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UPDATE

Polar Clouds and Sulfate Aerosols

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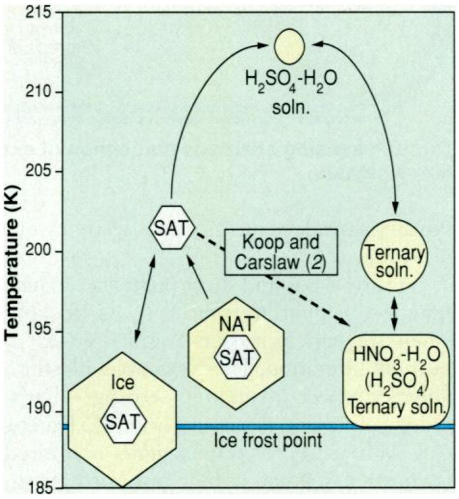
It is now well established that heterogeneous chlorine activation reactions on polar stratospheric clouds (PSCs) play a central role in polar ozone depletion. In contrast, the chemical composition and formation mechanism of the polar clouds is still a topic of considerable debate (*1*). Theoretical work by Koop and Carslaw on page 1639 of this issue (*2*) provides a piece to the puzzle of how one kind of PSC (type I) forms over and over again throughout the winter.

Several years ago, nitric acid trihydrate (NAT) was favored as the main ingredient of type I PSCs (*3*). It was thought that the global sulfate aerosols froze and formed sulfuric acid tetrahydrate (SAT) at the cold polar temperatures and that crystalline SAT then provided a good nucleating surface for NAT. However, laboratory work has shown that neither of these two steps occurs readily (*4*). In addition, some type I PSCs are not composed of NAT (*5*, *6*).

A new picture of PSC formation has recently emerged. Low-temperature liquid sulfuric acid aerosols can absorb significant quantities of HNO_3 (*7*), forming ternary solutions of H_2SO_4-HNO_3-H_2O. As temperatures plunge further, the ternary solutions absorb more HNO_3 and H_2O, forming PSC particles that are essentially binary solutions of HNO_3-H_2O. Recent work has indicated that these liquid PSCs may actually activate chlorine more efficiently than frozen NAT particles (*8*).

Although liquid sulfate aerosols do explain the presence of liquid PSCs, lidar data indicate that crystalline PSCs also exist at temperatures above the ice equilibrium temperature (or ice frost point) (*5*). It has been assumed that evaporation of crystalline PSCs (either ice or NAT) leaves a frozen sulfate core, probably in the form of SAT (see figure). Laboratory work has suggested that in the atmosphere, SAT remains frozen until a temperature of 210 to 215 K (*9*). This high temperature may never occur during the polar winter, and thus, SAT could remain frozen for the entire season. However, it has also been shown that SAT is not a good nucleating surface for PSCs (*4*). Thus, until recently, experimental results coupled with the two formation mechanisms described above implied that after crystalline PSCs formed once and left behind a frozen core, additional PSC growth would be hindered. PSCs could only form after either the temperature warmed to cause SAT melting or cooled to 189 K, where ice could condense. Neither of these possibilities occurs frequently enough to explain the observations of PSCs throughout the winter.



Closing the loop. Conversion of cloud particles from crystalline to liquid through the melting of SAT upon cooling (dashed line), which then permits PCSs to form again.

Koop and Carslaw (*2*) get us out of this dilemma by showing that SAT can melt upon moderate cooling in the atmosphere to form a supercooled ternary solution particle of H_2SO_4-HNO_3-H_2O (see figure). They suggest that the presence of HNO_3 in the atmosphere can help regenerate liquid sulfate aerosols, allowing the cycle of PSC formation to begin again. Adsorption of HNO_3 onto SAT causes the crystal to melt at temperatures well below the temperature of 210 to 215 K measured for SAT in the absence of HNO_3. This melting temperature depends only on the pressures of water and nitric acid in the atmosphere and occurs at a temperature several degrees above that at which NAT was seen to grow on SAT in laboratory experiments. Thus, if SAT does form in the atmosphere, this theory predicts that it will melt back to a ternary solution before NAT can directly condense, solving the mystery of how PSCs continue to form late in the polar winters. Formation of crystalline PSCs should not prevent subsequent formation of liquid PSCs on the same sulfate particles. Still, the issue of how crystalline PSCs form in the first place is unresolved.

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