Reports

Vitrification Temperature of Water

Abstract. *The vitrification temperature* (T_g) *of water is an elusive quantity because of the great difficulty in supercooling water sufficiently without initiating its crystallization. Water depresses the vitrification temperature of glycerol (184°K) monotonously, and this property has been used for derivation of an estimate of its* T_g. *The result, 127° ± 4°K (−146° ± 4°C), is the temperature below which water presumably exists as a brittle, glassy substance.*

It is widely believed (*1, 2*) that any substance will undergo vitrification if it can be supercooled sufficiently below the melting point without inception of crystallization. Vitrification is readily achieved in many such substances as polymers, ceramics, and polyhydroxy compounds. In contrast, I find only one detailed report on the possible formation of vitreous water (*3*). The vitrification (glass-transition) temperature (T_g) of water, which is important in several areas of meteorological and other investigation, can apparently be considered a largely unknown quantity. I have used the ability of water to depress T_g for glycerol for obtaining what I believe to be a sufficiently close estimate of T_g for pure water.

Glycerol (*4*) was diluted with varying amounts of distilled and deionized water that were determined by titration (*5*). Each sample so characterized was introduced in 10-g amounts into a thin-walled, cylindrical aluminum cell that was then immersed in liquid nitrogen. After vitrification of the specimen, which occurred within seconds, the cell was rapidly transferred to an isopentane bath kept at 130°K; it was held buoyant therein by suspension from a Mettler balance reading to 1 mg. The measurement consisted in recording the buoyant weight of the cell as the temperature of the isopentane bath was increased by 1°K/min, the location of the T_g being indicated by a distinct discontinuity in the slope of a plot of buoyant weight versus temperature; this plot was linear over at least 20°K on either side of the T_g. Thus this procedure essentially amounted to determination of the temperature at which the coefficient of thermal expansion of the samples increased abruptly; such an event invariably accompanies the devitrification of substances.

Variation in the heating rate from 0.5° to 2°K/min resulted in values for the T_g that were identical within the experimental error (±1°K); furthermore, the location of the T_g, as observed upon heating through this temperature, was identical with that determined by cooling below it in the few instances when cooling was employed. An estimate of the accuracy of the method was provided by measurement of T_g for undiluted glycerol [moisture content, 0.0310 ± 0.0001 percent by weight (*6*)]; T_g occurred at 184°±1°K, in good agreement with the mean value of five independent determinations (185°K) on glycerol samples of generally unspecified but presumably low moisture content (*1*).

Results for several glycerol specimens diluted with water are reported in Fig. 1. Measurements on samples containing less than about 60 percent glycerol by weight were not made after the observation that such compositions crystallized at least partially upon immersion in either liquid nitrogen at 77°K or isopentane at 130°K. Figure 1 shows a monotonic decrease by water of the T_g for glycerol in the well-known manner in which the T_g of polymers is depressed after dilution with a substance of low molecular weight. In polymer-diluent systems, successful use has been made of the empirical relation

$$T_g = T_{g1} + T_{g2}\, w_2 + K w_1 w_2$$

to describe the results over an extended (*7*) or the entire (*8*) concentration range of the respective binary systems. In this instance T_g, T_{g_1}, and T_{g_2} are the glass-transition temperatures of solution, pure water, and pure glycerol, respectively; w_1 and w_2 are the weight fractions of water and glycerol, respectively; and K is a constant, characteristic of the glycerol-water system. A smooth line, as in Fig. 1, was drawn through the experimental data, and several points from this line were used for plotting the quantity $(T_g - T_{g2})/w_1$ versus w_1. The resultant plot was linear except where w_1 was less than 0.05 [as w_1 approaches zero, the quantity $(T_g - T_{g2})/w_1$ quickly becomes indeterminate]; accordingly, the data were extended by very short extrapolation to $w_1 = 0$. The intercept of the linear plot at $w_1 = 0$ gave the quantity $(T_{g1} - T_{g2} + K)$, and the slope (*9*) gave $-K$. The constant K equaled − 27° ± 2°K. The value of T_{g_1} the vitrification temperature of water, was thereby computed at 127°K within about 4°K (− 146° ± 4°C).

The result arrived at in this indirect manner is remarkably close to the temperature, 126°±2°K, at which Pryde and Jones (*3*) observed sudden increase in the heat capacity of a block of porous copper, containing water held in a fine state of subdivision, that had previously been rapidly cooled in liquid oxygen; they were able to repeat this observation of this system only once, and other procedures employed by them apparently failed to yield vitreous water. Their final conclusion (*3*), which took

Table 1. Various estimates of T_g for water (°K). ΔH_v for water at 375°K is taken as 6.7 × 10^{-13} erg per molecule. The conclusion of Kobeko *et al.* was based on observation that T_g for reportedly anhydrous sulfuric acid (specific gravity, 1.84) was identical with T_g for $H_2SO_4 \cdot 2H_2O$ (146°K). Prvde and Jones observed apparent devitrification at 126° ± 2°K but could not confirm the finding.

T_g/T_m (0.50–0.67)	T_g/T_b (0.25–0.33)	$\Delta H_v/kT_g$ (38–53)	Kobeko *et al.* (*10*)	Pryde and Jones (*3*)	Mine
137–183	93–123	90–126	146	123–148	127 ± 4

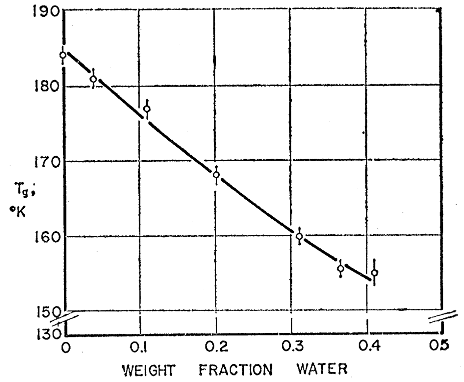

Fig. 1. Depression of the vitrification (glass-transition) temperature, T_g, of glycerol (184° ± 1°K) by addition of water. A smooth line has been drawn through the experimental points in order to reduce the error in the graphic procedure for the estimation of T_g for pure water.

into account earlier observations (*10*) of the vitrification temperature of two aqueous solutions of sulfuric acid, was that T_g for water lies between 123° and 148°K.

Various empirical rules have been proposed for prediction of T_g for a particular substance on the basis of the known magnitudes of other transition temperatures or other quantities characteristic of the substance. Thus it has been observed that T_g/T_m lies (*1*) between 0.50 and 0.67, T_g/T_b lies (*2*) between 0.25 and 0.33, and $\Delta H_v/kT_g$ (where ΔH_v is the molecular heat of vaporization of water at T_b, and k is Boltzmann's constant) lies (*2*) between 38 and 53. Table 1 lists three experimentally derived estimates of T_g for water, and estimates of the predicted range within which T_g should occur, as the estimates are computed by use of these three empirical rules.

Meteorological studies of formation of cloud and snow have been hampered by inability to supercool water by more than about 40°C. This circumstance is universally attributed to the ubiquity of foreign particles (motes) that induce nucleation prematurely and heterogeneously. In order to eliminate motes from water samples and subsequently to supercool these samples by about 35° to 40°C several techniques have been devised, including (i) copious distillation and deionization (*11*); (ii) suspension of water droplets at the interface between two liquids (*12*), or coating of such droplets with an inert skin (*13*); and (iii) production of very fine water droplets in cloud chambers (*14*). My success in supercooling water by more than 115°C (Fig. 1) was gained at the expense of gross contamination (more than 60 percent by weight) with glycerol. Nevertheless I suggest that the search for a suitable solute, that in trace amounts could suppress the crystallization of water, might prove considerably more rewarding than any of the sample purification and size-reduction procedures that I have just mentioned.

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References and Notes

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Mass of Vesta

Abstract. *The asteroid 197 (Arete) approaches asteroid 4 (Vesta) within 0.04 astronomical unit once every 18 years. It may therefore be possible to determine the mass of Vesta from observations of Arete. From 72 observations a value of (1.20 ± 0.08) × 10^{-10} solar mass was derived, the indicated uncertainty being a probable error.*

Asteroid 197 (Arete) approaches asteroid 4 (Vesta) within 0.04 astronomical unit once every 18 years. Since its discovery in 1879 there have been five such approaches—in 1885, 1903, 1921, 1939, and 1957.

It may therefore be possible to determine the mass of Vesta from observations of Arete. A discussion of 59 observations led to the value (1.17 ± 0.10) × 10^{-10} solar mass, the indicated uncertainty being a probable error (*1*). A final discussion of the observations will be possible as soon as the search for older observations has been completed. In the meantime, a new analysis of 72 observations in 28 oppositions was made by comparison with two orbits. Orbit 1 was a numerical integration which did not take account of any Vesta perturbations. Orbit 2 was a numerical integration which included the effect of Vesta. The value 1.17343 × 10^{-10} solar mass, used for the mass of Vesta, was obtained in the aforementioned preliminary solution. The extra figures have no physical significance and were dropped in the quoted results, but they were retained in the construction of orbit 2 for computational convenience. The residuals before the differential corrections were obtained from P. Herget and C. Bardwell of the Cincinnati Observatory.

The whole period from 1879 to 1966 was divided into five basic differential correction intervals, each having the time equivalent to one of the five approaches near the middle. Fifteen combinations of basic differential correction intervals were considered, each consisting of one, two, three, four, or five basic differential correction intervals. For each of the 15 combinations three solutions were made. One was a correction of orbit 1 for an adjustment of the position-velocity vector at the epoch; the second was a correction of orbit 1 with a determination of the mass of Vesta included. The third solution was a correction of orbit 2 consisting of an adjustment of the position-velocity vector and the determination of a correction to the value used for the mass of Vesta in constructing orbit 2.

No meaningful results were obtained where only one or two basic differential correction intervals were considered. Table 1 shows the results for the cases where at least three basic differential correction intervals have been used. The corrections of orbits 1 and 2 in each case lead to the same value for the mass of Vesta.

For the cases where three or four differential correction intervals were used, the results indicate some, although not complete, consistency among themselves and with the solution covering the whole period. The reason for the incomplete consistency may be the paucity of observations. The final analysis, when additional observations are available, may show whether the increase in the number of the observations would increase consistency and