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Humidity, Ice, and Nitric Acid

R. S. Gao *et al.* report average relative humidity, with respect to ice, of over 130% in the vicinity of low-temperature cirrus clouds and contrails (Reports, "Evidence that nitric acid increases relative humidity in low-temperature cirrus clouds," 23 Jan., p. 516). To account for this, the authors "propose that HNO_3 molecules adsorbed on cirrus cloud particles under [nitric acid trihydrate (NAT)] stability conditions combine with surface H_2O molecules to form NAT or NAT-like molecules that interfere with the uptake of water molecules on the ice surface more than with evaporation." The ice particles so modified are designated Δ-ice.

This explanation violates the second law of thermodynamics. Quantitatively, Gao *et al.* assume $\alpha_{\Delta\text{ice}} < \alpha_{\text{ice}}$ while $Q_{e,\Delta\text{ice}} \approx Q_{e,\text{ice}}$ ($\alpha \leq 1$ is the condensation coefficient, or fraction of surface collisions that contribute to ice growth, and Q_e is the evaporation flux). To conform with the second law, there must be a proportional reduction in $Q_{e\Delta\text{ice}}$: $Q_{e\Delta ice}/Q_{e,\text{ice}} = \alpha_{\Delta\text{ice}}/\alpha_{\text{ice}}$; otherwise, the Δ-ice surface could be used as a passive one-way membrane in violation of microscopic reversibility and the second law. Imagine, for example, a plug of ice condensed inside a toroidal ring at constant temperature. Let one surface of the ice plug be modified so as to form Δ-ice and the other be unchanged. The ring is coated inside to prevent ice nucleation, and water vapor is permitted to diffuse around. With $Q_{e\Delta\text{ice}} \approx Q_{e,\text{ice}}$ for evaporation and uniform pressure in the ring requiring $Q_{c\Delta\text{ice}} = Q_{c,\text{ice}}$ for the collisional surface flux, there will be fewer growth collisions (because $\alpha_{\Delta\text{ice}} < \alpha_{\text{ice}}$) and net evaporation from the Δ-ice surface (also net condensation on the unmodified ice surface), inducing a current of water vapor around the ring--a perpetual motion machine! Gao *et al.* may be on firmer ground in their analogy to antifreeze proteins, which slow the approach to equilibrium, but they should not invoke one-way surface structures in violation of the second law.

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Response
Our Report presents observations of elevated relative humidity with respect to a flat surface of pure hexagonal ice (RH_i) in low-temperature cirrus clouds in the upper troposphere. Our observations led us to assert that the air parcels with elevated RH_i were in mass balance with respect to the condensed phase, i.e., there was no net ice particle growth. Because this ice-vapor system was in mass balance with an RHi greater than 100%, we further asserted that the low-temperature ice surfaces were in a state distinct from the lowest energy equilibrium state of hexagonal ice. As an attempt to explain our observations, we put forth the concept of Δ-ice, which is ice with a surface impurity of HNO_3 under ambient conditions that yield stability of the NAT phase. We offered several lines of support for the existence of Δ-ice, including the analogy with the action of antifreeze proteins in fish.

McGraw is correct that the second law of thermodynamics does not allow arbitrary one-way surface fluxes. We respectfully disagree, however, that his argument applies to Δ-ice. Although the exact cause (and existence) of the Δ-ice supersaturation awaits laboratory investigation, there are two general ways that Δ-ice might achieve a steady-state partial pressure higher than the ice equilibrium vapor pressure. First, Δ-ice could have a surface energy that is higher than that of an infinite flat surface of pure ice. Examples of this are ice with an increase in surface curvature similar to that proposed to explain the action of antifreeze proteins, or ice for which the outer portion of the particles might not be hexagonal ice. Second, both $Q_{e,\Delta\mathrm{ice}}$ and $\alpha_{\Delta\mathrm{ice}}$ could be zero (arrested growth) for a limited RH_i range above 100%. In this case, McGraw 's arguments are moot because the Δ-ice surface is effectively invisible to the H_2O vapor. If we assume that Δ-ice corresponding to our first option is configured as one surface in McGraw 's toroid experiment, the H_2O current is now due to the ice and Δ-ice surface energy differences and will accordingly cease when this energy difference dissipates into heat.

To clarify the Δ-ice mechanism in a related but somewhat different way, we suggest considering the standard cloud physics growth equation

$$f = c\,(\alpha_1 p_{\mathrm{vap}} - \alpha_2 p_{\mathrm{sat}}) \quad (1)$$

where f is the net flux of H_2O molecules to an ice surface, c is a proportionality factor, α_1 and α_2 are coefficients, and p_{vap} and p_{sat} are the H_2O vapor pressure and saturation vapor pressure with respect to an infinite flat surface of pure ice, respectively. The assumption of $\alpha_1 = \alpha_2$ leads to the equilibrium solution

$$p_{\mathrm{vap}} = p_{\mathrm{sat}} \quad (2)$$

To use Eq. 1 to describe a system other than pure flat ice, the terms α_1 and α_2 must be reevaluated, and p_{sat}, as defined above, no longer represents the equilibrium vapor pressure of the system. An important case is the increase in equilibrium vapor pressure above curved pure ice surfaces (Kelvin effect). In this case, for example, the value of α_2 is greater than α_1 and at equilibrium $p_{\mathrm{vap}} > p_{\mathrm{sat}}$ (1). For Δ-ice, α_1 and α_2 are not known a priori. In the context of Eq. 1, our Report presented evidence that α_1 is decreased when HNO_3 impurity molecules are present. We further asserted that the evaporative flux ($\sim\alpha_2 p_{\mathrm{sat}}$) was not altered by surface HNO_3, on the basis of limited laboratory observations.

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References and Notes

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2. We thank D. M. Murphy for helpful discussions.