixtures of ordinary water, silica and sodium oxide.

We acknowledge support from the Office of Naval Research.

(Received, March 22nd, 1971; Com. 349.)

<sup>1</sup> R. Davis, *Chem. Eng. News*, 1970, **48**, 7.

<sup>2</sup> D. Rousseau, *Science*, 1970, **171**, 170.

<sup>3</sup> R. Sosman, "The Phases of Silica," Rutgers University Press, New Brunswick, N.J., 1965, p. 338.

<sup>4</sup> International Critical Tables, Vol. 7, McGraw Hill, New York, 1930, p. 95.

<sup>5</sup> B. Deryaguin and N. Churayev, "Investigation of the Properties of Water II," presented to the 44th National Colloid Symposium, Lehigh University, June, 1970.