The evaporation rate, free energy, and entropy of amorphous water at 150 K

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Measurement of the rates of evaporation of amorphous water (a) and ice (i) near 150 K can be interpreted as giving a measure of their free energy difference, $\Delta_i^a G$ (150 K)$=1100\pm100$ J/mol, which, together with the known enthalpy difference and heat capacity data, suggests a residual entropy difference of $\Delta_i^a S$ (0)$=-0.7\pm2.2$ J/(K mol) at absolute zero. Previous theoretical estimates of $\Delta_i^a S$ (0), which are much larger, did not allow the amorph to be connected with normal liquid water by a reversible thermodynamic path at atmospheric pressure. The present value allows such a connection. © *1996 American Institute of Physics.* [S0021-9606(96)50525-8]

INTRODUCTION

We report measurements of the rates of evaporation of amorphous water (a) and ice (i) near 150 K and suppose that their ratio gives a measure of their free energy difference which, together with the known enthalpy difference and heat capacity data, suggests a residual entropy difference of $\Delta_i^a S$ (0)$=-0.7\pm2.2$ J/(K mol) at absolute zero. The residual entropy of ice,[1–4] due to the frozen-in proton disorder is 3.4 J/(K mol), so the residual entropy of the glass, 2.7 ± 2.2 J/(K mol), does not violate the third law.

The residual entropy of glassy water is of considerable theoretical significance. It has been shown previously[5] that in order for supercooled and amorphous water to be connected by a reversible isobaric path, the residual entropy of glassy water must satisfy strict bounds imposed by thermodynamic consistency. If these bounds are not satisfied, continuity is impossible, and glassy water is a distinct phase. Although this question has been discussed theoretically,[5–7] the key quantity, that is to say the residual free energy of glassy water, has not been measured. In this paper we measure the evaporation rate of amorphous water and ice at 150 K. From this measurement we calculate the residual free energy of the glass, and discuss the implications for the continuity problem.

Our thermodynamic interpretation of the evaporation rates rests on some untested assumptions. It is not altogether clear that the free energy of a glass can be defined or measured unambiguously. For instance, Simon[8] argued cogently that there is no point in speaking of the equilibrium vapor pressure of a glass because the equilibrium vapor pressure of a condensed phase should be measured under conditions where it coexists in equilibrium with the vapor, but an individual glass would change through a sequence of different glasses if it was allowed to evaporate and recondense. The same objection applies to solubility measurements[9] or to any other method which relies on equilibrating a glass with another phase. Fowler and Guggenheim[10] dismiss Simon's argument as ''too drastic''.

There is still debate about whether glassy water becomes a liquid before it freezes to ice near 150 K. Simon's objection does not apply if the amorph is a supercooled liquid near 150 K. From spectroscopic studies of the rates of isotope exchange processes in the glass, Fisher and Devlin[11] conclude that the very weak glass transition reported[7,12,13] near 130 K is a manifestation of the onset of molecular rotation in the glass, rather than transformation to a diffusing liquid, and that the glass freezes directly to ice near 150 K without passing through an intermediate liquid state. We refer to our unfrozen deposit as the amorph to avoid specifying whether it is a glass or liquid.

The Gibbs free energy difference between two condensed phases, 1 and 2, of the same substance, is related to the ratio of their vapor pressures, when the vapor is ideal, by[14]

$$\Delta_1^2 G = RT \ln\{p_2/p_1\}. \tag{1}$$

In the experiments described below, we measure the rate of evaporation under a vacuum of 10^{-10} Torr, which prevents recondensation. The sticking coefficient of water on ice is unity over the range of temperature of our experiments.[15,16] A sticking coefficient of unity means that all molecules that impinge on the ice surface lose sufficient energy to become trapped in a bound state. Under this condition, the adsorption rate is equal to the surface collision rate, which from elementary kinetic theory is directly proportional to the pressure p above the surface. At equilibrium the adsorption and evaporation rates are equal, and p is the vapor pressure. Consequently, the evaporation rate r_e is proportional to the equilibrium vapor pressure. Assuming that it

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makes sense to speak of the equilibrium vapor pressure of the amorph, p_a, we have $r_{e,a}/r_{e,i}=p_a/p_i$. The free energy difference between the amorph and ice is then given by

$$\Delta_i^a G = RT \ln\{r_{e,a}/r_{e,i}\}. \quad (2)$$

EXPERIMENT

The experimental apparatus for the molecular beam measurements at Pacific Northwest National Laboratory has been described previously.[15–18] In brief, a quadruply differentially pumped molecular beam of H_2O (D_2O) was used to dose the Ru(001) sample. For most of the experiments, the beam was quasi-effusive and had a velocity profile characteristic of a 300 K Maxwellian distribution. A variable energy (2–50 kcal/mol) supersonic nozzle beam source was also employed in several experiments. In all cases, the incident H_2O (D_2O) beam flux was between 0.01 and 0.1 monolayers/s. The flux is defined in terms of ice monolayers, where 1 ML$=1.056\times10^{15}$ molecules/cm^2. This definition corresponds to the H_2O coverage in the $\sqrt{3}\times\sqrt{3}\,R30°$ ice-like bilayer on Ru(001)[19] with a Ru(001) lattice constant of 2.70 Å.[20]

The highly collimated beam has a circular profile of ~0.35 cm diameter. This beam can intercept the ~1.2 cm diameter Ru(001) sample at incident angles as large as 70° from the surface normal without overfilling the target. Dosing with this H_2O (D_2O) flux source enables precise and reproducible H_2O (D_2O) exposures to be attained without appreciable adsorption on surfaces other than the Ru(001) crystal. The beam dosing technique also allows the condensation coefficient to be determined directly by the beam reflection technique of King and Wells.[15,16,21] The incident, scattered, and desorbed fluxes of H_2O (D_2O) are detected in an angle-integrated manner by measuring the H_2O (D_2O) partial pressure in the scattering chamber with a quadrupole mass spectrometer. The mass spectrometer is positioned to prevent a line-of-sight view of the Ru(001) surface. The Ru(001) single crystal resides in an UHV surface analytical chamber with a base pressure $<1\times10^{-10}$ Torr. The Ru(001) surface was cleaned and characterized by low energy electron diffraction and Auger electron spectroscopy using previously published procedures. The crystal was attached to a liquid nitrogen-cooled Dewar and heated resistively. The sample temperature could be varied between 85 and 1500 K under computer control with a precision of better than ±0.1 K and an absolute accuracy of ±2 K.

RESULTS

Amorphous films 30–1000-molecular layers thick were grown by vapor deposition at a rate of 0.05 monolayer/s onto the Ru(001) substrate at 85 K. The evaporation rate was measured as the sample was heated or cooled at a linear rate of 0.6 K/s. At the highest temperature the desorption rate of about 1 monolayer/s corresponds to a vapor pressure of about 10^{-6} Torr so only 1 desorbing molecule in $\sim10^4$ can readsorb. Under these conditions the experiment measures the free desorption rate, which for a sticking coefficient of unity is directly proportional to the vapor pressure. The amorphous deposits freeze in the 155 to 165 K range. From other studies[7,12,13,22–25] it is known that glassy water freezes to cubic ice 1.

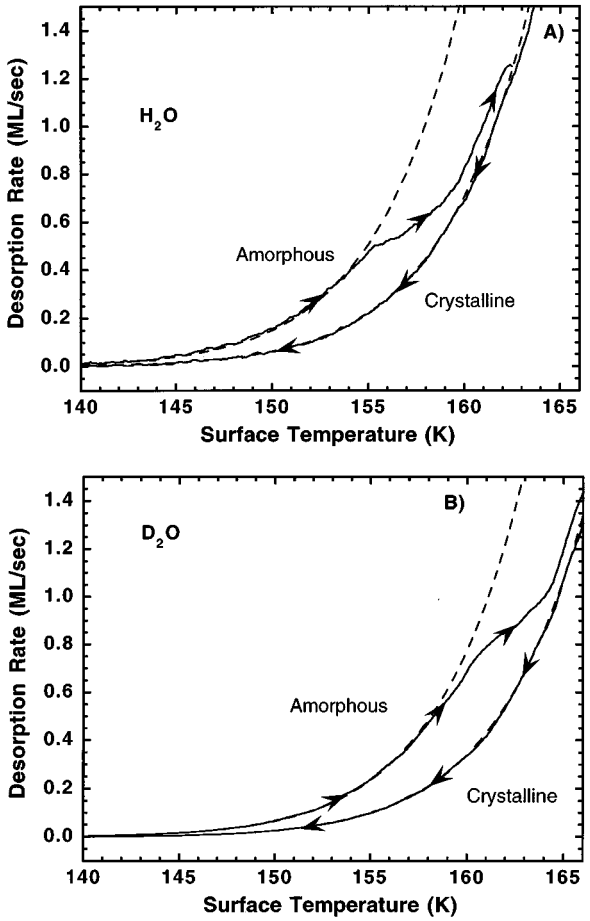

FIG. 1. The desorption rate from 100-monolayer-thick films of amorphous H_2O (A) and D_2O (B) as they are heated and cooled at a rate of 0.6 K/s. The hysteresis is due to the freezing of the films to cubic ice 1, which is more stable and evaporates slower. The arrows on the curves indicate the direction of the temperature ramp. The dashed lines are Arrhenius fits to the desorption rates.

The experimentally determined desorption rate for both the H_2O amorph and crystalline ice is displayed in Fig. 1(A). In this experiment a 100-molecular layer-thick film is deposited on an 85 K substrate. The film is subsequently heated from 85 to 163 K and then immediately cooled back to 85 K after which it is reheated to 200 K to desorb the entire film. The initial heating/cooling cycle exhibits a pronounced hysteresis in which the desorption rate is higher upon heating than cooling. This hysteresis is absent in subsequent heating/cooling cycles and arises from the irreversible transformation of the amorph into crystalline ice during the initial heating. The higher desorption rate observed for the amorph is a manifestation of the excess free energy of the metastable phase. As the amorph crystallizes the measured desorption rate approaches that of the crystalline ice phase in the temperature range of 155 to 163 K. The kinetics of the crystallization are discussed in detail elsewhere.[26] The

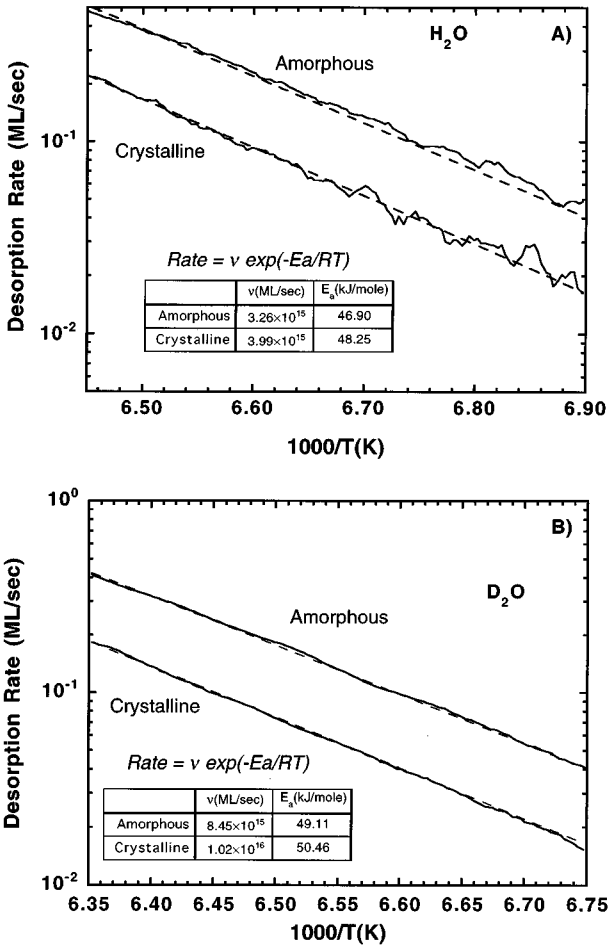

FIG. 2. Arrhenius plots of the desorption rate from amorphous and crystalline H_2O (A) and D_2O (B). The dashed lines are fits corresponding to the parameters tabulated in the figure, which were obtained by constraining the desorption activation energy difference to be the calorimetrically measured heat of freezing of the amorph to cubic ice 1 near 150 K. The uncertainty in the tabulated Arrhenius parameters is $\pm 20\%$ in ν and $\pm 2\%$ in E_a.

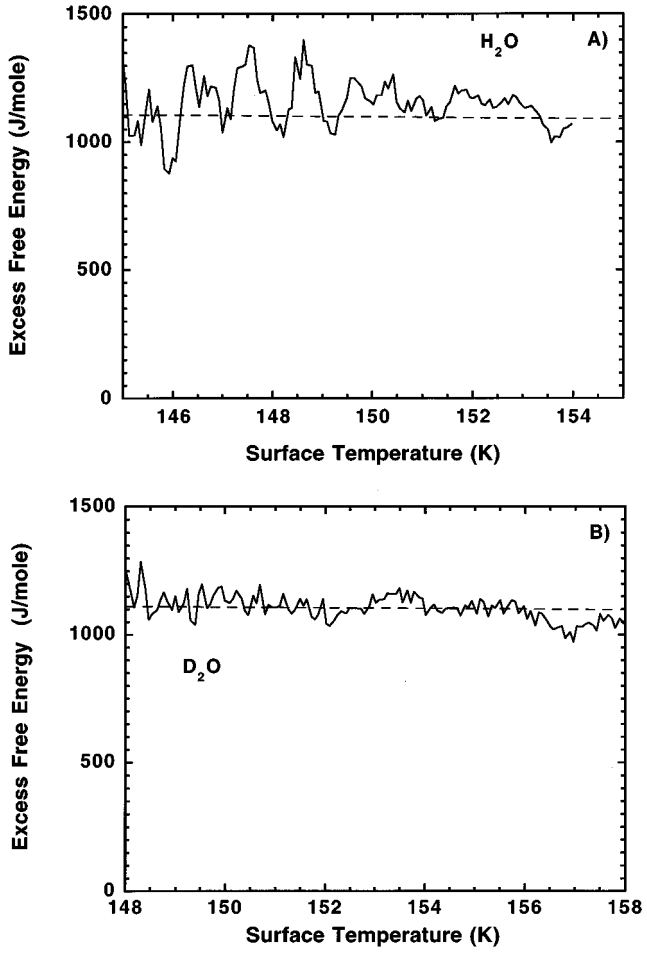

FIG. 3. The excess Gibbs free energy of the amorphous films of H_2O (A) and D_2O (B) relative to cubic ice 1, calculated from Eq. (2). The solid line is a point-by-point ratio of the experimental data and the dashed line is calculated from the Arrhenius parameters tabulated in Fig. 2.

dashed lines displayed in Fig. 1 represent Arrhenius fits (cf. Fig. 2) to the desorption rates for the amorph and crystalline ice films. Figure 1(B) shows analogous results obtained for D_2O. These experiments have been repeated many times for a variety of incident beam fluxes and film thicknesses and the results are reproducible.

Figure 2(A) shows Arrhenius plots of the desorption rates for the H_2O amorph and crystalline ice in the temperature range of 145 to 155 K. Because of the limited temperature range over which the amorph desorption rate is large enough to measure precisely without the influence of crystallization, reasonable fits can be obtained with a variety of Arrhenius parameters. We free-fit the experimental desorption rate for crystalline ice and obtain parameters in good agreement with previous measurements of H_2O desorption from ice multilayers.[16,27–29] To extract Arrhenius parameters for the amorph desorption rate we constrain the desorption activation energy difference to be the calorimetrically measured heat of freezing of the amorph to cubic ice 1 near 150 K:[7,12,22]

$$\Delta_i^a H(150\ \mathrm{K}) = 1350 \pm 150\ \mathrm{J/mol}. \tag{3}$$

The error allowed for $\Delta_i^a H$ in Eq. (3) is large enough to accommodate differences between samples of different origin[12,22] and different freezing temperatures,[7] as well as the small difference [50 J/mol (Ref. 24)] between the enthalpy of cubic and hexagonal ice. Both the higher evaporation rate of the amorphous films relative to the crystalline films, and the value of the activation energy obtained from the Arrhenius fit to the crystalline data are consistent with the measurements of Sack and Baragiola[29] on vapor-deposited ice films. Figure 2(B) shows analogous Arrhenius plots for D_2O. The signal-to-noise ratio is appreciably higher for the D_2O data due to the lower background pressure of D_2O in the UHV chamber.

The difference in free energy between crystalline ice and the amorph was calculated from Eq. (2). The solid lines in Fig. 3 are the free energy differences calculated directly from the experimentally measured rates at each temperature for both H_2O and D_2O. The dashed lines in Fig. 3 are calculated from the constrained Arrhenius fits displayed in Fig. 2. The slopes of the lines give the entropy difference $\Delta_i^a S = -(\partial \Delta_i^a G / \partial T)$, but they have an uncertainty of near

100% because of the limited temperature range in which the evaporation rate is large enough to measure accurately.

At 150 K, for both H_2O and D_2O, the measurements, displayed as solid lines in Fig. 3, yield

$$\Delta_i^a G(150\ \text{K}) = 1100 \pm 100\ \text{J/mol}. \tag{4}$$

From Eqs. (3) and (4) we obtain the small entropy difference

$$\Delta_i^a S(150\ \text{K}) = 1.7 \pm 1.7\ \text{J/(K mol)}, \tag{5}$$

which is consistent with the small slope of the dashed lines (derived from the Arrhenius parameters in Fig. 2) shown in Fig. 3.

The heat capacities of ice[1,3] and the amorph[13,25] have been measured and the entropy difference can also be expressed as

$$\Delta_i^a S(150\ \text{K}) = \Delta_i^a S(0) + \int_0^{150\ \text{K}} (\Delta_i^a C_p/T)\,dT$$

$$= \Delta_i^a S(0) + 2.4 \pm 0.5\ \text{J/(K mol)}. \tag{6}$$

$\Delta_i^a C_p$ is the heat capacity of the amorph relative to ice and $\Delta_i^a S(0)$ is the entropy difference at absolute zero. Johari[30] calculated the integral term in Eq. (6) from the data of Sugasaki *et al.*[25] up to 136 K to be 2.1 J/(K mol). We used the estimate[5,7,12,13] $\Delta_i^a C_p = 3.6$ J/(K mol) from 136 to 150 K and we estimate the total error in the integral to be about 0.5 J/(K mol). Equations (5) and (6) then yield

$$\Delta_i^a S(0) = -0.7 \pm 2.2\ \text{J/(K mol)}. \tag{7}$$

The calorimetric value of $\Delta_i^a S(0)$ is not known because there is no known reversible path connecting glassy water to a state of known entropy. Previous theoretical estimates[5,30–33] give values in the range 3.5 to 6 J/(K mol) while a value of $\Delta_i^a S$ (150 K) derived from experiment by Whalley *et al.*[34] using the assumption that the transformation from ice to an amorphous solid at 77 K corresponds to the extrapolated ice-water freezing line, agrees with Eq. (5).

RESOLUTION OF THE CONTINUITY PROBLEM

It has been shown[5] that the previous theoretical estimates of $\Delta_i^a S(0)$ rule out the possibility of connecting glassy water to normal liquid water along a thermodynamically reversible path at atmospheric pressure. If there is a reversible path connecting amorphous water at $T_1 = 150$ K to supercooled water at $T_2 = 236$ K, the lowest temperature to which the thermodynamic properties of supercooled water are known,[5,35] then thermodynamics requires[5] that

$$\Delta_i^a S(T_1) = \Delta_i^a S(T_2) - [\Delta_i^a H(T_2) - \Delta_i^a H(T_1)]/T_2 + \Sigma_t[\Delta H(T_t)/T_2 - \Delta S(T_t)] - \int_{T1}^{T2} \Delta_i^a C_p (1/T - 1/T_2)\,dT, \tag{8}$$

where $\Sigma_t[\Delta H(T_t)/T_2 - \Delta S(T_t)]$ sums the enthalpy and entropy changes at any first order phase changes that might occur in the amorphous branch at temperatures T_t along the path between T_1 and T_2. At a reversible first order change $\Delta H(T_t)/T_t = \Delta S(T_t) > 0$, where Δ indicates the change on going from the phase which is stable below T_t to the phase which is stable at higher temperature. It follows that $\Sigma_t[\Delta H(T_t)/T_2 - \Delta S(T_t)] < 0$ because $T_t < T_2$. The integral term is necessarily positive since $\Delta_i^a C_p > 0$ and $T < T_2$. The remaining terms on the right-hand side of Eq. (8), which have all been measured,[5,7,12,13,22,35] therefore put an upper bound on $\Delta_i^a S(T_1)$, which yields[5]

$$\Delta_i^a S(T_1) \leqslant 2.9\ \text{J/(K mol)}. \tag{9}$$

The equality in Eq. (9) can hold only if the last two terms in Eq. (8) are zero, which requires that there are no first order phase changes along the path and $\Delta_i^a C_p = 0$ at all temperatures between T_1 and T_2. However,[5,7,12,13] $\Delta_i^a C_p \approx 3.6$ J/(K mol) near T_1 and[35] 65 J/(K mol) at T_2 and it must satisfy

$$\Delta_i^a H(T_2) - \Delta_i^a H(T_1) = \int_{T1}^{T2} \Delta_i^a C_p\,dT. \tag{10}$$

Equation (10) is satisfied by a linear interpolation of $\Delta_i^a C_p$ between its values at T_1 and T_2. With that interpolation the bound becomes $\Delta_i^a S(T_1) \leqslant 1$ J/(K mol) which is consistent with our measured value. Whatever the form of $\Delta_i^a C_p$, it is clear that $\Delta_i^a S(T_1)$ must be substantially smaller than the upper bound in Eq. (9).

Because the residual entropy of ice is known[1–4] to be 3.4 J/(K mol) and the residual entropy of the glass cannot be less than zero, a lower bound is $\Delta_i^a S(0) \geqslant -3.4$ J/(K mol), which gives, taking account of the error quoted in Eq. (6), $\Delta_i^a S(T_1) \geqslant -1.5$ J/(K mol). Thus, our measured value lies between the upper bound required for continuity between the glass and liquid water and the lower bound imposed by the third law.

CONCLUSIONS

Our results show that the ratio of the evaporation rates of ice and the amorph is consistent with both solids having about the same entropy at absolute zero. That conclusion relies on Eq. (2), which is plausible, but possibly incorrect. One consequence of the small entropy of the glass is that it is now possible to contemplate a reversible path connecting glassy water to normal liquid water. Theoretical estimates of the entropy of the glass[5,30–33] ruled out such a path and led to the idea that glassy water is a distinct phase.[5] That may still be the case but the argument for it is now much less compelling.

The concept of the ''entropy of a glass'' can have different meanings, depending on whether one approaches it from the point of view of experimental thermodynamics or statistical mechanics.[36] An individual glass is just one of $\exp\{\gamma N\}$ possible glasses, where γ is of order unity and N is the number of molecules.[31,33,36–41] From a statistical point of view, if the individual glasses have approximately the same entropy then the entropy associated with all the glasses is greater than the entropy of an individual glass by γNk. In a preliminary communication[38] of the present results the small entropy difference between the ice and the glass was taken to suggest that it is the entropy of the individual glass that

determines its evaporation rate. However, simulation studies of the vapor pressure of glassy crystals of dimers[39,40] clarify that issue. They show clearly that the vapor pressure of an individual glassy crystal is correctly predicted when the entropy of the glass is taken to be the entropy of one glass plus γNk. We take that conclusion to be applicable to glasses in general, and glassy water in particular, in which case the entropy that we measure is the same as the entropy of classical thermodynamics, and there is no distinction between the entropy of glassy or liquid water at 150 K.

An important question remains. Glasses are expected to have a substantial residual entropy at absolute zero,[10] corresponding to the entropy associated with those degrees of freedom which become frozen in at the glass transition. There are two contributions to the expected residual entropy of glassy water, positional and rotational. The orientation of the water molecules in ice is frozen-in so that ice is a glassy crystal[1–4] below 100 K. As a result, ice has a residual entropy of 3.4 J/(K mol). Fisher and Devlin's study[11] suggests that a similar freezing in of the rotations occurs in glassy water around 130 K. Frozen-in rotational disorder may contribute a bit less to the residual entropy of the glass than it does to ice because different orientations are likely to have different energies in the glass.[30] But one would expect an additional contribution of 3 to 6 J/(K mol) to the residual entropy of the glass due to the frozen-in positional disorder.[5,30–33] That contribution seems to be missing from the residual entropy estimated here. An explanation for the apparent anomaly may be provided by a simulation study of model tetravalent network glasses,[41] which indicates the possibility of an essentially unique ideal glass with no residual entropy. Liquid helium provides an example[10] of a translationally disordered system with no residual entropy.

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